

**Assessment of natural and anthropogenic
hydrocarbon inputs using PAHs as tracers.
The Fraser River basin and Strait of Georgia
(1987-1997)**

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Executive Summary

Natural and anthropogenic hydrocarbons which enter surface waters both directly from runoff and discharges and indirectly from atmospheric deposition and exchange are efficiently adsorbed onto suspended particulate matter and sediments. The quantities and relative proportions of these hydrocarbons allow an assessment of contamination patterns in marine and freshwater ecosystems. To perform such an assessment for the Fraser River basin, hydrocarbon data collected by federal and municipal sampling programs over the last decade from the Fraser River, six lakes within the Fraser basin and marine sediments from the Strait of Georgia have been synthesised. The resulting large, complex data set includes samples of surface sediment, suspended particulate matter and dated sediment cores. These samples have been analysed for a large suite of compounds in the hydrocarbon family including parent (unsubstituted) polycyclic aromatic hydrocarbons (PAHs), alkyl-substituted PAHs, alkanes, terpanes, hopanes and steranes.

The data have been interpreted by analysing relationships among the hydrocarbon compounds and classes and by the application of multivariate statistical techniques. Where available, ^{210}Pb dated sediment cores have been used to reveal the evolution over time of the hydrocarbon patterns (and concentrations) and therefore to infer change brought on by human activities or, in some cases, natural diagenetic processes. The wide spatial distribution of samples in the Fraser drainage basin and the Strait of Georgia, has been a key factor in the interpretation of geochemical and contaminant processes, as well as the comparison of anthropogenic impacts between regions.

Overall, the hydrocarbon data reveal that what was once a pristine basin with varied natural hydrocarbon geochemistry is now impacted by human activities. Pristine background sediments contain imprints of combustion (natural forest and prairie fires) and weathering of soils containing higher plant PAH, natural petroleum components and algal production. Over the past century this natural background has been augmented by variable amounts of hydrocarbon compounds through combustion (liquid fuels, coal and wood), discharge of petroleum products, and through processing or disturbance of terrestrial woody material. PAH concentrations now exceed either provincial or interim federal sediment quality guidelines in the city of Kamloops, in most post-1970 core sections from Kamloops Lake, at most locations sampled in the Fraser River estuary and Vancouver Harbour and in all sections analyzed in both cores from the Strait of Georgia. Some of these hydrocarbons have entered the aquatic systems directly *via* atmospheric deposition but, undoubtedly, much of the input comes through runoff, municipal treatment plants and industrial effluent.

We infer multiple hydrocarbon sources from human activities including oil and refined oil products, burning of coal, liquid fuels and wood, and the disturbance of terrestrial ecosystems by activities such as logging and road building and, more indirectly, by pulping woody material. Although widespread petroleum contamination is evident in alkane profiles, PAH distributions, biomarkers and alkane unresolved complex mixtures or UCMs, the clearest evidence of contamination is associated with nearby activities (e.g., roads, wastewater treatment plants, urban areas), and remote areas remain relatively pristine. Combustion products from human activities can be identified, although not as unequivocally as the petroleum products.

Within the entire region, Vancouver Harbour exhibits the heaviest PAH contamination due to large and varied contaminant sources from its large population and industry.

The following is a summary of results relative to specific regions within the study area:

In Moose Lake and Stuart Lake concentration spikes in certain PAH compounds, or changes in PAH ratios toward the core surface imply impacts from activities such as road building or logging in the drainage basin. Stuart Lake is also interesting in that the sediments contain relatively high proportions of alkyl-substituted PAHs, suggesting petrogenic (petroleum-derived) inputs. Because these inputs predate the industrial era and have not changed much in this century, we infer the sources to be natural (shales, coal, bitumens). Chilko Lake shows virtually no identifiable impact from human activities. Kamloops Lake, in contrast, clearly shows impacts from petroleum and pulp-mill activities in recent sediment layers (e.g., enhanced alkyl PAH, hydrocarbon UCM, retene). Lakes nearest to the large population centres on the coast (Harrison Lake, and to a lesser extent Nicola Lake) exhibit combustion PAHs that increased over the background fluxes in the early 1900s, and peaked during approximately the 1950s. These PAHs likely reflect atmospheric inputs of fuel-combustion products from the Greater Vancouver urban region, with the PAH concentration decrease reflecting the switch from coal to liquid fuels after the Second World War.

Throughout the Fraser River, chronic inputs of petroleum are evident in suspended sediