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Sources and significance of alkane and PAH hydrocarbons in Canadian arctic rivers

By:

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Management Perspective

As part of Environment Canada's contribution to the Northern Contaminants Program, hydrocarbon concentrations were quantified in suspended sediment and water samples collected in 1993 and 1994 from 11 Arctic rivers (including the Mackenzie River) draining into the Canadian Archipelago or Hudson's Bay. This information was combined with similar Mackenzie data from 1987 (plus bottom sediment data from lakes in the Mackenzie delta and the Beaufort sea shelf) for the purpose of assessing the geochemistry of the alkanes and PAHs, inferring their sources, and characterizing their loading to the arctic marine environment. Alkane concentrations were similar for all the arctic rivers, but PAH concentrations were 10 to 100-fold higher in the Mackenzie River than in the Nunavut rivers because of a geological source in the Mackenzie valley. Suspended and bottom sediment samples from the Mackenzie commonly contained PAHs in excess of interim sediment quality guidelines. There is a need to ascertain whether the concentrations are having an effect on fish or other biota.

Key Words: PAH, alkane, petroleum, water quality guideline, sediment quality guideline, hopne, sterane, arctic rivers

Sources et incidence des alcanes et des hydrocarbures aromatiques polycycliques (HAP) dans les fleuves de l'Arctique canadien.

Sommaire à l'intention de la direction

Cette étude est une contribution d'Environnement Canada au Programme de lutte contre les contaminants dans le Nord. Elle a pour objet la mesure des concentrations d'hydrocarbures dans des sédiments en suspension et dans des échantillons d'eau prélevés en 1993 et 1994 dans onze fleuves de l'Arctique, dont le Mackenzie, qui se jettent dans la région de l'Archipel canadien ou la baie d'Hudson. Cette information a été comparée avec des données similaires recueillies pour le Mackenzie en 1987, ainsi qu'avec des données obtenues à partir de sédiments du fond prélevés dans des lacs du delta du Mackenzie et sur la plate-forme de la mer de Beaufort. Ces données ont servi à la détermination géochimique des alcanes et des HAP détectés, à l'identification de leurs sources et à la caractérisation de leur charge sur l'environnement marin arctique. L'étude a permis de constater que les concentrations d'alcanes étaient semblables dans tous les fleuves de l'Arctique. Par contre, les concentrations d'HAP se sont révélées dix à cent fois plus élevées dans le Mackenzie que dans les fleuves du Nunavut, ce qui est attribuable à la présence d'une source géologique de ces composés dans la vallée du Mackenzie. En effet, les échantillons de sédiments en suspension et de sédiments du fond en provenance du Mackenzie contenaient souvent des concentrations d'HAP excédant les limites fixées par les lignes directrices provisoires de qualité des sédiments. Il importe de déterminer si ces concentrations ont une incidence sur les poissons et sur d'autres biotes.

Mots clés : HAP, alcane, pétrole, lignes directrices sur la qualité de l'eau, lignes directrices de qualité des sédiments, hopane, stérane, fleuves de l'Arctique.

Abstract

Hydrocarbon measurements have been made on dissolved and particulate samples collected in 1987, 1993 and 1994 from the Mackenzie River delta and in 1993 for 10 smaller northern rivers that drain into the Canadian Archipelago or Hudson's Bay. The Mackenzie River has proved to be both spatially and temporally variable in hydrocarbon concentration. During summer the alkane and PAH (polycyclic aromatic hydrocarbon) content of suspended particulate in the Mackenzie River is sufficiently homogenous to use the SPM (suspended particulate matter) load to estimate hydrocarbon load. The Mackenzie River appears to transport a compositionally uniform mixture of particulate PAH, derived mainly from petrogenic sources and containing small (2- and 3-ring) and multi-ring (4- to 6-ring) PAHs which, according to their methylphenanthrene, hopane and sterane ratios, have similar hydrocarbon sources and maturity. Immature bitumens and shales from the Devonian Canol formation that outcrop into the lower Mackenzie river valley are most likely the principal petroleum source to the river. The ten smaller rivers have mean suspended particulate alkane concentrations (ng/g) similar to the Mackenzie River during summer, but PAH concentrations are approximately 10 times lower for the parent PAHs and 100 times lower for alkyl PAHs. The difference between the smaller rivers and the Mackenzie is exacerbated when hydrocarbon concentration is expressed volumetrically (ng/L). Alkyl PAHs have not been detected except in the Coppermine and Hayes Rivers indicating little or no petroleum-related hydrocarbons in the smaller rivers. This lack of petrogenic material is likely the single most important factor contributing to PAH concentration differences between the Mackenzie River and other arctic rivers. Particulate samples from the Mackenzie River and all smaller Canadian rivers have a resolved higher alkane pattern with a well-defined OEP (odd-even predominance) consistent with a major source in terrestrial, higher plant material. Sediment samples (suspended and bed) from the Mackenzie delta and shelf have natural PAHs concentrations that exceed interim sediment quality guidelines for the protection of aquatic life. What effect these elevated PAH concentrations may have on exposed biota is not presently known.

Résumé

Des mesures d'hydrocarbures ont été faites sur des échantillons dissous et particulaires prélevés en 1987, 1993 et 1994 dans le delta du Mackenzie, et en 1993 dans dix petits fleuves nordiques qui se jettent dans la région de l'Archipel canadien ou la Baie d'Hudson. Il en ressort que les concentrations d'hydrocarbures dans le Mackenzie varient en fonction du lieu et du moment des prélèvements. Au cours de l'été, la teneur en hydrocarbures aromatiques polycycliques (HAP) et en alcanes des particules en suspension dans le Mackenzie est suffisamment homogène pour qu'on puisse se servir de la charge des particules en suspension pour évaluer la charge d'hydrocarbures. Le Mackenzie transporte un mélange particulaire d'HAP dont la composition semble uniforme et principalement d'origine pétrogénétique. Ce mélange contient des HAP dont le nombre de cycles est petit (2 à 3 cycles) ainsi que des HAP polycycliques (4 à 6 cycles). Si l'on se fie aux proportions de méthylphénanthrène, de hopane et de stérane qu'ils contiennent, ces HAP sont de sources et de maturité similaires. Les bitumes immatures et les schistes argileux de la formation dévonienne de Canol qui affleurent dans la vallée du bas Mackenzie constituent probablement la principale source de pétrole dans la rivière. Les dix petits fleuves ont des concentrations moyennes (ng/g) d'alcane particulaire en suspension similaires à celles du Mackenzie pendant l'été. Par contre, leurs concentrations d'HAP sont 10 fois inférieures pour ce qui est des HAP d'origine et 100 fois inférieures en ce qui concerne les HAP d'alcoyle. La différence entre les petits fleuves et le Mackenzie ressort encore davantage quand la concentration d'hydrocarbures est exprimée en volume (ng/l). On n'a détecté des HAP d'alcoyle que dans les fleuves Coppermine et Hayes, ce qui indique qu'il y a peu ou pas d'hydrocarbures pétroliers dans les petits fleuves. Cette absence d'apport pétrogénétique est probablement le seul facteur prépondérant qui explique les différences de concentration en HAP entre le Mackenzie et les autres fleuves de l'Arctique. Des échantillons particulaires en provenance du Mackenzie et de tous les petits fleuves présentent une composition en alcanes résolue plus élevée avec une prédominance impaire-paire bien définie qui laisse entendre une source en matières terrestres provenant de plantes supérieures. Les échantillons de sédiments (en suspension ou du fond) du delta et de la plate-forme du Mackenzie contiennent des concentrations en HAP qui dépassent les limites fixées par les lignes directrices provisoires de qualité des sédiments pour la protection de la vie aquatique. On ne connaît pas pour le moment l'incidence de ces concentrations élevées d'HAP sur les biotes.

Sources and significance of alkane and PAH hydrocarbons in Canadian arctic rivers

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Key Words: PAH, alkane, petroleum, water quality guideline, sediment quality guideline, hopane, sterane, arctic rivers

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Abstract

Hydrocarbon measurements have been made on dissolved and particulate samples collected in 1987, 1993 and 1994 from the Mackenzie River delta and in 1993 for 10 smaller northern rivers that drain into the Canadian Archipelago or Hudson's Bay. The Mackenzie River has proved to be both spatially and temporally variable in hydrocarbon concentration. During summer the alkane and PAH (polycyclic aromatic hydrocarbon) content of suspended particulate in the Mackenzie River is sufficiently homogenous to use the SPM (suspended particulate matter) load to estimate hydrocarbon load. The Mackenzie River appears to transport a compositionally uniform mixture of particulate PAH, derived mainly from petrogenic sources and containing small (2- and 3-ring) and multi-ring (4- to 6-ring) PAHs which, according to their methylphenanthrene, hopane and sterane ratios, have similar hydrocarbon sources and maturity. Immature bitumens and shales from the Devonian Canol formation that outcrop into the lower Mackenzie river valley are most likely the principal petroleum source to the river. The ten smaller rivers have mean suspended particulate alkane concentrations (ng/g) similar to the Mackenzie River during summer, but PAH concentrations are approximately 10 times lower for the parent PAHs and 100 times lower for alkyl PAHs. The difference between the smaller rivers and the Mackenzie is exacerbated when hydrocarbon concentration is expressed volumetrically (ng/L). Alkyl PAHs have not been detected except in the Coppermine and Hayes Rivers indicating little or no petroleum-related hydrocarbons in the smaller rivers. This lack of petrogenic material is likely the single most important factor contributing to PAH concentration differences between the Mackenzie River and other arctic rivers. Particulate samples from the Mackenzie River and all smaller Canadian rivers have a resolved higher alkane pattern with a well-defined OEP (odd-even predominance) consistent with a major source in terrestrial, higher plant material. Sediment samples (suspended and bed) from the Mackenzie delta and shelf have natural PAHs concentrations that exceed interim sediment quality guidelines for the protection of aquatic life. What effect these elevated PAH concentrations may have on exposed biota is not presently known.

Introduction

Assessing and predicting the contaminant load carried by rivers is fundamental to understanding the processes of contaminant transport to the Arctic marine environment. Northward flowing rivers drain 10^7 km^2 of northern Asia, northern Europe and North America and discharge about 3300×10^9 m^3 of water into the Arctic Ocean each year (Aagaard and Carmack, 1989). Northern rivers, which integrate widespread atmospheric contaminant deposition and point sources, have the potential to serve as major conduits of contaminants to the Arctic Ocean.

Prior to this study, hydrocarbon loadings to the Arctic Ocean from North American rivers could be estimated only by reference to studies conducted in the Mackenzie River delta in 1987 (Yunker et al., 1991b; Yunker et al., 1993; Yunker and Macdonald, 1995). The similarity in hydrocarbon composition between samples from the Mackenzie delta and the contiguous shelf established the Mackenzie River as the primary source of terrigenous debris and petrogenic hydrocarbons to the shelf (Yunker et al., 1993; Yunker et al., 1995). The hydrocarbons included the higher plant *n*-alkanes (C_{23}-C_{33}), the primarily petrogenic lower *n*-alkanes (C_{15}-C_{19}), isoprenoids (e.g., pristane and phytane) and diagenetic hopanes, and PAHs (polycyclic aromatic hydrocarbons) with mixed petrogenic and combustion origins (Yunker et al., 1993).

The Mackenzie is the largest single source of sediment to the Arctic Ocean (Carson et al., 1998; Macdonald et al., 1998) and fourth largest in discharge (Milliman and Meade, 1983; Brunskill, 1986; Macdonald and Thomas, 1991). It has an extensive, diverse, drainage basin (1.8×10^6 km^2) with large headwater lakes and many different tributaries (Brunskill, 1986). The interannual variability in the freshwater discharge (± 25%) and sediment loading are large and require long time series to determine accurately (Carson et al., 1998; Macdonald et al., 1998; Macdonald, 2000).

Given the large interannual variability of the Mackenzie River, there is a need to establish whether there are relationships between SPM, flow and hydrocarbon composition that can be used to provide more robust estimates of hydrocarbon loading. Furthermore, because the Mackenzie River is exceptionally turbid and because it drains vast and varied ecozones that extend far to the south, it provides a dubious proxy for the many smaller, truly arctic rivers in the Northwest

Territories (NWT) and Nunavut. These smaller rivers are likely to differ in the strength and sources of hydrocarbons, as well as in the degree of partitioning between solid and dissolved phases. To address these issues, this work uses hydrocarbon data collected in 1987 for the Mackenzie River and in 1993 and 1994 for the Mackenzie River and ten smaller northward-flowing Canadian rivers. Whereas the Mackenzie River drains directly into the Arctic Ocean, the smaller rivers drain either into the Canadian Archipelago (Coppermine, Burnside, Ellice, Back and Hayes Rivers) or Hudson Bay (Lorillard, Quoich, Thelon, Dubawnt and Kazan Rivers; Figure 1). The combined annual flow of these smaller rivers is approximately 113×10^9 m^3, which is about 33% of the Mackenzie River flow (Macdonald et al., 2000).

Here, we present concentration and composition data for alkanes and PAHs in suspended particulate and dissolved phases of northern rivers. We compare the hydrocarbon geochemistry of these two classes of compounds, infer their source, and characterize their loading to the arctic marine environment. We then discuss the likelihood of PAH-induced biological effects in these rivers by comparing the observed concentrations with interim Canadian water and sediment quality guidelines for the protection of aquatic life.

Methods

Sample Collection

1987 Samples

Mackenzie River suspended particulate samples were collected in the three principal channels of the outer delta (East, Middle and Reindeer) during the June and July freshet (spring flood) in 1987 (Yunker et al., 1990; Yunker et al., 1991b; Yunker et al., 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; nominal pore size 2.7 and 0.7 μm respectively) and by integrated collection over 1 to 3 days using a continuous flow centrifuge. Samples were also obtained by direct filtration from under the ice at Station 1 in the nearshore Beaufort Sea (off the East channel) in late winter, early spring and late spring (salinity = 0 in all cases), and from the mouth of the East channel in late summer (Yunker and Macdonald, 1995). In June and July concurrent dissolved phase hydrocarbon samples were obtained by passing 0.7 μm filtered water

through Chromosorb T Teflon resin (Manville Corp.) columns using Seastar *in situ* water samplers (Green, 1986; Yunker et al., 1994). Dissolved phase sample volumes were 306 ± 109 L (mean ± SD) with a range of 203-446 L (n=6). Preparation and blank characteristics of the Chromosorb T columns have been described (Yunker et al., 1989). All wetted surfaces for the collection of both particulate and dissolved samples 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 Ponar (0.06 m^2; Station 1) and Smith-McIntyre (0.12 m^2; Stations 4 and 5) grab samplers.

1993 and 1994 Samples

The 1993 and 1994 Mackenzie River samples were collected at mid-channel sites just before the delta at the confluence of the Arctic Red River near to the town of Tsiigehtchic (formerly Arctic Red River), in the middle delta along the east channel near the town of Inuvik, and along the west channel near Aklavik (Figure 1). These locations have been designated Arctic Red, Inuvik and Alkavik, respectively. Samples were collected by pumping from 1m depth during both high flow conditions (June to September in both years) and low flow conditions (March of 1994 only). Gram quantities of SPM were obtained using a stainless steel Alfa-Laval continuous-flow centrifuge with a pump rate of 4 L/min. Dissolved phase samples were obtained by collecting the centrifugate in multiple 18 L stainless steel tanks. The number of tanks collected (normally 2 to 6) was defined by the total volume required to complete the chemical analyses. All wetted surfaces of the sampling equipment, transfer utensils, etc. were Teflon, glass, aluminum or stainless steel that had been appropriately cleaned with organic solvents to minimize sample contamination.

Sediment samples from four lakes in the Mackenzie delta were obtained from the central part of each lake in March 1994 using a Browns corer pushed into the lake bottom using a pole attached to the corer (Graf Pannatier, 1997). Samples were collected through a hole drilled through the ice with an ice auger and were kept from freezing until subsampling in the laboratory. The ice did not reach the lake bottom at any of the locations sampled. The core diameter was 6.7 cm and the core length differed in each lake (11 cm in Lake 5, 21 cm in Lake 6, 31 cm in Lake 3 and 35 cm in Lake 7). Cores were sectioned into slices of 2 cm thickness, except for the surface sample (1 cm).

The arctic rivers in the NWT and Nunavut were accessed by air during July, 1993 when they were on the descending limb of the annual spring melt hydrograph. All sampling sites were at or near Water Survey of Canada gauging stations (Figure 1). Samples of SPM were obtained by filtration through pre-combusted, solvent-washed GF/C filters (nominal pore size 1.2 μm). Filtrate samples (108 L representing the dissolved phase) were collected in stainless steel tanks like those employed for the Mackenzie samples. The same precautions were also used to minimize sample contamination.

Analytical Methods

1987 Samples

Methods of sample extraction and analysis have been reported in Yunker *et al.* (1990; 1991b; 1992). Briefly, prior to extraction samples were spiked with an internal surrogate standard mixture containing 13 perdeuterated *n*-alkanes and PAHs. Samples were digested in methanol/NaOH at 55 °C for 4 h, washed with methanol and extracted on a shaker table with dichloromethane/methanol (9:1). The alkane standards were [$^2H_{26}$]dodecane, [$^2H_{50}$]tetracosane and [$^2H_{74}$]hexatriacontane. The PAH standards used for quantification spanned the range of PAHs quantified and included [$^2H_8$]naphthalene, [$^2H_8$]acenaphthylene, [$^2H_{10}$]acenaphthene, [$^2H_{10}$]anthracene, [$^2H_{10}$]pyrene, [$^2H_{12}$]chrysene, [$^2H_{12}$]benzo[*k*]fluoranthene, [$^2H_{12}$]benzo[*a*]pyrene, [$^2H_{14}$]dibenz[*a,h*]anthracene and 1-methyl[$^2H_{10}$]naphthalene. Sample extracts were separated into fractions on a 1 × 10 cm silica gel column using pentane (3 × 1 mL) and the column was eluted first with pentane (25 mL) and then dichloromethane (18 mL) to obtain the F1 (alkanes, hopane triterpanes) and F2 (PAHs) fractions. Samples were analysed 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.

The PAHs quantified are listed in Table 1. For the original quantification of the 1987 samples, concentrations of 2-methylnaphthalene and 2,6/2,7-, 1,3/1,7- and 1,6-dimethylnaphthalene were referenced to 1-methylnaphthalene and concentrations of 3-, 2-, 9/4-, and 1-methylphenanthrene were calculated based on an average response factor for phenanthrene and 2,6/3,5-dimethylphenanthrene (Yunker et al., 1992). When the 1993 and 1994 samples were analysed a

much larger number of alkyl PAH standards were available for determination of alkyl PAH concentrations. Because the response factor ratios for the 1993/1994 data set exhibited little variation (2.1 % relative SD for 2-methylnaphthalene and 5.8 % for 2,6/2,7-, 1,6-, 2,3/1,4-, 1,5- and 1,2-dimethylnaphthalene relative to 1-methylnaphthalene, and 3.0 % for 2- and 1-methylphenanthrene relative to phenanthrene; n=9 for all) despite much larger variations in the actual response factors, these ratios could be used to obtain better concentration estimates for the 1987 samples. Accordingly, these response factor ratios have been used to recalculate concentrations of 2-methylnaphthalene and of the four monomethylphenanthrenes, and to extend quantification to all of the dimethylnaphthalenes.

1993 and 1994 Samples

Suspended sediment samples were soxhlet extracted using an azeotropic mixture of hexane/acetone (300 mL) in the presence of activated copper to remove sulfur. Lake sediments were freeze-dried and then soxhlet extracted with dichloromethane (300 mL) for 18 hours with activated copper. Prior to extraction, samples were spiked with an internal surrogate standard mixture containing [$^2H_8$]naphthalene, 1-methyl[$^2H_{10}$]naphthalene, [$^2H_8$]acenaphthylene, [$^2H_{10}$]acenaphthene, [$^2H_{10}$]fluorene, [$^2H_{10}$]anthracene, [$^2H_{10}$]pyrene, [$^2H_{12}$]chrysene and [$^2H_{12}$]benzo[*a*]pyrene. Water samples were extracted with dichloromethane using a Goulden Large Sample Extractor (Goulden and Anthony, 1985) and spiked with the same internal surrogate standard. Sediment and water extracts were dried with Na_2SO_4, concentrated using Rotary evaporation, base washed with 10M NaOH, re-dried, solvent exchanged with hexane, concentrated, and separated into two fractions using a silica gel column (35 × 1.2 cm). The column was first eluted with hexane (50 mL) and then with dichloromethane/hexane (1:1, 50 mL) to obtain F1 (alkanes) and F2 (PAHs), respectively.

Identification and quantitative determination of the *n*-alkanes involved use of a HP-5MS capillary column in a Hewlett-Packard 5971 GC-MSD operated in Selected Ion Monitor mode. A 2 μL sample was injected in splitless mode with a time delay of 1.25 minutes after injection. The initial oven temperature of 50°C was held for 2 minutes and then programmed to increase by 50°C/min to 100 °C; held again for 2 minutes, increased again at 6°C/min to 300°C, and held for a further 10 minutes. The injector temperature was 250°C and the transfer line was 280°C. The

carrier gas was helium with an initial column head pressure of 15 psi. The system was equipped with Electronic Pressure Control and operated in constant flow mode. The detector filament and the multiplier were turned on at 6 minutes. GC conditions for determination of PAHs were identical to those for the *n*-alkanes except for the temperature program. The initial oven temperature of 60°C was held for 2 minutes and then programmed to increase by 10°C/min to 150 °C, followed by an increase at 3°C/min to 280°C, then 10°C/min to 300°C and finally held for 5 minutes. Quantification was achieved using a single point calibration (external standard mix injected after every tenth sample with updating of instrument retention times and responses).

All sampling and analytical replicates have been averaged before producing the concentration summaries in Tables 2 and 3.

Corroborative Analyses

Sediments from six core sections (one in duplicate) from the four lakes in the Mackenzie delta were also analysed for PAHs by Axys Analytical Services Ltd. of Sidney, B.C. This laboratory has performed most of the recent PAH analyses for sediment samples from the Arctic Ocean, and their methods provide good agreement in PAH concentrations and distributions with the 1987 Mackenzie River/Beaufort Sea samples (Yunker et al., 1996 and unpublished). Analyses included the perdeuterated surrogate standards [$^2H_8$]naphthalene, [$^2H_{10}$]acenaphthene, [$^2H_{10}$]phenanthrene, [$^2H_{10}$]pyrene, [$^2H_{12}$]chrysene, [$^2H_{12}$]benzo[*a*]pyrene, [$^2H_{12}$]perylene, [$^2H_{14}$]dibenz[*a,h*]anthracene, [$^2H_{12}$]benzo[*ghi*]perylene, and 2-methyl[$^2H_{10}$]naphthalene. Samples were spiked with surrogate standard, ground with anhydrous sodium sulphate, packed into a column and eluted with methanol (150 mL) followed by dichloromethane (250 mL). The eluate was backwashed with sodium hydroxide solution followed by extracted water and dried over anhydrous sodium sulphate. The extract was concentrated in a Kuderna-Danish flask, activated copper added and transferred onto a silica gel column (Biosil, 10 g; 5% deactivated). The column was eluted first with pentane (25 mL, alkane fraction) and then dichloromethane (25 mL, PAHs). Analyses used multiple ion detection (MID) mode, a Finnigan Incos 50B GC/MS with a Varian 3400 GC and a Restek Rt_X-5 column (0.25 mm i.d./0.25 μm film) and helium carrier gas. A minimum of two ions were acquired for each target analyte and surrogate standard.

For the six samples the average difference between laboratories was 49 ng/g (range 2-108 ng/g) for the Σ 178-278 parent PAH total and 160 ng/g (3-240 ng/g) for the alkyl PAHs. These concentration differences are generally within one SD of the mean concentration for the suspended particulate and sediment samples (Tables 2 and 3).

Results and Discussion

Physical Setting

The dominant hydrologic feature of arctic rivers is the large contrast between freshet (May, June, July) when over 30% of the annual discharge may occur in a single month, and winter inflow, which contributes only 5 – 10% of the total annual flow (Macdonald et al., 2000). Freshet for the Mackenzie River is less extreme than it is for smaller, genuinely arctic rivers because the Mackenzie contains three large headwater lakes (Lake Athabasca, Great Slave Lake and Great Bear Lake) whereas the smaller rivers often freeze entirely during winter and discharge almost all of their annual moisture accumulation during a brief spring thaw. For most northern rivers the bulk of the suspended solid transport occurs in association with the spring freshet. For example, the Mackenzie River discharges about 70% of the freshwater between May and September (Figure 2) and more than 90% of the particulate is delivered during June, July and August. Beginning in mid-May the Mackenzie River increases dramatically from low, winter flow to maximum flow within a few weeks, and thereafter flow decreases gradually to winter levels by the end of November. SPM concentrations are low (typically ca. 2 mg/L) in winter, but increase dramatically with river flow in the approach to freshet and exhibit large variance related to episodic flow "events" in the drainage basin (Yunker et al., 1995; Carson et al., 1998; Macdonald et al., 2000).

Flow variations in the Liard River and smaller tributaries in the Cordillera Mountains of the western part of the drainage basin are largely responsible for the flow variability of the Mackenzie River. This region contains a large amount of erodible surface material and a deeper active layer than the Pre-Cambrian Shield rock and tundra terrain characteristic of the east side of the river (Brunskill, 1986; Carson et al., 1998). As might be expected from the large relief of the Cordillera (elevations 2000 - 2500 m), rivers here are characterised by higher total dissolved

solids and suspended sediments than rivers to the east (e.g., Milliman and Syvitski, 1992). As a result, most of the water and sediment that passes through the Mackenzie delta originates in the Cordillera rivers downstream of Great Slave Lake (Brunskill, 1986; Carson et al., 1998).

For the years when hydrocarbon data were collected (1987, 1993 and 1994), summer Mackenzie River flows at Arctic Red River were generally below average (estimated at $2.5 \pm 0.3 \times 10^{11}$ m^3 for1973-1994; mean ± SD), but the onset of freshet was earlier in 1993 and 1994, and the maximum flow was noticeably above average in 1993 (Figure 2). Cumulative flow from May to November decreased in the order of 1993 to 1987 to 1994 (2.4, 2.3 and 2.2 x 10^{11} m^3, respectively). The annual flows for all three years were within 1 SD of the 1973-1994 average flow, but only 1993 fell within the 95% confidence limit of the mean flow ($2.5 \pm 0.12 \times 10^{11}$ m^3). Annual inputs of fine sediment (<0.125 mm; fine sand, silt and clay) to the Mackenzie delta were also below the 1974-1994 average (124 ± 42 Mt) in these years, with 1993 being the closest to the average, followed by 1987 and then 1994 (113, 85 and 79 Mt, respectively; Carson et al., 1998). Only the sediment load in 1993 was within the 95% confidence limit for the 1974-1994 load (124 ± 19 Mt).

The Mackenzie River is the predominant source of fine sediment to the delta, providing an average of 96 Mt during the period 1974-1994 (Carson et al., 1998). The Arctic Red and Peel Rivers (Figure 1) each contribute an additional 7.3 and 21 Mt of suspended sediment, respectively, for a cumulative average of 124 Mt for the May to October period (Carson et al., 1998). In the Mackenzie River the peak sediment load occurs in June, coinciding with peak flows in the Liard River (Carson et al., 1998). The Mackenzie River load remains high from May through August, however, while the majority of the sediment input from the Arctic Red and Peel Rivers is confined to May and June.

The Inuvik station and the three outer delta stations primarily receive sediment from the Mackenzie and Arctic Red Rivers (Figure 1). Approximately 85% of the water and 73% of the sediment supplied to the head of the delta by the Mackenzie, Arctic Red and Peel Rivers flows past the East, Middle and Reindeer Channel locations that were sampled in 1987 (Carson et al., 1999). In the mid-delta (between Inuvik and Aklavik), 87% of the suspended sediment load passes through the Middle Channel. In the southwestern delta and at Aklavik the Peel River

provides most of the suspended particulate, but the Mackenzie River also contributes a portion of the suspended sediment. The Mackenzie River portion can be expected to increase at Aklavik as the Peel River contribution declines after the end of June. Most of the sediment that discharges into Shallow Bay on the west side of the delta originates in the Peel River (Carson et al., 1999).

During summer, SPM concentrations are generally highest at Arctic Red River (where the Mackenzie River is still contained in one channel) and generally decrease after the river has split into multiple channels in the delta (Table 2). The 1993 suspended particulate samples contained mostly silt (4.8 – 46.9%) and clay (53.1 –94.8%), with only a small amount of sand (0.01 – 2.4%). Overall the clay content was consistently lowest at the Arctic Red station (60.8 – 62.1%), and was generally higher but more variable at Inuvik (77.3 – 94.8%) and Aklavik (53.1 – 84.7%). At Inuvik the clay content was lowest in June and highest in September, while at Alkavik the clay content was highest in July and lowest in September. At all three locations the highest sand content was observed at the sampling time closest to freshet. No particle size data are available for 1987 or 1994.

While flow rates and concentrations of suspended solids often correlate (due to resuspension of fine-grained bottom sediment with increasing discharge), very large systems such as the Mackenzie River exhibit more complex behaviour because various tributaries deliver SPM at different times and locations relative to the delta (Macdonald et al., 2000). Because local rainstorms in summer and fall can cause floods that rival spring snowmelt (Brunskill, 1986), sediment transport is episodic and SPM concentrations at a given time can vary widely between the different Cordilleran rivers. As a result, while the log of the SPM increases with river flow at the Arctic Red River confluence in most instances (Figure 3), high SPM concentrations (i.e., > 500 mg/L) can also occur at much lower flows than would be predicted by a log SPM *vs.* flow model. Hence, the transport of particle-associated compounds such as hydrocarbons can not be predicted simply from river flow.

The lakes sampled in the middle and outer Mackenzie Delta (Figure 1) are permanently connected to the main river by small distributary channels (Graf Pannatier, 1997). While these lakes generally remain turbid throughout the open water season (due to regular input of sediment), most of the sediment input occurs during annual flooding as part of the spring freshet. These lakes, therefore, can collect hydrocarbons directly from the atmosphere or from

productivity in the lake as well as receive sediments and organic material at least seasonally from the Mackenzie River.

In Lake 7 in the middle delta (Figure 1), sediments exhibit annual varves that are consistent with the ^{137}Cs profile, indicating that the lake has received continuous sediment deposition with little or no disturbance post-deposition (Graf Pannatier, 1997). In Lake 6 the annual varves are absent, but the ^{137}Cs downcore profile and total inventory indicate continuous sedimentation, suggesting that surface mixing has occurred in the lake with little or no sediment loss. Hence, for these two lakes the surface sediments would only contain material deposited during the 1993 open-water season. In contrast, sediments in Lakes 3 and 5 in the outer delta have well defined ^{137}Cs profiles, but the sedimentation rates are lower than in the middle delta (Table 3) and the total ^{137}Cs inventories are lower than expected from atmospheric deposition. Because sill elevations are lower for lakes in the outer delta, it is likely that frequent erosional losses of sediment from the lakes have occurred during storm surges or periods of heavy rain. Graf Pannatier (1997) has estimated that an average of 50% of the sediment has been removed post-deposition from the lakes in the outer delta, hence the cores from these lakes may be less reliable for the interpretation of hydrocarbon profiles than the two continuous cores from the middle delta.

Physical characteristics of the ten smaller NWT and Nunavut Rivers have been less intensively studied than the Mackenzie River. The terrain between the Mackenzie River and Hudson Bay is predominantly comprised of Pre-Cambrian Shield rocks and tundra with a shallow active layer (Brunskill, 1986; Carson et al., 1998). As a result the rivers draining the tundra, including those underlain by the Shield, are characterized by low total dissolved solids and suspended sediments (Brunskill, 1986; Macdonald et al., 2000).

In 1993 the peak water discharge occurred in June for eight of these rivers. Most of the flow occurred in a brief pulse in the Burnside, Ellice, Back, Quoich and Thelon Rivers, while the discharge declined more slowly throughout the summer in the Coppermine, Dubawnt and Kazan Rivers. Flow data are not available for the other two rivers for 1993, but historically (1973-1992) the peak water discharge has occurred in late June or early July. From 1990-1992 the Hayes consistently exhibited a brief pulse, while flow in the Lorillard River declined more slowly after freshet. For logistical reasons sampling in these rivers had to occur after the spring freshet with the result that the major flux of SPM could already have passed before sampling. At

the time of sampling (July 20-22) SPM concentrations in most of the rivers were ca. 1 mg/L, which is essentially equivalent to the Mackenzie River in winter. SPM concentrations in the Coppermine, Ellice and Hayes Rivers (8.4 to 26 mg/L) were noticeably higher, however (Table 4).

Hydrocarbon Concentrations on Suspended Particulate and Sediment

Mackenzie River

Hydrocarbon concentrations can be expressed either as the concentration on the suspended particulate itself (ng/g) or the concentration of particulate hydrocarbon in the river (ng/L). On either basis there is no discernible relationship between alkane and PAH concentration data for the Mackenzie River and the sampling location (Station 1, East, Middle and Reindeer channels stations in the outer delta, Inuvik, Aklavik or Arctic Red stations; Figure 1) or the season (with samples from all locations from March/April, June, July and August/September grouped together). This lack of correlation suggests that the above-mentioned decline in sediment input from the Arctic Red and Peel Rivers after the end of June has had little influence on hydrocarbon concentrations in the delta.

A relationship does emerge when samples are grouped by year and date of sampling (Figures 4 and 5). Expressed either as ng/g on the particulates or ng/L in the water, alkane and PAH concentrations are low in late winter (March and early April), when the Mackenzie River flow and SPM are still low, and are generally much higher in spring and summer (May-September), when river flow and SPM are high (Table 2). The post-freshet elevation in hydrocarbon concentration is particularly apparent for the ng/L data (Figures 4 and 5).

Post-freshet total alkane concentrations on suspended particulate are comparable in 1987 and 1994, but are much lower in 1993 (Figure 4). Total PAH concentrations are also lowest in 1993, but 1994 concentrations are only slightly lower than in 1987 (Figure 5). The same alkane and PAH relationships between years are maintained if particulate concentrations are expressed on a µg/g organic carbon (OC) basis (Table 2). On a volume basis the post-freshet mean concentrations of total alkanes and PAHs transported by the river are highest in 1994, lowest in 1993 and intermediate in 1987 (Figures 4 and 5).

There is very little difference in mean ng/g concentrations of alkanes and PAHs (i.e., totals, lower and higher alkanes, parent and alkyl PAHs) between sediment from lakes in the middle and outer delta and in the nearshore Beaufort Sea and post-freshet suspended particulate from the Mackenzie River in 1987 and 1994 (Tables 2 and 3). Furthermore, concentration ranges for delta and marine sediment are almost entirely within the ranges for Mackenzie River suspended particulate for each hydrocarbon class and there are no systematic trends downcore in the lake sediments despite large variations in the sediment accumulation rate (Table 3) and regime (Graf Pannatier, 1997).

Mean concentrations do generally decrease from river particulate, to the middle and then the outer delta lakes, and then to Beaufort Sea sediment, but the differences are not significant (Table 3). On a μg/g OC basis, mean concentrations in the lake sediments also are not significantly different from the means for 1987 and 1994 suspended particulate (Tables 2 and 3). This similarity of hydrocarbon concentrations is evidence of the source-sink connection between the Mackenzie River and the lakes, which become flooded by the Mackenzie each summer, and the Beaufort Shelf, which receives the bulk of its sediments from the river (Yunker et al., 1991b; Macdonald et al., 1998).

Based on the lake sediment core data, the low concentrations observed in 1993 for Mackenzie River suspended particulate are not representative of the recent history of the river, particularly for the alkanes (Tables 2 and 3). The anomalously low hydrocarbon concentrations observed in 1993 were not accompanied by any change in the alkane and PAH distributions and therefore appear to reflect simple dilution. Possible explanations could include, therefore, larger than usual inputs of particulates from an inorganic source (e.g., glacial till), larger river flow at freshet (Figure 2), or an unusually large contribution of sediment from a tributary impoverished in organic material.

When alkane and PAH data for all three years are pooled, the ng/L hydrocarbon concentrations in the Mackenzie River exhibit a linear correlation with SPM ($p < 0.001$, $\nu = 34$; Figure 6). Yunker *et al.* (1991b) previously observed this relationship in the 1987 data, but within a much lower SPM range, and Fernandes and Sicre (2000) have recently described a correlation between *n*-alkane concentrations and OC and SPM values in the Ob' and the Yenisei Rivers. In the Mackenzie the higher alkanes and alkyl PAHs produce a much better correlation with SPM (r^2 =

0.79 and 0.72, respectively) than do the lower alkanes and Σ 178-278 parent PAHs ($r^2 = 0.57$ and 0.54, respectively), which suggests that higher plant debris and petroleum components are more strongly associated with suspended particulate material than are the lower alkanes or parent PAHs. Correlations between these parameters and OC are very poor ($r^2 = 0.079 - 0.089$), however, suggesting that the simple relationship between soil erosion and riverine hydrodynamics inferred for the Ob' and the Yenisei Rivers (Fernandes and Sicre, 2000) does not extend to the Mackenzie River.

Smaller NWT and Nunavut Rivers

Suspended particulate in the ten smaller rivers has mean ng/g concentrations of the lower and higher alkanes that are similar to the Mackenzie River during summer, but PAH concentrations are approximately 10 times lower than in the Mackenzie for the parent PAHs and 100 times lower for alkyl PAHs (Table 2). There is also considerable concentration variation between the individual rivers: total alkane concentrations range from 1190 ng/g in the Coppermine River to 51,000 ng/g in the Back River, while total PAH concentrations range between 8.0 ng/g in the Hayes River to 250 ng/g in the Kazan River. Limited published data for other arctic rivers suggests that this range of PAH concentrations is comparable to that observed in the large Siberian rivers (Fernandes and Sicre, 1999). Suspended particulate concentrations for a slightly reduced set of PAHs (Σ 178-278 parent PAHs plus the methylphenanthrenes but not the methylnaphthalenes) range from 7 to 103 ng/g in the Ob' River estuary and from 24 to 444 ng/g in the Yenisei River estuary. As well, unpublished concentration data cited by Fernandes et al. (1999) for the Lena River are comparable to those for the Ob' and the Yenisei Rivers.

Hydrocarbon data exhibit slightly less variability for the smaller Canadian rivers when expressed on an organic carbon or a volume basis, but a much larger concentration difference between these smaller rivers and the Mackenzie River emerges when data are expressed in these units (Table 2). The concentration order for the rivers also shifts with the change in units (and frequently with the hydrocarbon parameter). For example, on a volume basis the total alkane concentrations now range from 3.4 ng/L in the Kazan River to 56 ng/L in the Back River, while total PAH concentrations range between 0.03 ng/L in the Quioch River and 0.6 ng/L in the Coppermine River. On a volume basis the highest suspended particulate PAH concentration for the smaller Canadian rivers is less than for the Eurasian Rivers: concentrations range from 0.1 to

2.2 ng/L in the Ob' estuary and from 0.1 to 3.2 ng/L in the Yenisei estuary (Fernandes and Sicre, 1999).

The various rivers exhibit large variations in flow, SPM, particulate alkane concentration and the percentage of the SPM that is organic carbon (Tables 2 and 4). The large variation in organic carbon content of the suspended particulate (1.47% of the SPM in the Coppermine River to 73.7% in the Quoich River) is particularly noticeable. The rivers that drain into the Archipelago exhibit the largest differences in higher alkane concentration: the Coppermine and Hayes Rivers have the lowest concentrations (670 and 1200 ng/g, respectively), the Ellice and Burnside Rivers are intermediate and the Back River has the highest concentration (45,000 ng/g), whereas for Chesterfield inlet and Hudson Bay, the Kazan River is lowest (2100 ng/g), the Lorillard, Quoich and Thelon Rivers are intermediate and the Dubawnt River is highest (27,000 ng/g).

There is no apparent relationship between river flow or length of time since freshet at sampling and the SPM, carbon or alkane concentrations (Table 4). However, higher plant alkane concentrations generally increase with the percentage carbon (particularly for the rivers flowing into the Archipelago), suggesting that a large portion of the particulate with high carbon content is plant detritus (Eglinton and Hamilton, 1967; Meyers and Ishiwatari, 1993). The rivers flowing into Hudson Bay generally flow through more vegetated areas (Wedel, 1992), and these rivers generally have higher concentrations of both carbon and the higher plant *n*-alkanes (Table 4). For the rivers that drain into the Archipelago, the highest alkane concentrations are coincident with the highest parent PAH concentrations (Back and Burnside Rivers. 210 and 160 ng/g, respectively). For the rivers that drain into Hudson Bay however, the Kazan River has the lowest alkane concentration, but the highest PAH concentration (250 ng/g).

Alkyl PAHs are only detectable in suspended particulate from the Coppermine (15 ng/g) and Hayes (0.27 ng/g) Rivers. This lack of alkyl PAHs is likely the single most important factor contributing to PAH concentration differences between the Mackenzie River and other arctic rivers (this work and Fernandes and Sicre, 1999).

Hydrocarbon Concentrations in the Dissolved Phase

Mackenzie River

A full assessment of the quantity of hydrocarbons transported by a river must include dissolved-phase hydrocarbons. Due to operational limitations of the sampling, however, the "dissolved phase" includes hydrocarbons that are truly dissolved as well as hydrocarbons that are contained on fine and colloidal particles that have passed through the filter (1987 samples) or centrifuge (1993 and 1994 samples) used to remove larger particulate (Yunker et al., 1994).

Various methods (solvent extraction, filtration and column exchange, centrifugation) have been used to estimate dissolved hydrocarbon load for the Mackenzie River. Comparison between data produced using these methods is made difficult because the quantity of lipid assigned to the "dissolved and colloidal" phase highly depends on the procedure used to collect the sample (e.g., Gómez-Belinchón et al., 1988; Yunker et al., 1991a; Yunker et al., 1994; Gustafsson et al., 1996; Gustafsson and Gschwend, 1997). In general methods that use resin column extraction tend to undersample colloidal material because the exchange of lipid from the very fine particulate and colloidal material to the dissolved phase is slow in comparison to the residence time of the water sample in the column. In contrast dichloromethane extraction will often produce a sample where the fine particulate and colloidal phases have made a substantial contribution.

For the Mackenzie River, dissolved PAH concentrations estimated by solvent extraction in 1993 and 1994 are generally about 10 times higher than the concentrations estimated by resin column adsorption in 1987 (Table 5). Higher alkane concentrations are about twice as high in 1993 than in 1987, while the lower alkanes are about 20 times higher in 1993. Concentration ranges overlap (or nearly overlap) for the different compound classes. Concentration ranges for resin column *vs.* solvent extraction are, respectively, 0.5-9.9 and 9.8-140 ng/L for the lower alkanes, 7.6-35 and 21-85 ng/L for the higher alkanes, 0.6-1.6 and 2.9-38 ng/L for the Σ 178-278 parent PAHs, and 1.1-10 and 12-280 ng/L for the alkyl PAHs. The high alkyl PAH concentration (and SD) for the March 1994 samples (Table 5) is due to high concentrations of the monomethylnaphthalenes (250 and 78 ng/g) in the two samples from the Arctic Red station (naphthalene was also high in these samples, 240 and 83 ng/g, respectively).

With resin column extraction, hydrocarbons in the dissolved phase were a small fraction of the total hydrocarbon (Table 5), making only a small contribution to the total flux (Yunker et al., 1991b). With solvent extraction however, the dissolved phase was a significant fraction of the total flux in summer 1993 and March 1994, but was much lower for the post-freshet samples from 1994 (Table 5). The high dissolved phase contribution during March 1994 is to be expected given the low SPM during late winter, but the elevated summer 1993 values are harder to explain. However, if the 1993 dissolved fraction concentrations are referenced to the more typical summer 1994 particulate phase concentrations (see above), then the post-freshet contribution of PAHs to the dissolved phase is comparable in 1993 and 1994 (percentages in brackets in Table 5).

The centrifuge method, used for suspended particulate sampling in 1993 and 1994, efficiently removes coarse and high density particulate (estimated at >90% of mineral particles >0.45 μm; Envirodata, 1987) but is less efficient for fine and low density particulate. The stacked GF/D and GF/F glass fibre filter method used in 1987 removes most particles > 0.7 μm from dissolved fraction samples. Hence, compounds such as the higher plant *n*-alkanes which are strongly associated with terrigenous debris and coarse particles (Prahl and Carpenter, 1983; Yunker et al., 1994), exhibit the best agreement in concentration between the 1987 and 1993/94 samples (Table 5). In contrast the lower alkanes and the parent and alkyl PAHs are not confined to the larger particulate (Yunker et al., 1994), and the 10-20 fold increase in concentration with samples obtained by centrifuge most likely reflects higher amounts of fine, low density particles in the samples.

Smaller NWT and Nunavut Rivers

Solvent extraction produced comparable dissolved phase alkane concentrations in the Mackenzie River and the smaller Canadian rivers in 1993, while dissolved PAH concentrations were lower in the smaller rivers (Table 5). As with the ng/L particulate phase concentrations, the smaller rivers were homogeneous in dissolved phase concentration, but there is little correspondence in concentration trends between the two phases. Total alkane concentrations range from 55 ng/L in the Thelon River to 130 ng/L in the Lorillard River, while total PAH concentrations range between 13 ng/L in the Quioch River and 37 ng/L in the Back River. Because SPM

concentrations were very low in these rivers, the dissolved fraction was a high percentage of the hydrocarbon total (Tables 2 and 5).

Hydrocarbon Distributions

n-*Alkanes and Isoprenoids*

Because of their low susceptibility to microbial degradation compared to other types of organic matter, alkanes can be used to help establish the sources of organic matter in suspended particulate and sediments (Meyers and Ishiwatari, 1993). Freshwater and terrestrial biological systems typically produce two groups of odd-carbon alkanes: the algal alkanes (n-C_{17} with usually smaller amounts of n-C_{19} or n-C_{15}) and the plant wax alkanes (odd carbon alkanes from n-C_{23} to n-C_{33}, with a maximum at n-C_{27} or n-C_{29}; Eglinton and Hamilton, 1967; Meyers and Ishiwatari, 1993). During petroleum generation these basic distributions are modified by heat and pressure over geological time scales, to produce an alkane profile containing shorter chain length and even-carbon alkanes, as well as isoprenoids. Because organisms generally produce only the odd alkanes, the alkane odd-even predominance (OEP; Scalan and Smith, 1970) at n-C_{27} can provide a valuable indication of the amounts and freshness of biogenic components in sediments (Tables 2 and 3).

Alkane profiles for suspended particulate samples from the Mackenzie River, Mackenzie delta lakes, the Mackenzie shelf and the smaller Canadian rivers obtained in 1987, 1993 and 1994 have lower alkane (n-C_{13}-C_{20} plus pristane and phytane) and higher alkane (n-C_{21}-C_{34}) fractions that vary independently of one another. In most Mackenzie River and shelf samples the resolved, lower alkanes appear as a broad envelope of peaks that maximizes at n-C_{17}, pristane or n-C_{18} and has a petroleum origin (Yunker et al., 1993). Algal-related n-C_{17} appears as a prominent peak in a number of Mackenzie River suspended particulate samples (particularly those collected in July or September) and dominates the lower alkanes fractions in all samples from the smaller rivers. n-C_{17} is also the dominant alkane for all rivers except the Back River, indicating a substantial contribution of algal productivity to these samples.

Particulate samples from the smaller Canadian rivers all have a resolved higher alkane pattern with a well-defined OEP (Table 2) that is consistent with a major source in terrestrial, higher plant material (Eglinton and Hamilton, 1967). For five of these river samples an OEP could not

be calculated because the even carbon *n*-alkanes were undetectable. Most samples from the Mackenzie River and shelf also have a well defined OEP. A few Mackenzie River (Inuvik, July and September 1993 and March 1994; Arctic Red, March 1994) and smaller river (Back and Thelon Rivers) samples have a distinct predominance of n-C_{33} alkane, which suggests a large contribution of peat to the sample. The predominance of peat in winter samples from the Mackenzie River has been noted previously (Yunker et al., 1993).

The 1993 and 1994 samples of suspended particulate from the Mackenzie River generally have a lower OEP for the higher plant *n*-alkanes than the 1987 samples (Table 2). Part of this difference may be due to differences in water flow through the centrifuge: the 1993/1994 samples were collected using a flow of 4 L/min., while the 1987 samples were obtained by direct filtration or by using the centrifuge with a flow of 1 L/min. At lower flow rates a centrifuge traps lower density plant debris more efficiently and higher OEP values (comparable to those obtained by direct filtration) would result (cf. Yunker et al., 1993).

Four Mackenzie River suspended particulate samples that have particularly elevated higher alkane concentrations (Figure 4) have little or no OEP. The lack of an OEP is often an indication that recent inputs of oil have occurred, but none of these samples have a noticeable UCM (unresolved complex mixture). The UCM is a broad envelope that typically extends from phytane to n-C_{33} (usually centred near n-C_{25}) that is characteristic of petroleum (e.g., Wakeham, 1976). These four samples are Aklavik, March 1994 (higher alkanes 227,000 ng/g or 5500 ng/L), Arctic Red, June and July 1994 (higher alkanes 15,000 ng/L) and Inuvik, August 1994 (still has a small OEP but higher alkanes are 62,000 ng/g).

All suspended particulate samples collected in the Mackenzie River in 1993 have a visible UCM in m/z 57 ion alkane chromatograms, while the UCM is negligible or absent for samples collected in 1987 and 1994. An envelope also is present in two low-level samples obtained in March 1994 (Inuvik and Arctic Red), but a large portion of the envelope appears to be baseline noise, not an UCM. The 1993 samples from the Back, Burnside, Ellice and Dubawnt Rivers had an UCM, while the Quoich River did not. Most of the samples with an UCM also have a higher alkane OEP, indicating that petroleum present is highly weathered with few resolved alkanes to interfere with the higher plant alkane OEP. The reason for the differences in UCM content between years and sampling locations is not known.

The Mackenzie delta lake cores generally have an alkane OEP that is lower than in sediments of the nearshore Mackenzie shelf (Table 3). The OEP is most depressed (< 1.20) in a few sediment core sections from Lakes 7 and 3 that have markedly elevated concentrations of the higher alkanes (> 18,000 ng/g). This low OEP could indicate either a higher bacterial activity or a lower flux (or retention) of terrestrial higher plant debris in the lakes (Eglinton and Hamilton, 1967; Brassell and Eglinton, 1983). A third possibility is that inputs of petroleum hydrocarbons are higher in the delta lakes than in the nearshore marine regime. In support of this latter possibility, there is a significant trend in the lake cores for the OEP at C_{27} to decrease with increasing concentrations of the higher alkanes ($r^2 = 0.40$, $p < 0.001$, $\nu = 47$, log alkane *vs.* OEP; $r^2 = 0.69$ with one high OEP outlier removed), and all samples with higher alkane concentrations in excess of 10,000 ng/g have an OEP that is less than 1.3. Because higher alkane concentrations are all below this level in the nearshore sediments, this suggests either that the petroleum hydrocarbons tend to settle preferentially in the delta, and/or that they are degraded in the marine regime before they can accumulate in sediments. n-C_{17} is not elevated in near-surface core sections from the lakes, indicating that algal productivity is low.

In all seasons the dissolved phase samples collected by resin column extraction in the Mackenzie River in 1987 had a well defined OEP for the higher alkanes (Yunker et al., 1991a; Yunker et al., 1994; Table 5). Dissolved phase samples collected by solvent extraction in both the Mackenzie River and the smaller rivers in 1993 had on average no OEP, although some samples did have a small OEP (particularly at lower carbon number, centred at n-C_{23} and n-C_{25}). The 1993 samples also had much higher concentrations and proportions of the lower alkanes. Fine particulate samples collected in the Mackenzie River in 1987 also had a low OEP (Yunker et al., 1994), suggesting that fine particulate that has passed through the centrifuge is dominating the alkane profile for the 1993 samples.

n-C_{17} was present intermittently in the dissolved phase of Mackenzie River samples from all years and locations, but this algal alkane was evident in most of the samples from the smaller Canadian rivers. n-C_{17} could appear in the dissolved phase either from the lyzing of algal cells during sampling or, for the 1993 samples, the passing of finer algal material through the centrifuge.

Hopane and Sterane Biomarkers

Hopanes and steranes are stable 4- and 5-ring hydrocarbons that primarily originate, respectively, in bacterial cell walls and in algal and terrestrial plant sterols (Ourisson et al., 1979; Mackenzie et al., 1982; Ourisson et al., 1987). The structures of these natural, biogenic compounds are diagenetically modified by heat and pressure over geological time scales as organic matter is converted into petroleum or coal. The modifications occur in predictable ways resulting in well defined and characteristic series of the rearranged, diagenetic isomers of these hopane and sterane biomarkers in organic rich sediments and sedimentary rocks, petroleum source rocks, crude oils, coals, etc. (Peters and Moldowan, 1993). Because these biomarkers are more stable than other petroleum components such as the resolved alkanes, the hopanes and steranes can serve as conservative indicators (and tracers) of petroleum that has entered the Mackenzie River *via* oil seeps or the erosion of bitumens or organic-rich rocks (e.g., Volkman et al., 1992; Yunker et al., 1993; Prince et al., 1994; Bieger et al., 1996; Hostettler et al., 1999).

The hopane profiles (based on m/z 191 chromatograms) for the samples of river suspended particulate and lake sediment from the middle and outer delta in 1994 are very similar to profiles published previously for samples of river suspended particulate and shelf sediment from 1987 (Yunker et al., 1993). In all samples the diagenetic 17α(H),21β(H)-hopanes and 17β(H),21α(H)-moretanes that maximize at the C_{30} hopane make up most of the hopane series, and biogenic 17β(H),21β(H)-hopanes are only minor constituents (not shown). Samples of river suspended particulate (both 1987 and 1994) and sediment (both lake and shelf) also have very similar relative abundances of the 27, 28 and 29 carbon regular steranes (Figure 7) and consistent values for a number of sterane- and hopane-based maturity and source parameters (Figures 8 and 9). The uniformity of these biomarkers and maturity indicators indicates that the river particulates and lake and shelf sediments have a common (and likely relatively constant) source of hydrocarbons.

To further investigate potential petroleum sources to the delta, hopane and sterane ratios for particulate and sediment samples can be compared to published data for oils and petroleum source rocks obtained from exploration wells drilled in the lower Mackenzie corridor (Figure 1; Snowdon et al., 1987; Feinstein et al., 1988). This data set includes samples of crude oil from Norman Wells (two Devonian era oils from the producing oil field plus two Cretaceous era oils

from non-producing wells) and samples of organic-rich rocks and bituminous shales from the major petroleum producing strata (the Devonian Canol and Bluefish formations and the Cretaceous Slater River formation). The Canol and Bluefish strata underlie the Mackenzie corridor from outlet of Great Bear Lake almost to the Mackenzie delta, while the Slater River strata occurs south of Great Bear Lake (Feinstein et al., 1988). The Canol formation has been established as the source for Norman Wells oil (Snowdon et al., 1987; Feinstein et al., 1988).

The Devonian samples (two Norman Wells production oils and all Canol and Bluefish samples) plot in the lower centre of the sterane ternary diagram and overlap the cluster of suspended particulate and sediment samples from the delta and shelf (Figure 7). The Cretaceous oils and source rocks form a separate group that plots on the upper left (both oils have the same sterane proportions and their symbols overlap). Hence, the main petroleum source for the delta is most likely Devonian-era oils or source rocks. Terrestrial sourced oils such as the Paleogene oils from strata under the Mackenzie delta (and the offshore Beaufort Sea) generally have even higher proportions of the C_{29} steranes and would be shifted further towards the lower right of the plot than the Devonian samples (Curiale, 1991; Peters and Moldowan, 1993; not shown).

The extent of isomerisation of hopane and sterane biomarkers from the original biological configuration is widely used to assess the thermal maturity of oils and bitumens (Peters and Moldowan, 1993). Because some isomerisation reactions require less energy (and can proceed at lower temperatures), examination of a range of maturity parameters gives a better indication of the thermal maturity of a sample than just one parameter. For example, isomerisation at the C-22 position in 17α(H),21β(H)-hopanes occurs earlier than any of the sterane modifications. Of the parameters shown in Figures 8 and 9, the C_{32} hopanes generally reach maturity first followed by 20S/(20S + 20R) and then ββ/ββ +αα for the C_{29} steranes. Once a parameter has reached thermal equilibrium it generally remains constant at higher maturities (e.g., the 22S/22S + 22R ratio will remain constant while sterane ratios continue to change). The correlation diagram shown in Figure 8 is probably the most widely-used and effective tool for determining the thermal maturity of petroleum source rocks or oils (Peters and Moldowan, 1993; Faure et al., 2000).

Samples from the Mackenzie River and Beaufort Sea generally have very consistent proportions of the different thermal maturity parameters (Figures 8 and 9). All parameters are below the levels that signify thermal equilibrium (Peters and Moldowan, 1993) and indicate, particularly for the steranes, that the predominate petroleum source to the delta is less mature than most of the oils (including the two Norman Wells production samples) and source rocks. The hopanes are closest to maturity — 22S/22S + 22R proportions for the C_{31} and C_{32} hopanes are 0.53 ± 0.04 and 0.55 ± 0.02, respectively (mean ± SD; n = 25) as compared to equilibrium values of 0.55 and 0.58 — suggesting that the source reservoir(s) is in the early stages of oil generation (Peters and Moldowan, 1993). The two sterane parameters (Figure 8) provide somewhat conflicting results in that the parameter that usually reaches maturity first (20S/20S + 20R) is indicating a lower maturity than the late-maturing parameter ($\beta\beta/\beta\beta + \alpha\alpha$). Here it is likely that the 20S/20S + 20R proportions are being depressed by the presence of biogenic C_{29} steranes with the natural 20R configuration, which would underestimate the maturity. Hence, because the $\beta\beta/\beta\beta + \alpha\alpha$ proportion does not include any biogenic steranes, it is most likely a more reliable indicator of petroleum maturity for environmental samples.

Snowdon et al. (1987) and Feinstein et al. (1988) have found that the Ts/Ts + Tm proportion (18α(H)-22,29,30-trisnorneohopane, Ts, relative to 17α(H)-22,29,30-trisnorhopane, Tm) is one of the most characteristic parameters for distinguishing Devonian petroleum sources in the lower Mackenzie corridor. Because Tm is a rearranged hopane, its production during petroleum diagenesis seems to be more dependent on the initial depositional environment than maturity, and it is often used to distinguish between source rocks (Peters and Moldowan, 1993). Suspended particulate and sediment samples from the delta and shelf generally have low Ts proportions (Figure 9), indicating that material from the Devonian Bluefish formation is not making a significant contribution. Hence, immature bitumens and shales from the Canol formation that outcrop into the river valley are the most likely petroleum source to the river. Mature Norman Wells crude oil could still be present, but its occurrence would have to be balanced by material with similar properties but lower maturity.

A number of the suspended particulate samples from the Arctic Red station contain high concentrations of distinctive, marine-derived C_{30} steranes (Moldowan, 1984; Curiale, 1991; Figure 10). In the Norman Wells, Mackenzie corridor and delta, and Beaufort Sea regions high

amounts of C_{30} steranes are characteristic of Cretaceous oils (Feinstein et al., 1988; Curiale, 1991). The C_{30} steranes were not elevated in any of the 1987 samples from the river or shelf, and are only slightly elevated in a few of the lake sediments (particularly in Lake 5; Figure 10). The ephemeral nature of the Cretaceous hydrocarbons suggests that they have only localized sources, and that they are likely introduced as oils that biodegrade relatively rapidly. In contrast, the uniformity and persistence of other hopanes and steranes in the Mackenzie delta and Beaufort Sea is consistent with a hydrocarbon source in relatively stable bitumens that will degrade only slowly. The observed uniformity also suggests that the principal hydrocarbon source(s) must be far enough south in the Mackenzie corridor so that the suspended particulate matter is well mixed before it reaches the delta.

PAHs

PAH molecular mass profiles for suspended particulate and sediment samples from the Mackenzie River, Mackenzie delta lakes and the Mackenzie shelf obtained in 1987, 1993 and 1994 have a predominance of 178 (phenanthrene plus anthracene) for the low mass parent PAHs and 252 (benzo[*b/j/k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene) and 276 (benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene) for the high mass PAHs (Yunker et al., 1993; Yunker et al., 1996; Graf Pannatier, 1997). The two components vary independently of one another, and the major parent PAH molecular mass constituent alternates between 178 and 252 (or occasionally 276) in individual river, delta and shelf samples. Profiles for the mono- and dimethylnaphthalenes (not shown) and monomethylphenanthrenes (Figure 11) are also relatively constant from sample to sample. The more volatile and relatively water soluble PAHs (naphthalene, and the mono- and dimethylnaphthalenes) exhibit much larger variations in concentration and distribution than the higher molecular weight PAHs.

PAH ratios have been used to determine PAH sources, classify samples by location and estimate the importance of combustion-derived PAH (Lipiatou and Saliot, 1991; Yunker et al., 1996; Budzinski et al., 1997; Yunker et al., 2000). The usual index of combustion and/or anthropogenic input is an increase in the proportion of the less stable and/or kinetically produced parent PAH isomers relative to the thermodynamically stable isomers (e.g., fluoranthene relative to pyrene or indeno[1,2,3-*cd*]pyrene relative to benzo[*ghi*]perylene) or to the molecular mass totals (Yunker and Macdonald, 1995). By comparing PAHs of the same molecular mass,

petroleum maturity (Yawanarajah and Kruge, 1994), with much more variation between samples (not shown).

Mean PAH ratios are strikingly uniform from year to year in the Mackenzie River and in sediments from different freshwater and marine locations (Figure 11). We can infer that this uniformity extends to at least the past 50 years from the consistency of downcore profiles of PAH ratios in sediments from the delta lakes (Graf Pannatier, 1997), and profiles from a core collected in the Canada basin north of the Beaufort shelf suggest the homogeneity extends much further into the past (Yunker et al. in preparation). The general uniformity of parent PAH ratios (Figure 11a and b) extends to all of the PAH molecular masses greater than 178 (i.e., also anthracene/178, benz[*a*]anthracene/228, benzo[*b/j/k*]fluoranthene/benzo[*b/j/k*]fluoranthene + benzo[*e*]pyrene, benzo[*a*]pyrene/benzo[*e*]pyrene + benzo[*a*]pyrene). Consistent 178/178+252+276 ratios (Figure 11c and d) reflect consistent transport by the Mackenzie River of a mixture of small (2- and 3-ring) and multi-ring (4- to 6-ring) PAHs (Yunker et al., 1993; Yunker et al., 1995) which, according to the methylphenanthrene ratios and the hopane and sterane ratio data presented above, have similar maturity. All of the above features reinforce the conclusion that the Mackenzie River dominates the regional hydrocarbon geochemistry (cf. Yunker et al., 1993).

The predominance of molecular mass 178 and 252 in Mackenzie River samples contrasts markedly with predominance of mass 202 and 252 usually observed in areas that receive direct anthropogenic input (Hites et al., 1980; Bates et al., 1984; Lipiatou and Saliot, 1991; Yunker et al., 1996). Suspended particulate samples collected in March 1994 had elevated fluoranthene/202 ratios and higher proportions of molecular mass 202 (fluoranthene and pyrene) at Inuvik, Aklavik and Arctic Red (Figure 11a). The indeno[1,2,3-*cd*]pyrene/276 ratio was also high (0.28) at the Arctic Red station, but indeno[1,2,3-*cd*]pyrene was undetectable in the other two samples (Figure 11b). Fluoranthene and indeno[1,2,3-*cd*]pyrene proportions are elevated in the long-range-transported aerosol (with its associated combustion PAHs) that manifests as Arctic haze in late winter (Daisey et al., 1981; Barrie, 1986; Patton et al., 1991; Halsall et al., 1997). Because the river SPM is still low at this time, atmospheric PAHs can more easily be detected in the river PAH composition. Atmospheric PAHs have also been observed in late

winter/early spring in suspended particulate and sediment trap samples from the nearshore Beaufort Sea (Yunker et al., 1995).

The suspended particulate sample with the elevated 178 proportion (0.69; Figure 11c) is the sample from Aklavik in March 1994 that had high alkane concentrations and a low OEP. A strong indication of petroleum hydrocarbons in the sample is further provided by the dominance of molecular mass 178 (phenanthrene plus anthracene) in the parent PAH profile and a high proportion of anthracene (anthracene/178 = 0.49). In most Mackenzie/Beaufort samples anthracene is typically only a few percent of phenanthrene, and such a high proportion of anthracene is more characteristic of coal or coal tar (Radke et al., 1990). Anthracene was also elevated at Station 1 in April and early May of 1987 (anthracene/178 = 0.15 and 0.09, respectively). These data suggest that, as in the case of atmospheric PAH, it may be easier to detect the presence of oil in the river before the summer increase in SPM.

Naphthalene and the molecular mass 202 PAHs (fluoranthene and pyrene) were the major PAHs in the smaller rivers. These PAHs, along with the general predominance of fluoranthene over pyrene, (Mean ± SD: 0.56 ± 0.09, range 0.41 - 0.71) implicates combustion (presumably from long range transport) as the major PAH source (Patton et al., 1991; Yunker et al., 1996; Halsall et al., 1997). Higher molecular weight PAHs were only trace constituents in most samples; the highest amounts were present in the Back River sample, where the molecular mass 252 PAHs were one-half the concentration of the mass 202 PAHs.

Lower MW PAHs (naphthalene, phenanthrene, the mono- and dimethylnaphthalenes) predominate in the dissolved phase samples obtained in both the Mackenzie River in 1987, 1993 and 1994 and the smaller rivers in 1993 (not shown). Similar profiles were also observed in the fine particulate and colloidal phase samples obtained in 1987 (Yunker et al., 1994), again suggesting that fine particulate that has passed through the centrifuge is responsible for the elevated PAH concentrations for the 1993 and 1994 samples (Table 5). For the Mackenzie River the predominance of naphthalene and 178 PAH in the dissolved and colloidal phases suggests a petrogenic origin; this is consistent with the predominance of petrogenic aliphatic hydrocarbons in the dissolved phase (Boehm, 1980; Albaigés et al., 1984; Gómez-Belinchón et al., 1988; Ehrhardt and Petrick, 1993).

Mackenzie delta suspended particulates and sediments from the delta lakes and Mackenzie shelf are characterised by high proportion of alkyl PAHs (Tables 2 and 3). The naphthalene or phenanthrene/anthracene homologue series totals always dominate, and the fluoranthene/pyrene series total is a more minor constituent (typically 50% of P/A; this work and Yunker et al., 1993). Alkyl homologue plots generally maximize at C_3 or C_2 for the naphthalenes, C_1 or C_2 for the phenanthrene/anthracenes, and C_1 or C_2 for the fluoranthene/pyrenes. These maxima at C_1 and higher for the PAH alkyl homologue series, establish a source in mature organic matter or petroleum for the majority of the alkyl PAHs (Laflamme and Hites, 1978; Wakeham et al., 1980; Sporstøl et al., 1983).

The lack of detection of alkyl PAHs in the particulate phase all of the NWT and Nunavut rivers except the Coppermine and Haynes Rivers implies an absence of petroleum derived hydrocarbons in the smaller rivers. However, alkyl PAHs are detectable in the water samples from these rivers, suggesting that these hydrocarbons are present in the fine particulate, colloidal or dissolved fractions in the smaller rivers. As in the Mackenzie River, petroleum is a possible source for these PAHs. However, phenanthrene, and the methyl-substituted naphthalenes and phenanthrenes have also been observed in peat samples obtained from the Beaufort Sea shoreline (Yunker et al., 1993), and peat may be a more likely origin for these PAHs in the smaller rivers than petroleum.

Comparison of PAH Concentrations to Canadian Water and Sediment Quality Guidelines

It is well established that PAHs and other hydrocarbons can induce biological effects, including tumors (e.g., Lockhart et al., 1992). The possibility that naturally high PAH concentrations might induce biological effects in the Mackenzie River and Beaufort Sea has been previously investigated (Yunker and Macdonald, 1995). All PAHs except 2-methyl naphthalene and phenanthrene were found to be below the concentrations believed to elicit toxic effects in bottom fish and other biota. Nevertheless, the naturally high baseline for PAHs may make biota in this region more susceptible to chronic or accidental spills of PAHs from oil production. Here we compare PAH concentrations in water, in suspended particulate and in sediment for the Mackenzie River and the ten smaller rivers (Tables 6-8) with recent interim water guidelines for

the protection of aquatic life for a variety of organic contaminants (Canadian Council of the Ministers of the Environment, 1998).

Although the interim sediment guidelines make no reference to their applicability to suspended particulate, most of the bed material in the lower Mackenzie River is sand (Carson et al., 1998), and a comparison to suspended particulate is likely to give a better — or more conservative — assessment of biotic exposure under summer flow conditions.

The interim water criteria are only exceeded for pyrene and benzo[*a*]pyrene in two 1994 samples (Inuvik and Aklavik in July 94) from the Mackenzie River delta (Table 6). These two samples had some of the highest SPM concentrations observed (816 and 1023 mg/L), which helped to elevate the PAH concentrations above the guidelines.

The interim sediment guidelines are exceeded far more frequently by suspended particulate and sediment samples (Tables 7 and 8). Most of the PAH concentrations over the guidelines are observed in the Mackenzie River under summer flow conditions. Naphthalene, fluorene, phenanthrene, chrysene, dibenz[*a,c/a,h*]anthracene and 2-methylnaphthalene have the most exceedences in the Mackenzie River and shelf. Phenanthrene and 2-methylnaphthalene in suspended particulate exceed criteria in a substantial proportion of the available samples in all three years, while naphthalene, fluorene, chrysene and dibenz[*a,c/a,h*]anthracene exceed criteria in two of the three years (not 1993). While pyrene and benzo[*a*]pyrene are consistently elevated only in 1987 Mackenzie River suspended particulate, benzo[*a*]pyrene has been identified elsewhere as a compound of concern in sediments from the region (Stich and Dunn, 1980). In contrast to the Mackenzie, the smaller rivers exceed the sediment criteria for only a few of the smaller PAHs (naphthalene, acenaphthylene and phenanthrene; Table 7).

Suspended particulate samples from the Mackenzie delta in all years sampled and sediment samples from both the Mackenzie delta and shelf clearly contain PAHs well in excess of interim sediment quality guidelines for the protection of aquatic life. There is an urgent need for further studies to establish the source(s) of these PAHs, their availability to biota and to ascertain whether they are having effects on bottom fish and other "high risk" biota (cf. Yunker and Macdonald, 1995).

Conclusions

The Mackenzie River has proved to be more variable in hydrocarbon concentration and content than was indicated by a single year of sampling at three stations in the outer delta in 1987. The differences observed in 1993 and 1994 are largely due to location: stations in the lower and middle to upper delta generally have higher SPM concentrations and, particularly for the Arctic Red station, are apparently closer to petroleum sources.

During summer flow, suspended particulate in the Mackenzie River is homogenous enough in alkane and PAH content that the linear relationship between ng/L hydrocarbon concentrations and SPM can be used to obtain a good approximation of the hydrocarbon load carried by the river. With SPM in mg/L, the slopes are 2.7 and 12 ng/mg for the lower and higher alkanes, respectively, and 0.52 and 1.0 ng/mg for the parent and alkyl PAHs. The standard error of the slope is less than 10% in each case, and all constants have been set to zero.

Suspended particulate in the ten smaller NWT and Nunavut rivers has mean concentrations of the lower and higher alkanes (in ng/g) that are similar to the Mackenzie River during summer, but PAH concentrations are approximately 10 times lower than in the Mackenzie for the parent PAHs and 100 times lower for alkyl PAHs. These PAH concentrations are comparable to the few data collected for the large Siberian rivers. A much larger concentration difference between the smaller rivers and the Mackenzie River emerges when data are expressed on a volume basis. The general non-detectability of alkyl PAHs in all rivers except the Coppermine and Hayes Rivers indicates an absence of petroleum derived hydrocarbons in the smaller rivers. This lack of petrogenic material is likely the single most important factor contributing to PAH concentration differences between the Mackenzie River and other arctic rivers.

For the Mackenzie River, dissolved PAH concentrations determined using solvent extraction in 1993 and 1994 are on average about 10 times higher than the concentrations determined using resin column adsorption in 1987. These differences are likely to arise from retention of different amounts of fine particulate by the particulate sampling methods used in the different studies.

Particulate samples from the Mackenzie River and all smaller Canadian rivers all have a resolved higher alkane pattern with a well-defined OEP that is consistent with a major source in terrestrial, higher plant material.

Hopane and sterane distributions and ratios exhibit a remarkably similar composition for river particulates and lake and shelf sediments. The uniformity of these biomarkers and maturity indicators suggests that the river particulates and lake and shelf sediments have a common (and likely relatively constant) source of hydrocarbons. Comparison to published data for oils and petroleum source rocks obtained from exploration wells drilled in the lower Mackenzie corridor indicates that the principal petroleum source for the delta is most likely immature bitumens and shales from the Devonian Canol formation that outcrop into the lower Mackenzie river valley. Mature Norman Wells crude oil could still be present, but its occurrence would have to be balanced by material with similar properties but lower maturity. A number of the suspended particulate samples from the Arctic Red station contain high concentrations of distinctive, marine-derived C_{30} steranes, suggesting local inputs of Cretaceous oils that biodegrade relatively rapidly.

Mean PAH ratios in the Mackenzie River, in sediments from various Mackenzie delta and shelf locations and in downcore profiles in sediments from the delta lakes are all similar. This uniformity reflects a compositionally uniform transport of a mixture of small (2- and 3-ring) and multi-ring (4- to 6-ring) PAHs which, according to their methylphenanthrene, hopane and sterane ratios, have similar hydrocarbon maturity.

Suspended particulates from the Mackenzie delta and sediment samples from both the Mackenzie delta and shelf contain PAHs in substantial excess of interim sediment quality guidelines for the protection of aquatic life. These elevated PAH concentrations indicate an urgent need to establish the source(s) and to ascertain whether they are having effects on bottom fish and other biota.

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Table 1. PAH parameters quantified in this study.

Parent PAHs	Molecular Mass	Σ 178-278 PAH	Alkyl PAHs	Alkyl PAH
Naphthalene	128		2-Methylnaphthalene	✓
Acenaphthylene	152		1-Methylnaphthalene	✓
Acenaphthene	154		2,6/2,7-Dimethylnaphthalene	✓
Fluorene	166		1,3/1,7-Dimethylnaphthalene	✓
Phenanthrene	178	✓	1,6-Dimethylnaphthalene	✓
Anthracene	178	✓	1,4/2,3-Dimethylnaphthalene	✓
Fluoranthene	202	✓	1,5-Dimethylnaphthalene	✓
Pyrene	202	✓	1,2-Dimethylnaphthalene	✓
Benz[*a*]anthracene	228	✓	2,3,6-Trimethylnaphthalene	✓
Chrysene/triphenylene	228	✓	2,3,5-Trimethylnaphthalene	✓
Benzo[*b/j/k*]fluoranthene	252	✓	3-Methylphenanthrene	✓
Benzo[*e*]pyrene	252	✓	2-Methylphenanthrene	✓
Benzo[*a*]pyrene	252	✓	2-Methylanthracene	✓
Perylene	252		9/4-Methylphenanthrene	✓
Dibenz[*a,c/a,h*]anthracene	278	✓	1-Methylphenanthrene	✓
Indeno[1,2,3-*cd*]pyrene	276	✓		
Benzo[*ghi*]perylene	276	✓		

Table 2. Hydrocarbon concentrations and ratios (mean ± SD) for suspended particulate from the Mackenzie River and the ten smaller rivers.

River/Season	Mackenzie River Low Flow (Mar-Apr)		Mackenzie River High Flow (May-Sep)			Smaller Rivers (Jul)
Year	1987	1994	1987	1993	1994	1993
Station	Stn. 1	Inuvik, Alkavik, Arctic Red	Stn. 1, East, Middle, Reindeer	Inuvik, Alkavik, Arctic Red	Inuvik, Alkavik, Arctic Red	
n	1	3	9	8	10	10 (5 for OEP)
SPM, mg/L	2.7	26 ± 1.8	124 ± 74	84 ± 38	490 ± 369	5.0 ± 8.2
Carbon % (POC/SPM)	3.39	0.66 ± 0.18	1.76 ± 0.65	2.22 ± 0.75	1.25 ± 0.29	25 ± 25
Lower alkane proportion	0.35	0.12 ± 0.11	0.37 ± 0.12	0.46 ± 0.06	0.16 ± 0.06	0.34 ± 0.21
Alkyl PAH proportion	0.64	0.60 ± 0.05	0.59 ± 0.02	0.65 ± 0.05	0.63 ± 0.08	0.07 ± 0.21
OEP C_{27}	1.68	1.18 ± 0.15	2.77 ± 0.71	1.96 ± 0.44	1.50 ± 0.53	2.52 ± 0.87
Concentration, ng/g [a]						
Lower alkanes	1400	1500 ± 550	5300 ± 1400	1100 ± 1100	2900 ± 2400	5400 ± 4200
Higher alkanes [b]	2600	7100 ± 5470	9600 ± 3900	1600 ± 1800	11800 ± 4000	14100 ± 13900
Σ 178-278	150	106 ± 30	1000 ± 200	320 ± 280	670 ± 380	93 ± 86
Alkyl PAH	260	167 ± 70	1400 ± 250	620 ± 560	1100 ± 500	1.5 ± 4.8
Concentration, µg/g OC [a]						
Lower alkanes	41	240 ± 83	350 ± 130	43 ± 14	250 ± 240	29 ± 16
Higher alkanes [b]	77	1000 ± 450	610 ± 280	59 ± 21	1000 ± 400	82 ± 61
Σ 178-278	4.4	16 ± 3.4	64 ± 20	14 ± 2.6	57 ± 43	0.45 ± 0.34
Alkyl PAH	7.7	25 ± 5.4	90 ± 29	26 ± 6.2	93 ± 60	0.10 ± 0.32
Concentration, ng/L [a]						
Lower alkanes	3.8	39 ± 14	680 ± 410	71 ± 51	1200 ± 1100	6.8 ± 3.1
Higher alkanes [b]	7.1	200 ± 160	1260 ± 980	96 ± 82	6400 ± 4700	21 ± 15
Σ 178-278	0.4	2.7 ± 0.8	120 ± 69	20 ± 8.7	260 ± 210	0.11 ± 0.06
Alkyl PAH	0.7	4.3 ± 2.0	170 ± 100	41 ± 21	500 ± 430	0.04 ± 0.13

[a] Alkane and PAH fractions are defined in Figure 4 and Table 1. Proportions are the ratio of the lower alkanes to the lower plus higher alkane total and the ratio of the alkyl PAH total to the Σ 178-278 parent PAH plus alkyl PAH total. The OEP C_{27} ratio is $(C_{25} + 6C_{27} + C_{29})/(4C_{26} + 4C_{28})$ (Scalan and Smith, 1970).

[b] The higher alkane concentrations for samples from Aklavik in March 1994 (227,000 ng/g, 30 times the mean of samples from Inuvik and Arctic Red at the same time) and Inuvik in August 1994 (62,000 ng/g, 5 times other summer samples) have been excluded. Carbon and µg/g OC data omit Aklavik, Jun 93 due to the anomalously low carbon content (0.07%).

Table 3. Hydrocarbon concentrations and ratios (mean ± SD) for sediment core samples from Mackenzie delta lakes and surficial sediments from the nearshore Mackenzie shelf.

	Middle Delta		Outer Delta		Mackenzie shelf
Location	Lake 6	Lake 7	Lake 3	Lake 5	Stations 1, 4 and 5
n	11	16	15 (16 for alkanes)	6	4 (3 for alkanes)
Carbon %	1.84 ± 0.15	1.58 ± 0.16	1.88 ± 0.33	2.19 ± 0.25	1.47 ± 0.15
Sedimentation rate, $g/cm^2 \times y$ [a]	0.65 ± 0.03	1.21 ± 0.06	0.33 ± 0.03	0.64 ± 0.02	–
Lower alkane proportion	0.31 ± 0.09	0.32 ± 0.10	0.21 ± 0.05	0.26 ± 0.05	0.24 ± 0.03
Alkyl PAH proportion	0.66 ± 0.05	0.66 ± 0.03	0.64 ± 0.03	0.62 ± 0.06	0.58 ± 0.03
OEP C_{27}	1.55 ± 0.36	1.53 ± 0.33	1.47 ± 0.46	1.46 ± 0.28	1.92 ± 0.10
Concentration, ng/g [b]					
Lower alkanes	4000 ± 590	4100 ± 720	2700 ± 810	3100 ± 180	2300 ± 200
Higher alkanes	9700 ± 4000	9900 ± 5900	11000 ± 4980	9300 ± 3100	7500 ± 510
Σ 178-278	530 ± 30	570 ± 81	420 ± 92	430 ± 15	910 ± 240
Alkyl PAH	1040 ± 200	1150 ± 240	760 ± 220	720 ± 160	1300 ± 460
Concentration, μg/g OC [b]					
Lower alkanes	220 ± 49	260 ± 56	150 ± 41	140 ± 22	160 ± 31
Higher alkanes	530 ± 210	630 ± 400	600 ± 260	430 ± 140	510 ± 64
Σ 178-278	29 ± 2.9	37 ± 7.2	23 ± 6.6	20 ± 2.8	69 ± 4.3
Alkyl PAH	57 ± 13	73 ± 17	42 ± 15	34 ± 7.3	100 ± 4.4

[a] Sedimentation rates based on measured ^{137}Cs profiles are from Graf Pannatier (1997).

[b] See Figure 4, Tables 1 and 2 for a definition of parameters.

Table 4. Vegetation, sampling and suspended particulate characteristics of the smaller rivers in the NWT and Nunavut.

River	Vegetation regime [a]	Annual flow [b] 10^9 m^3	Flow maximum 1993 [c], m^3/s	Weeks past freshet at sampling; flow percentage of maximum [c]	SPM mg/L	SPM Carbon %	SPM Higher alkanes ng/g
Rivers flowing into the Canadian Archipelago							
Coppermine	Taiga, high-heath tundra	10.5	1330	3-4 weeks; 60%	26.4	1.47	670
Burnside	Low-heath tundra	5.4	2050	4 weeks; 20%	0.93	13.0	13000
Ellice	Low-heath tundra	3.0	1540	5 weeks; 14%	8.4	3.90	4490
Back	Low-heath tundra	15.8	4970	4 weeks; 39%	1.1	24.4	45300
Hayes	Low-heath tundra	4.1	2810	–	9.2	4.50	122
Rivers flowing into Chesterfield Inlet and Hudson Bay							
Lorillard	Low-heath tundra	2.5	1510	–	1.1	10.4	16800
Quoich	Low-heath tundra	7.6	1580	4-5 weeks; 33%	0.3	73.7	13900
Thelon	Taiga, high-heath tundra	33.5	4710	3-4 weeks; 55%	1.3	20.2	17200
Dubawnt	Taiga, high-heath tundra	13.8	864	2-3 weeks; 79%	1.2	33.4	26700
Kazan	Taiga, high-heath tundra	16.9	1800	1 week; 95%	0.3	64.3	2100

[a] Vegetation regime information is from Wedel (1992).

[b] Annual flow data are from (Macdonald et al., 2000).

[c] Flow maximum and weeks past freshet data have been extracted from the HYDAT data base (Environment Canada, 1996). Data for 1993 are not available for the Hayes and Lorillard Rivers and the flow maximum is the average for 1990-1992.

Table 5. Dissolved fraction hydrocarbon concentrations and ratios (mean ± SD) for the Mackenzie River and the smaller Rivers.

River	**Mackenzie River**				**Smaller Rivers**
Date	Jun-Jul 1987	Jun-Sep 1993	Mar 1994	Jun-Aug 1994	Jul-Aug 1993
Location	East, Middle, Reindeer	Inuvik, Alkavik, Arctic Red	Inuvik, Alkavik, Arctic Red	Inuvik, Alkavik, Arctic Red	All Rivers
n	6	12 (8 for alkanes)	6	11	11
Lower alkane proportion	0.15 ± 0.11	0.53 ± 0.14			0.59 ± 0.13
Alkyl PAH proportion	0.80 ± 0.10	0.81 ± 0.04	0.81 ± 0.13	0.70 ± 0.14	0.87 ± 0.03
OEP C_{27}	2.36 ± 0.74	1.04 ± 0.16			0.99 ± 0.17
Concentration, ng/L [a]					
Lower alkanes	3.6 ± 3.3	61 ± 42	-	-	47 ± 23
Higher alkanes	21 ± 11	49 ± 24	-	-	30 ± 9
Σ 178-278	1.1 ± 0.5	12 ± 10	8.3 ± 3.1	13 ± 6.6	3.0 ± 1.9
Alkyl PAH	5.5 ± 3.3	44 ± 31	79 ± 100	34 ± 12	19 ± 6.5
Dissolved Fraction Percentage of Total [b]					
Lower alkanes	0.42	49 (5.1) [c]	-	-	86 ± 5.6
Higher alkanes	1.7	43 (0.8) [c]	-	-	63 ± 20
Σ 178-278	0.83	32 (4.0) [c]	75	8.1	97 ± 1.6
Alkyl PAH	2.5	47 (7.5) [c]	91	10	100 ± 0.5

[a] See Table 1 and Figures 4 and 5 for a definition of parameters.

[b] Percentages of the dissolved fraction relative to the corresponding ng/L suspended particulate concentrations of Table 1.

[c] Percentages in brackets compare the 1993 dissolved fraction concentrations to the more typical 1994 particulate phase concentrations.

Table 6. Numbers of water samples (suspended particulate plus dissolved phases) and their concentration ranges for samples that exceed interim Canadian federal water quality guidelines for the protection of aquatic life.

Compound	Freshwater Guideline	Mackenzie River Low Flow (Mar-Apr)		Mackenzie River High Flow (May-Sep)			Smaller Rivers
		1987	1994	1987	1993	1994	1993
n		1	3	6	8	10	10
	ng/L	Number of samples over the guideline (concentration range in ng/L)[a]					
Naphthalene	1100						
Acenaphthene	5800		–		–	–	–
Fluorene	3000						
Phenanthrene	400						
Anthracene	12						
Fluoranthene	40						
Pyrene	25					2 (27-40)	
Benz[*a*]anthracene	18						
Benzo[*a*]pyrene	15					2 (18-23)	

[a] A blank indicates no samples above the guideline; – indicates not analysed.

Table 8. Numbers of sediment samples and their concentration ranges for samples that exceed interim Canadian federal sediment quality guidelines for the protection of aquatic life.

Compound	Guidelines		Middle Mackenzie Delta		Outer Mackenzie Delta					Mackenzie shelf
	Freshwater	Marine	Lake 6	Lake 7	East [a]	Middle [a]	Reindeer	Lake 3 [a]	Lake 5	Stn. 1, 4, 5
n			11	16	6	6	6	15	6	4
	ng/g	ng/g	Number of samples over the guideline (concentration range in ng/g) [b]							
Naphthalene	34.6	34.6	11 (76-110)	16 (61-180)	4 (43-73)	6 (60-96)	6 (65-160)	14 (52-130)	6 (60-72)	4 (79-130)
Acenaphthylene	5.87	5.87	3 (120-150)						5 (96-152)	
Acenaphthene	6.71	6.71					1 (9.2)			3 (7.1-16)
Fluorene	21.2	21.2	11 (24-31)	16 (24-45)		2 (23-24)	3 (22-41)	8 (22-33)		4 (29-77)
Phenanthrene	41.9	86.7	11 (130-160)	16 (130-220)	6 (76-140)	6 (120-260)	6 (120-270)	15 (53-180)	6 (110-120)	4 (130-320)
Anthracene	46.9	46.9								
Fluoranthene	111	113								
Pyrene	53	153		2 (56-68)			1 (68)			1 (56)
Benz[*a*]anthracene	31.7	74.8								
Chrysene	57.1	108	11 (65-79)	16 (77-140)	1 (93)	5 (71-97)	6 (68-110)	9 (58-92)	5 (58-62)	4 (71-120)
Benzo[*a*]pyrene	31.9	88.8				1 (38)	1 (45)			2 (42-45)
Dibenz[*a,c/a,h*] anthracene	6.22	6.22	11 (7.1-10)	16 (7.0-18)	4 (6.3-16)	6 (6.3-25)	5 (11-24)	6 (6.4-8.0)	4 (7.0-8.6)	4 (11-22)
2-Methyl naphthalene	20.2	20.2	11 (36-250)	16 (110-330)	6 (37-170)	6 (120-220)	6 (130-300)	15 (56-260)	4 (42-150)	4 (150-300)

[a] The samples listed in Table 3 have been supplemented by 18 sediment samples from the three main channels of the outer Mackenzie delta that have only been analysed for parent PAHs and the methylnaphthalenes (Yunker et al., 1990; Yunker et al., 1991b).

[b] A blank indicates no samples above the guideline; – indicates not analysed.

Figures

Figure 1. Map of the principal rivers in northern Canada showing sampling locations **a)** on the ten smaller northward-flowing Canadian rivers and **b)** in the Mackenzie River delta. The area outlined by a dashed line in the central Mackenzie corridor is the region where organic-rich rock samples were obtained from exploration wells by Snowdon et al. (1987) and Feinstein et al. (1988).

Figure 2. Average Mackenzie River water flow at the Arctic Red River confluence for the years 1973-1994 (solid line) with individual flow profiles for the years 1987, 1993 and 1994 (dashed lines).

Figure 3. SPM *vs.* Mackenzie River flow at the Arctic Red River confluence using data from late May to early October.

Figure 4. Suspended particulate concentrations for the lower alkane (n-C_{13}-C_{20} plus pristane and phytane) and higher alkane (n-C_{21}-C_{34}) fractions with samples grouped by year and date of sampling. SPM data have been used to interchange ng/g and ng/L data.

Figure 5. Suspended particulate concentrations for the Σ 178-278 parent PAH and alkyl PAH fractions with samples grouped by year and date of sampling. SPM data have been used to interchange ng/g and ng/L data. PAH parameters are defined in Table 1.

Figure 6. Concentrations of **a)** the lower and higher alkanes and **b)** the Σ 178-278 and alkyl PAHs *vs.* the SPM for suspended particulate samples from the Mackenzie River.

Figure 7. Ternary diagram showing the relative abundances of the 27, 28 and 29 carbon regular steranes (20R 5α(H),14α(H),17α(H)-cholestane, and its 24-methyl and 24-ethyl derivatives) based on peak height ratios from m/z 217 mass chromatograms. Samples of river suspended particulate (both 1987 and 1994) and sediment (both lake and shelf) are shown by closed symbols. Samples of crude oil from Norman Wells, including two Devonian era oils from the producing oil field and two Cretaceous era oils from non-producing wells, and organic-rich rocks from the Devonian Canol and Bluefish formations and the Cretaceous Slater River formation from wells drilled in the Mackenzie corridor (Snowdon et al., 1987; Feinstein et al., 1988) are shown by open symbols.

Figure 8. Comparison of thermal maturity parameters based on isomerisation of asymmetric centres in the C_{29} steranes using m/z 217 peak heights for 20S/20R + 20S proportions of 5α(H),14α(H),17α(H)-ethylcholestane vs. ββ/ββ +αα proportions of the 20S and 20R diasteriomers of 5α(H),14β(H),17β(H)-ethylcholestane (ββ) and 5α(H),14α(H),17α(H)-ethylcholestane (αα). Dashed lines show the ratios for each parameter that typically indicate thermal maturity (Peters and Moldowan, 1993). The maturity trend line has been adapted from Faure et al. (2000). The river, oil and source rock samples are the same as in Figure 7.

Figure 9. Comparison of the 22S/22R + 22S proportions of 17α(H),21β(H)-bishomohopane vs. proportions of 18α(H)-22,29,30-trisnorneohopane (Ts) relative to 17α(H)-22,29,30-trisnorhopane (Tm) based on m/z 191 peak areas. The C_{32} hopane ratio is an index of thermal maturity, while Ts/Ts + Tm is both maturity and source dependent (Peters and Moldowan, 1993). A dashed line shows the typical C_{32} hopane ratio that indicates thermal maturity. The river, oil and source rock samples are the same as in Figure 7.

Figure 10. Ratio of the 30/29 + 30 carbon regular steranes for the 20R + 20S diasteriomers of 24-ethyl and 24-propyl substituted 5α(H),14β(H),17β(H)-cholestane based on peak height ratios from m/z 218 mass chromatograms.

Figure 11. Comparison of selected PAH ratios (mean ± 1SD, maximum and minimum) for samples of suspended particulate from the Mackenzie River, both under low flow and high flow regimes, to ratios for sediments from lakes in the middle and outer delta, the nearshore Mackenzie shelf and the ten smaller rivers. Also shown are ratios for atmospheric samples from Alert on northern Ellesmere Island (Patton *et al.*, 1991). Abbreviations refer to the ratios of a) fluoranthene (Fl) to fluoranthene plus pyrene (202), b) indeno(1,2,3-cd)pyrene (InPyr) to indeno(1,2,3-cd)pyrene plus benzo(ghi)perylene (276), c) 178 (phenanthrene plus anthracene) to 178 plus 252 (benzo[*b/j/k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene) and 276, and d) 2- and 3-methylphenanthrene to the monomethylphenanthrene total.

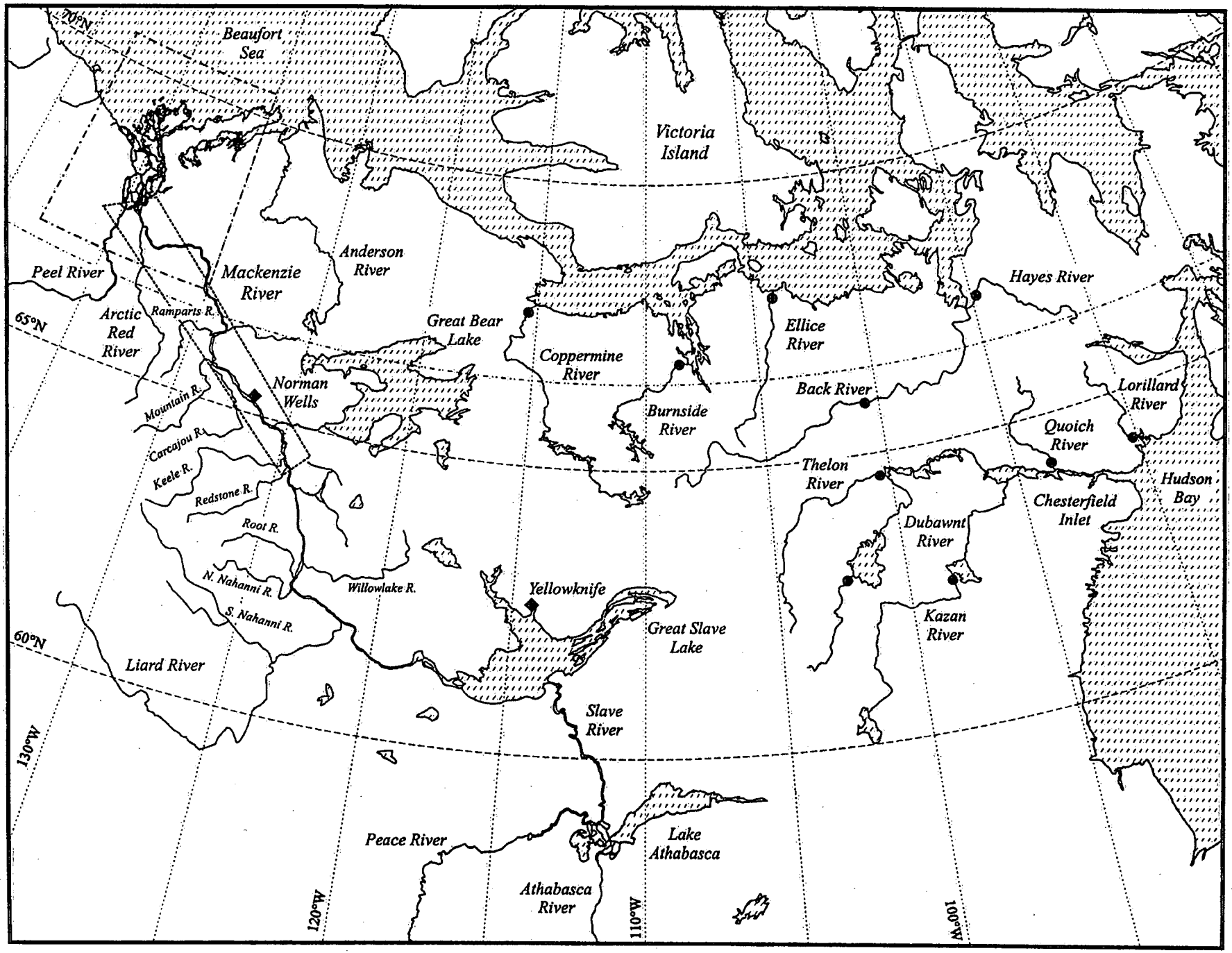
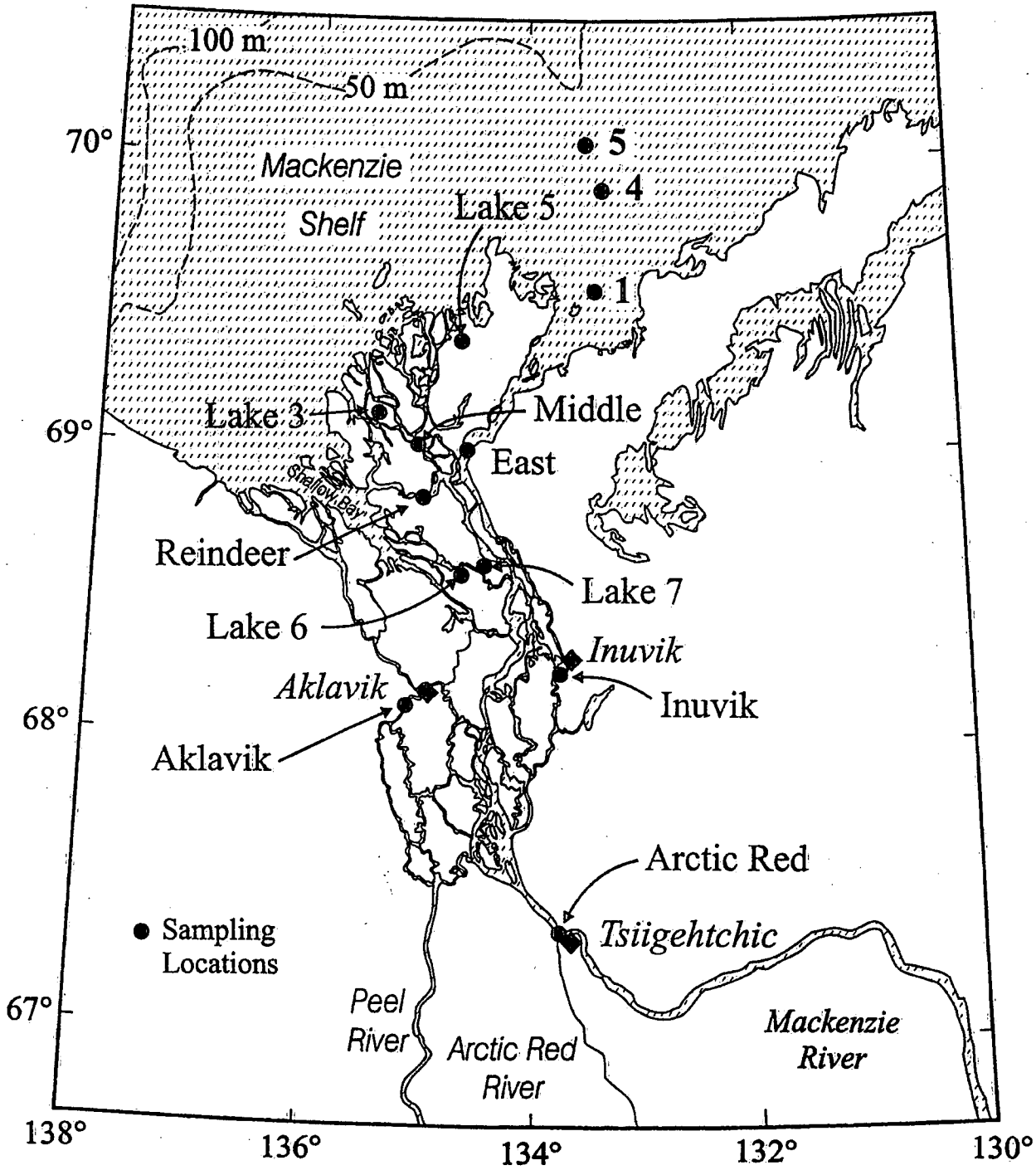

70°N
Beaufort Sea
Victoria Island
Anderson River
Mackenzie River
Peel River
Arctic Red River
Ramparts R.
65°N
Great Bear Lake
Coppermine River
Ellice River
Hayes River
Norman Wells
Mountain R.
Burnside River
Back River
Lorillard River
Quoich River
Carcajou R.
Keele R.
Thelon River
Hudson Bay
Chesterfield Inlet
Redstone R.
Root R.
Dubawnt River
N. Nahanni R.
Willowlake R.
Yellowknife
S. Nahanni R.
Kazan River
Great Slave Lake
60°N
Liard River
Slave River
130°W
Peace River
Lake Athabasca
Athabasca River
120°W
110°W
100°W

Figure 1a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Shallow Bay
Reindeer
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Inuvik
Inuvik
Aklavik
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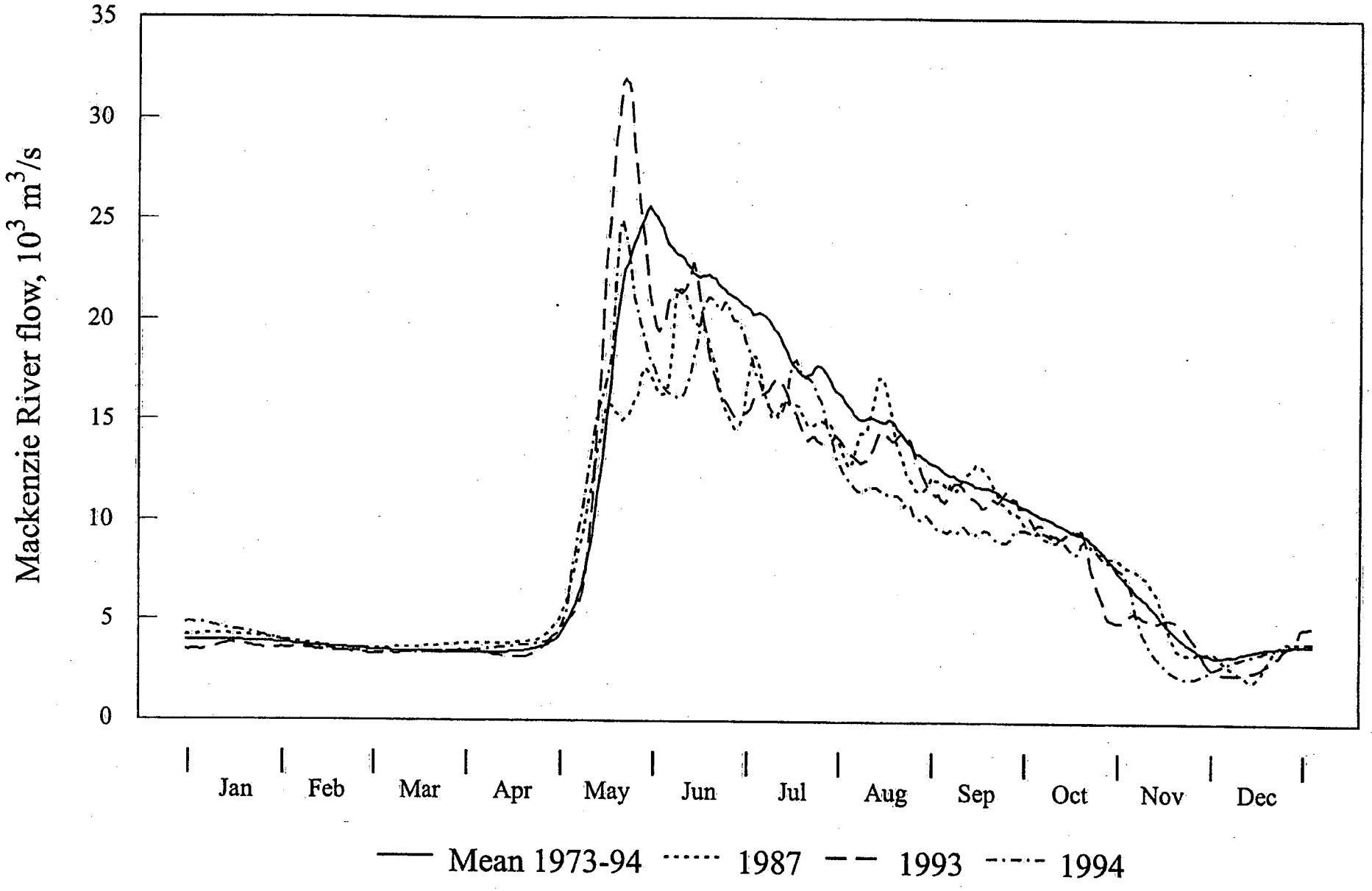
River

Figure 1b


Mackenzie River flow, 10^3 m^3/s
35
30
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20
15
10
5
0
Jan
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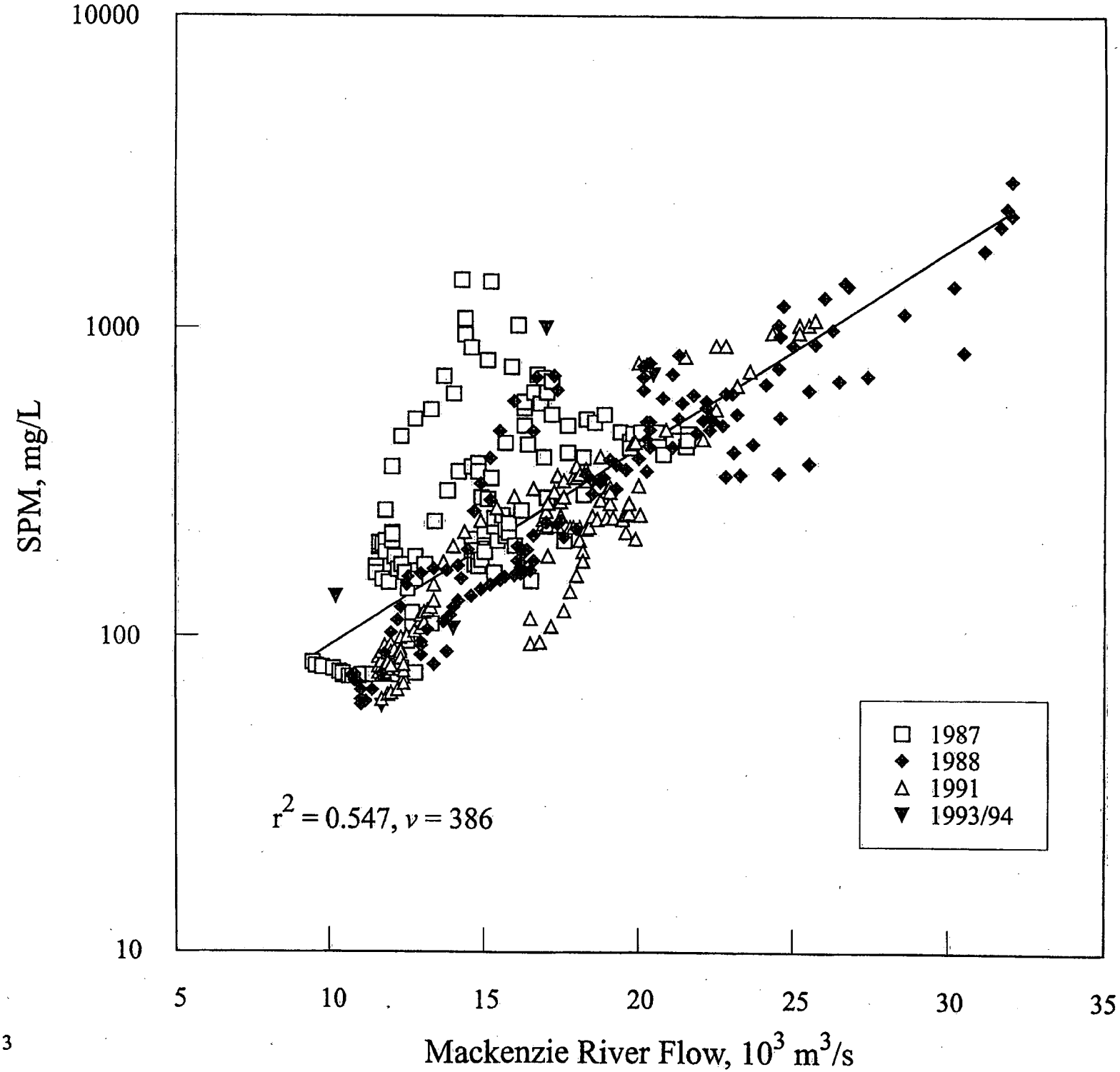
Nov
Dec
Mean 1973-94
1987
1993
1994

Figure 2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SPM, mg/L
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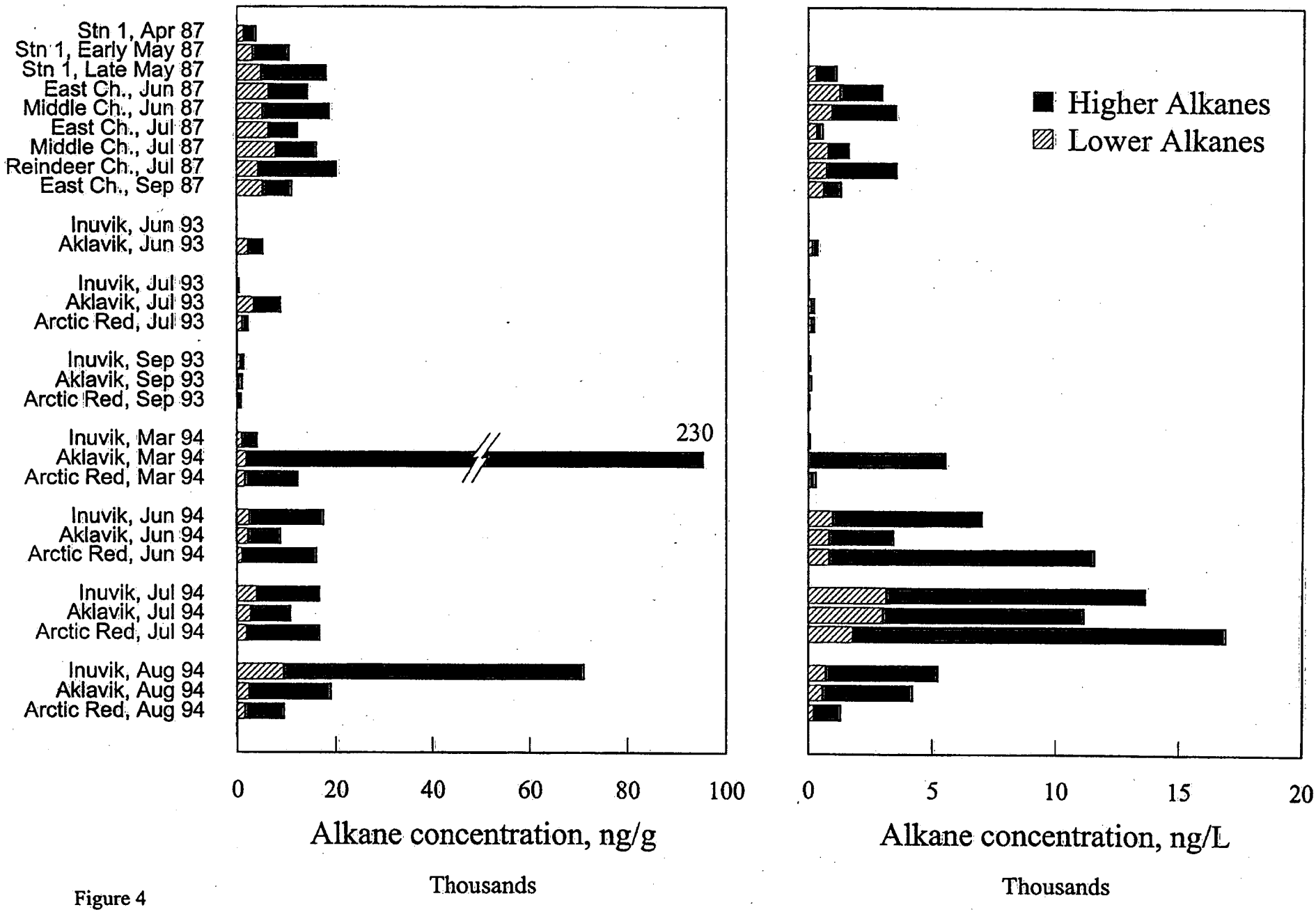
Mackenzie River Flow, 10^3 m^3/s
$r^2 = 0.547$, $\nu = 386$
1987
1988
1991
1993/94

Figure 3


Stn 1, Apr 87
Stn 1, Early May 87
Stn 1, Late May 87
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Middle Ch., Jun 87
East Ch., Jul 87
Middle Ch., Jul 87
Reindeer Ch., Jul 87
East Ch., Sep 87
Inuvik, Jun 93
Aklavik, Jun 93
Inuvik, Jul 93
Aklavik, Jul 93
Arctic Red, Jul 93
Inuvik, Sep 93
Aklavik, Sep 93
Arctic Red, Sep 93
Inuvik, Mar 94
Aklavik, Mar 94
Arctic Red, Mar 94
Inuvik, Jun 94
Aklavik, Jun 94
Arctic Red, Jun 94
Inuvik, Jul 94
Aklavik, Jul 94
Arctic Red, Jul 94
Inuvik, Aug 94
Aklavik, Aug 94
Arctic Red, Aug 94
230
0
20
40
60
80
100
Alkane concentration, ng/g
Thousands
Higher Alkanes
Lower Alkanes
0
5
10
15
20
Alkane concentration, ng/L
Thousands

Figure 4

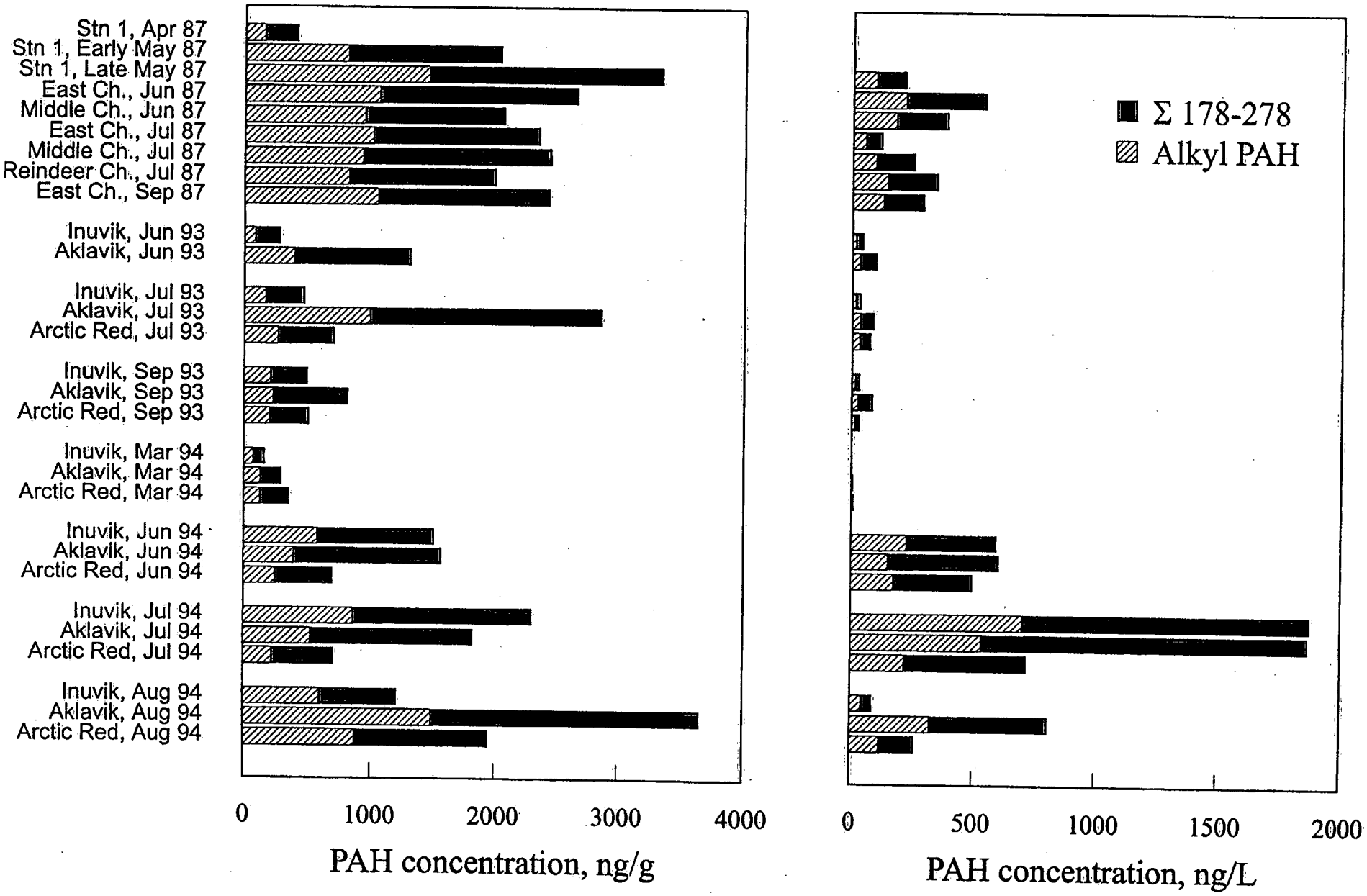
Stn 1, Apr 87
Stn 1, Early May 87
Stn 1, Late May 87
East Ch., Jun 87
Middle Ch., Jun 87
East Ch., Jul 87
Middle Ch., Jul 87
Reindeer Ch., Jul 87
East Ch., Sep 87
Inuvik, Jun 93
Aklavik, Jun 93
Inuvik, Jul 93
Aklavik, Jul 93
Arctic Red, Jul 93
Inuvik, Sep 93
Aklavik, Sep 93
Arctic Red, Sep 93
Inuvik, Mar 94
Aklavik, Mar 94
Arctic Red, Mar 94
Inuvik, Jun 94
Aklavik, Jun 94
Arctic Red, Jun 94
Inuvik, Jul 94
Aklavik, Jul 94
Arctic Red, Jul 94
Inuvik, Aug 94
Aklavik, Aug 94
Arctic Red, Aug 94
0
1000
2000
3000
4000
PAH concentration, ng/g
Σ 178-278
Alkyl PAH
0
500
1000
1500
2000
PAH concentration, ng/L

Figure 5

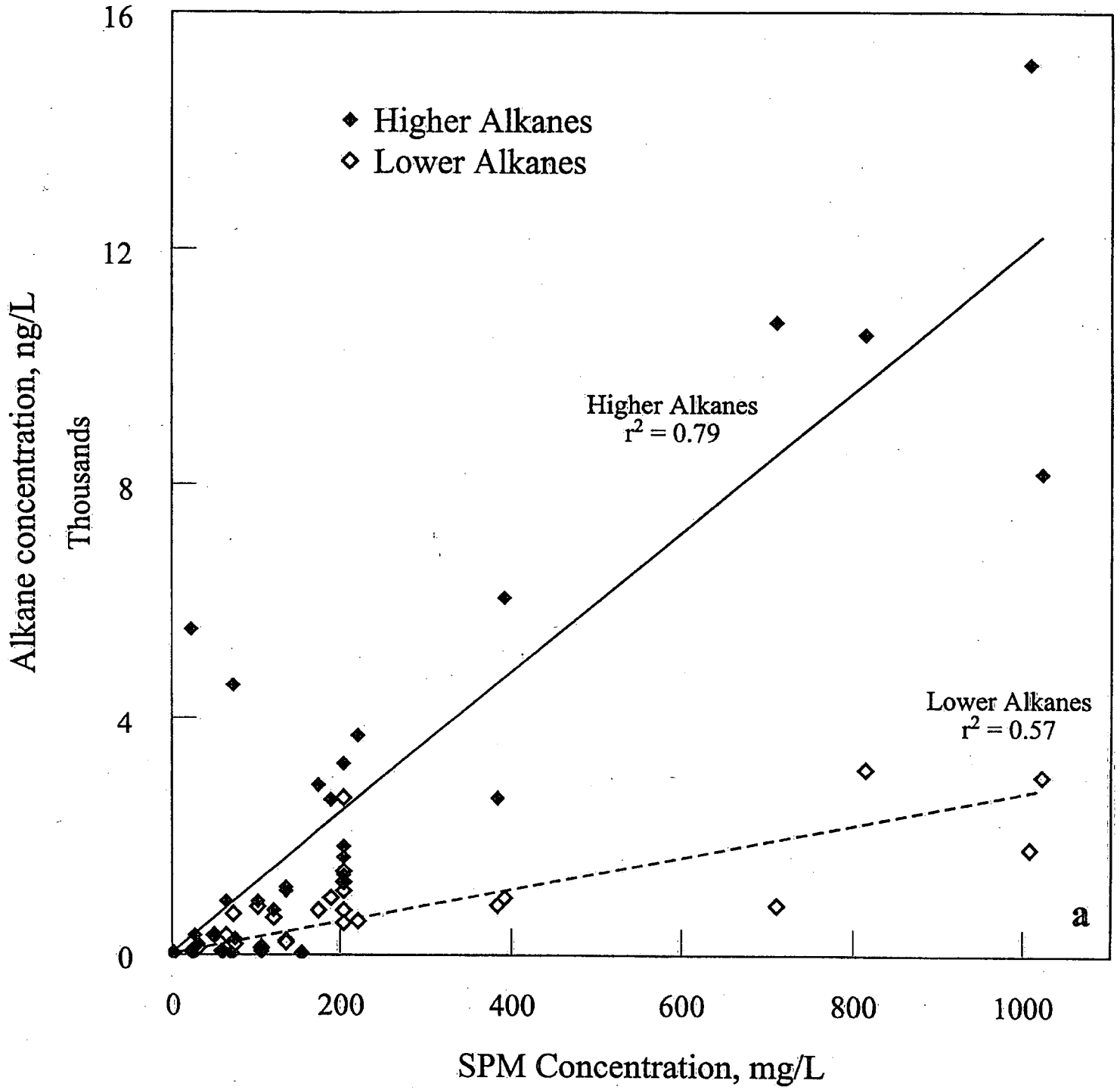
Higher Alkanes
Lower Alkanes
Higher Alkanes
$r^2 = 0.79$
Lower Alkanes
$r^2 = 0.57$
a
Alkane concentration, ng/L
Thousands
16
12
8
4
0
0
200
400
600
800
1000
SPM Concentration, mg/L

Figure 6a

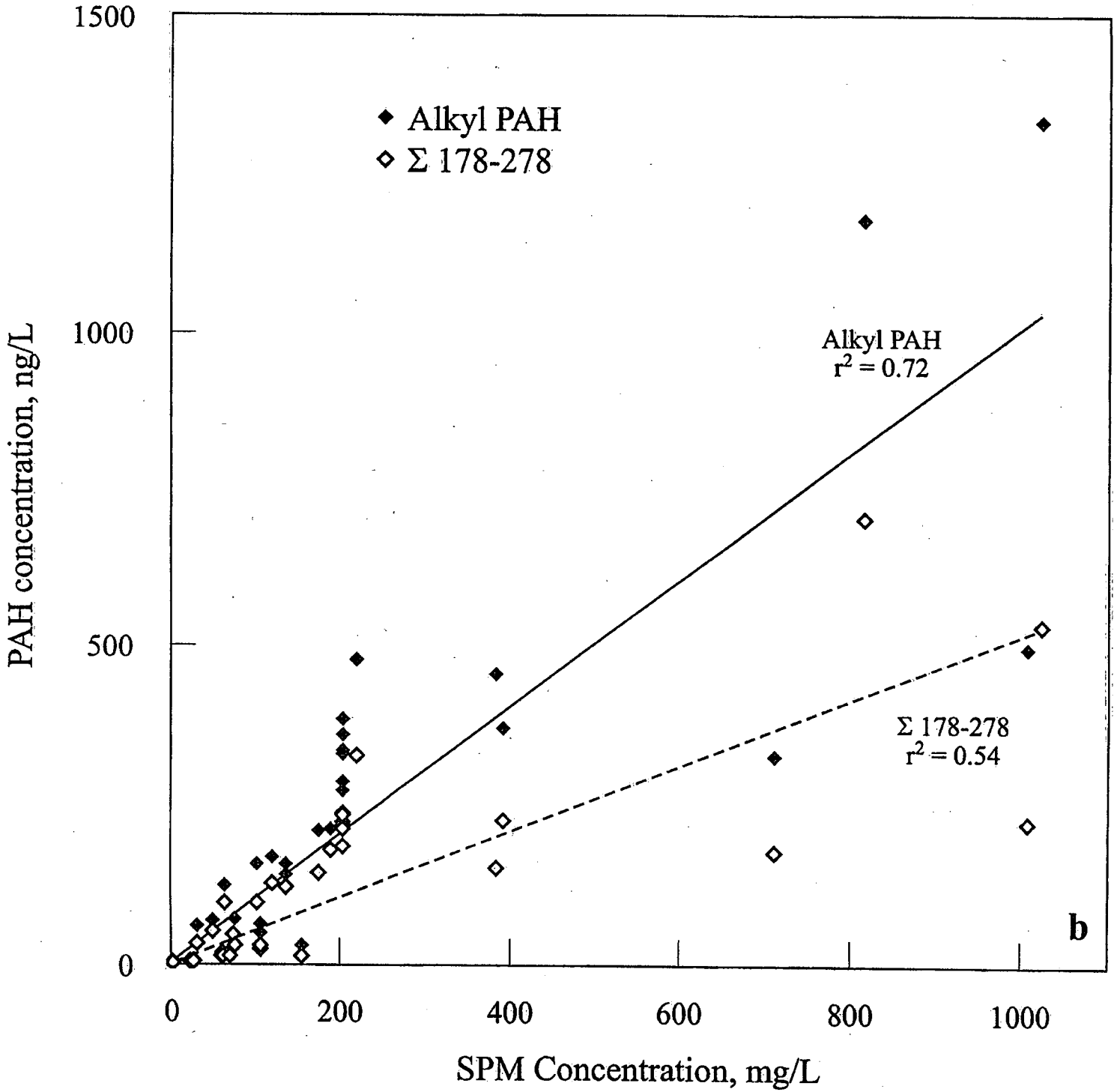
1500
1000
500
0
PAH concentration, ng/L
Alkyl PAH
Σ 178-278
Alkyl PAH
r² = 0.72
Σ 178-278
r² = 0.54
b
0
200
400
600
800
1000
SPM Concentration, mg/L

Figure 6b

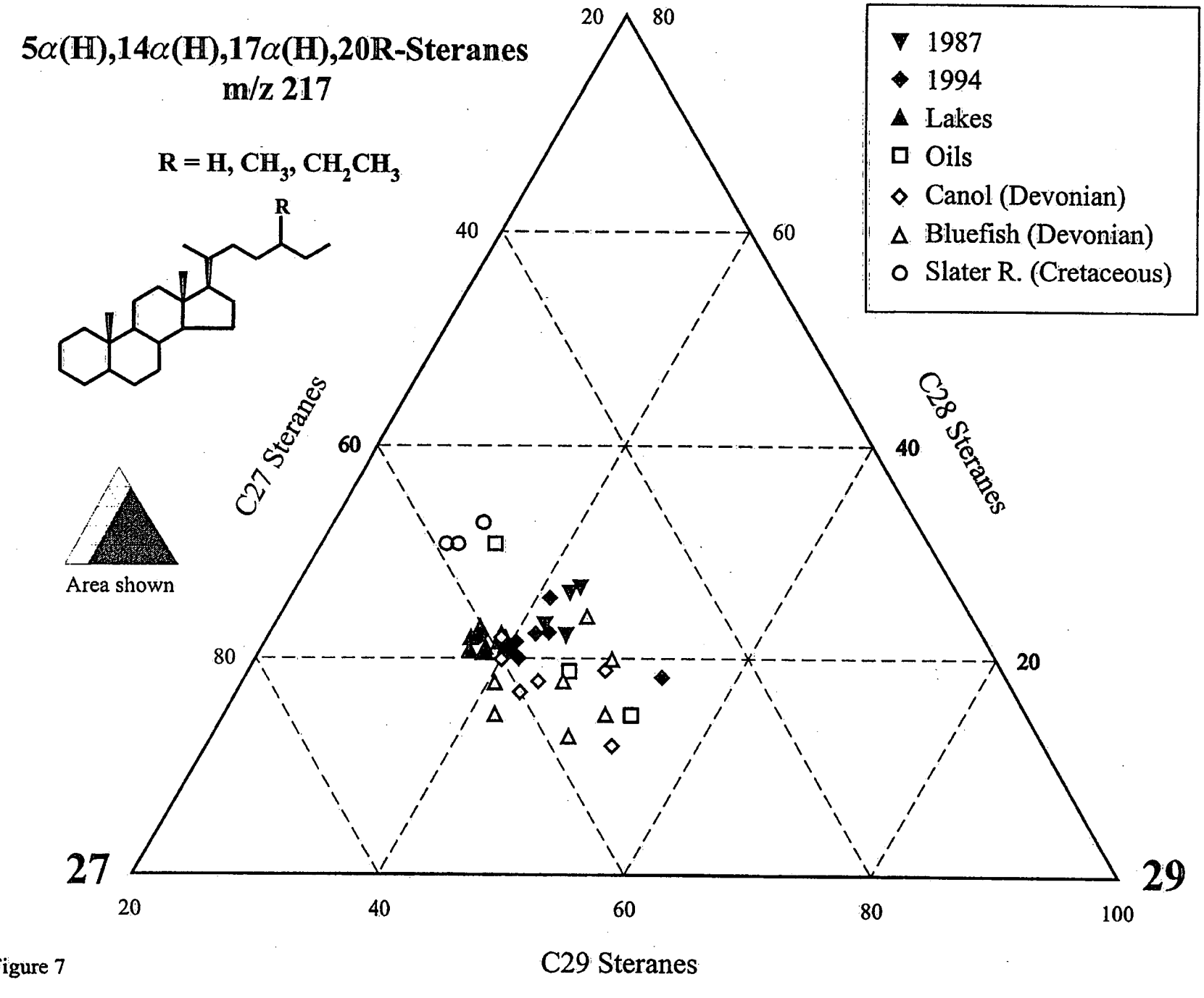
5α(H),14α(H),17α(H),20R-Steranes
m/z 217
R = H, CH3, CH2CH3
R
Area shown
1987
1994
Lakes
Oils
Canol (Devonian)
Bluefish (Devonian)
Slater R. (Cretaceous)
C27 Steranes
C28 Steranes
C29 Steranes
27
29
20
40
60
80
100

Figure 7

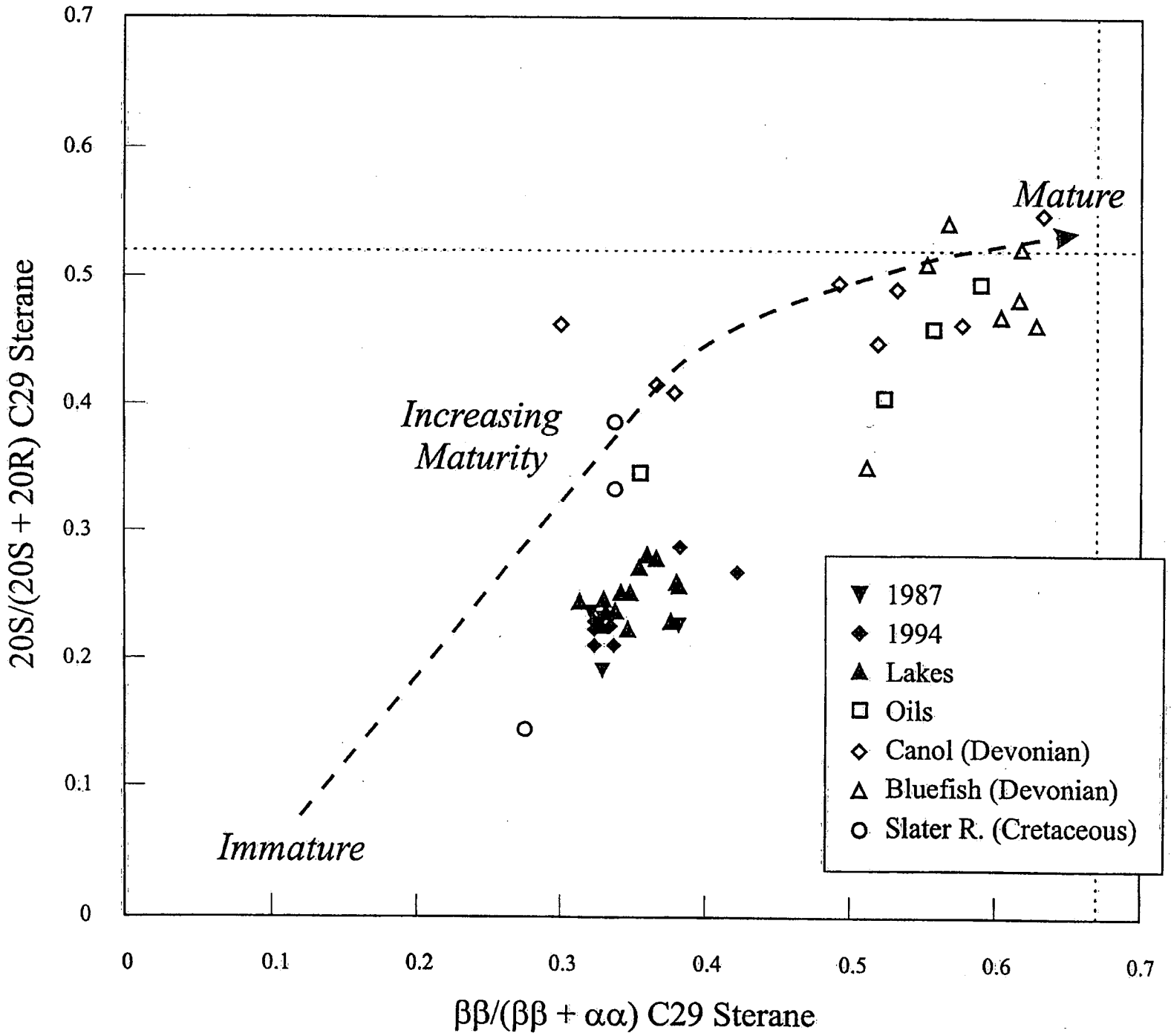
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20S/(20S + 20R) C29 Sterane
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
ββ/(ββ + αα) C29 Sterane
Mature
Increasing Maturity
Immature
1987
1994
Lakes
Oils
Canol (Devonian)
Bluefish (Devonian)
Slater R. (Cretaceous)

Figure 8

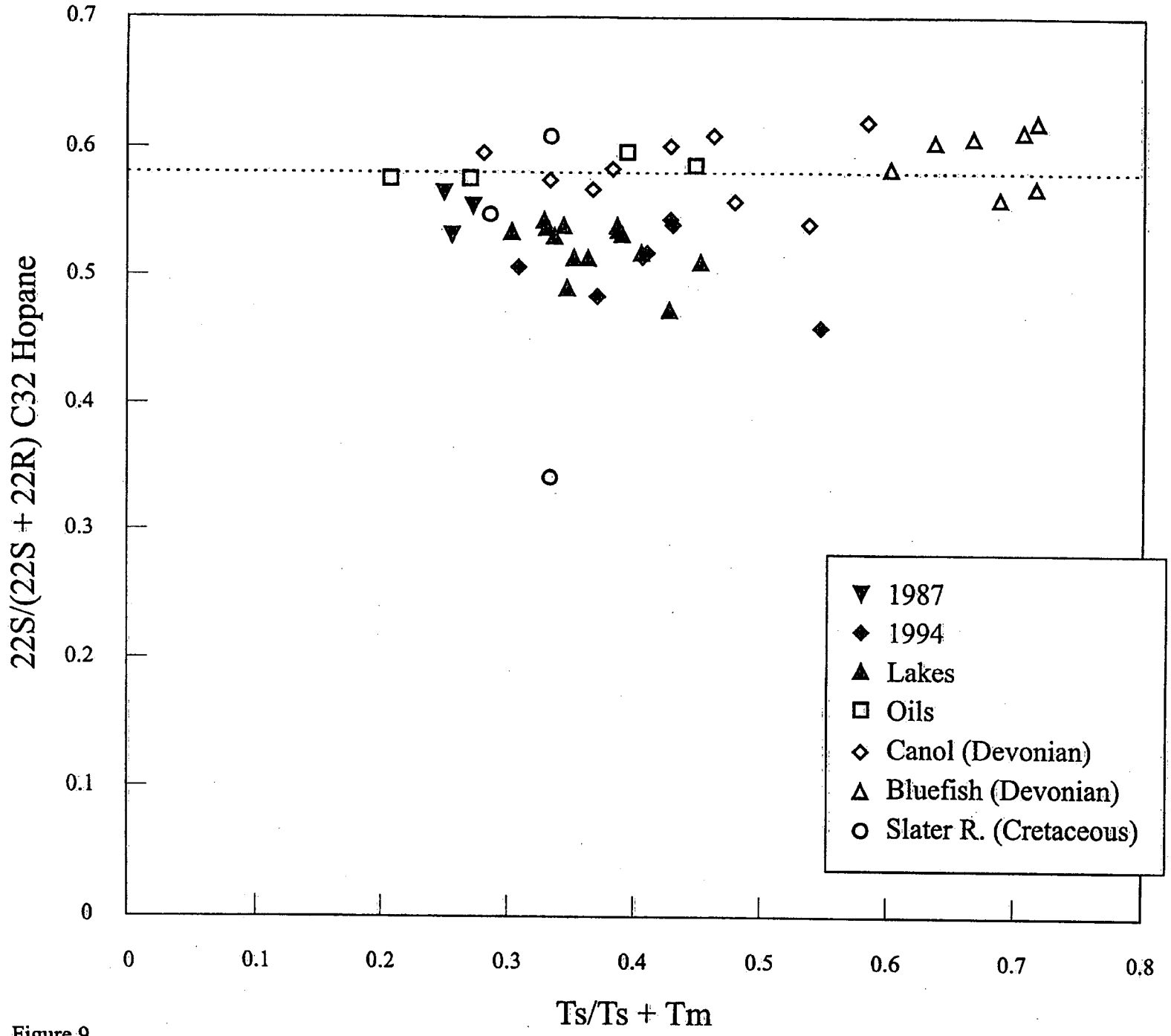
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
22S/(22S + 22R) C32 Hopane
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Ts/Ts + Tm
1987
1994
Lakes
Oils
Canol (Devonian)
Bluefish (Devonian)
Slater R. (Cretaceous)

Figure 9

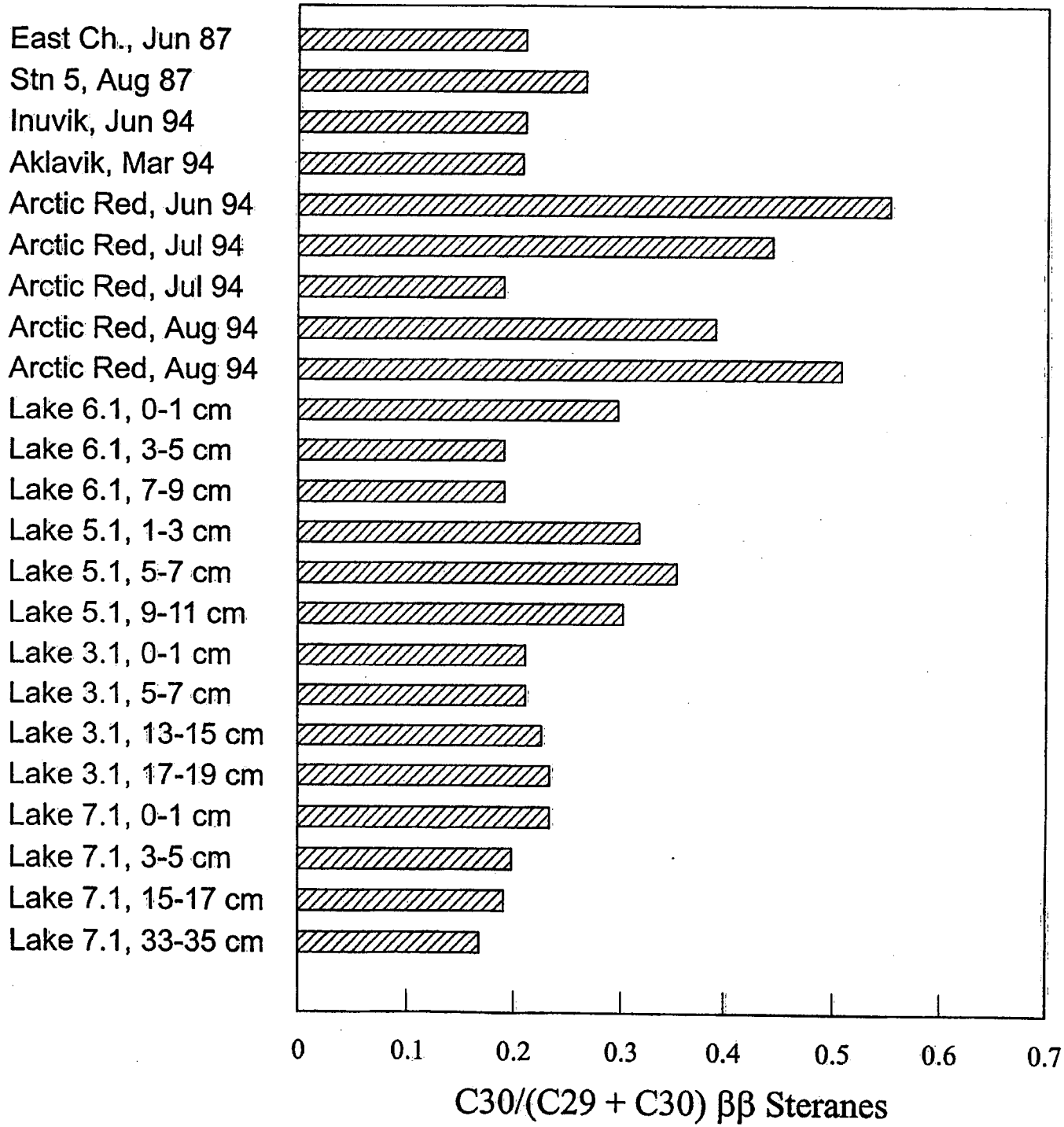
East Ch., Jun 87
Stn 5, Aug 87
Inuvik, Jun 94
Aklavik, Mar 94
Arctic Red, Jun 94
Arctic Red, Jul 94
Arctic Red, Jul 94
Arctic Red, Aug 94
Arctic Red, Aug 94
Lake 6.1, 0-1 cm
Lake 6.1, 3-5 cm
Lake 6.1, 7-9 cm
Lake 5.1, 1-3 cm
Lake 5.1, 5-7 cm
Lake 5.1, 9-11 cm
Lake 3.1, 0-1 cm
Lake 3.1, 5-7 cm
Lake 3.1, 13-15 cm
Lake 3.1, 17-19 cm
Lake 7.1, 0-1 cm
Lake 7.1, 3-5 cm
Lake 7.1, 15-17 cm
Lake 7.1, 33-35 cm
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
C30/(C29 + C30) ββ Steranes

Figure 10

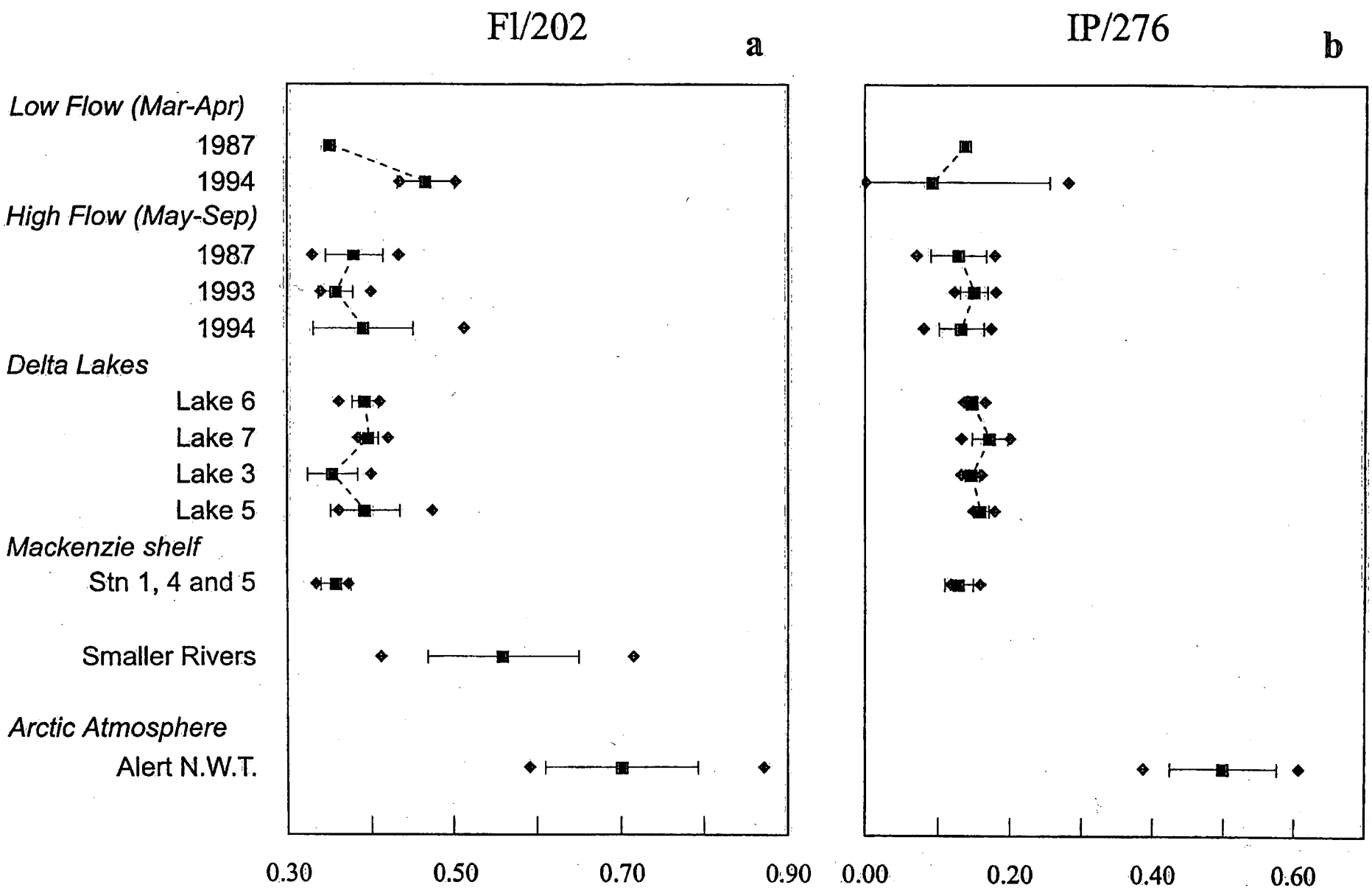

Figure 11a and b

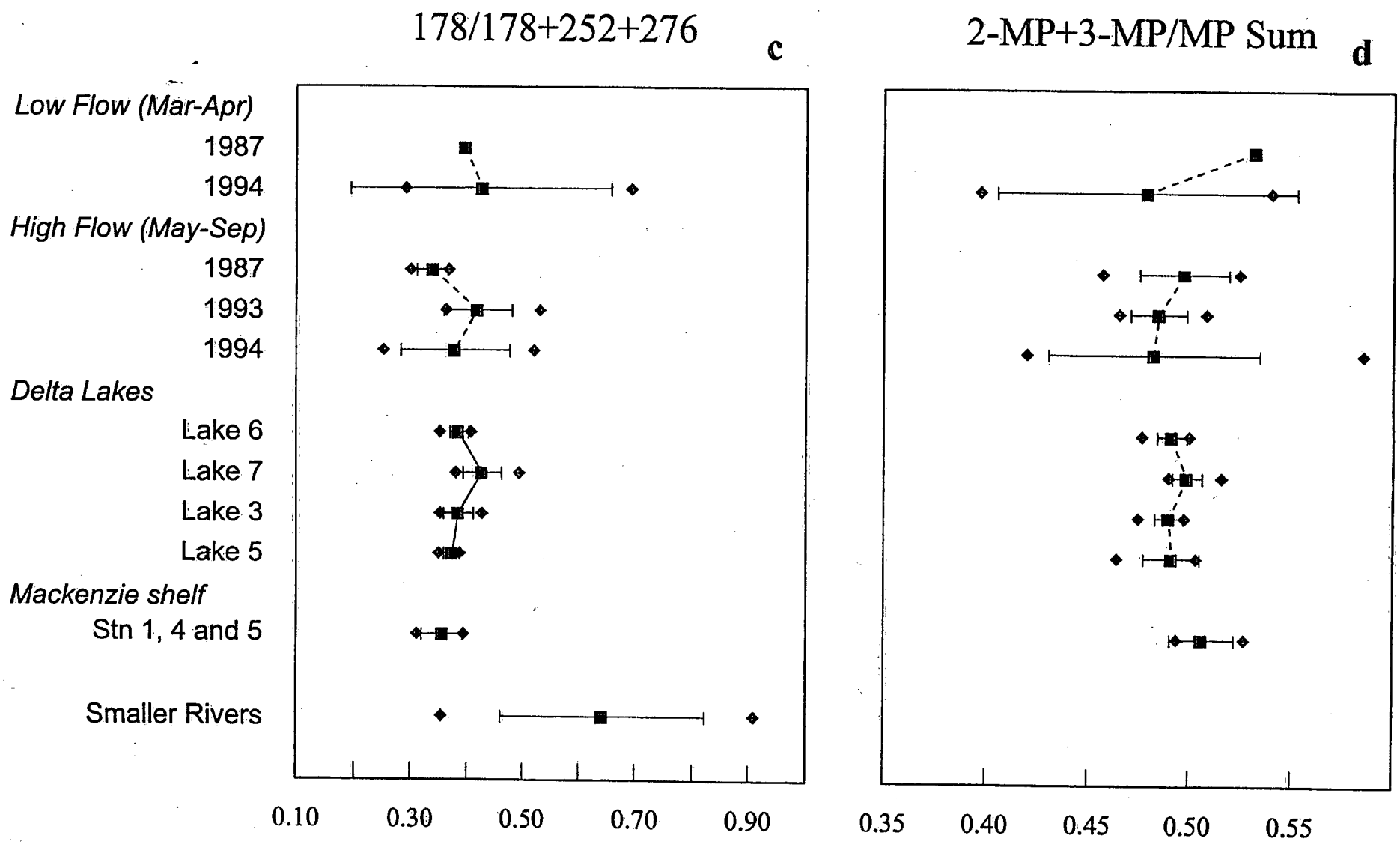

Figure 11c and d

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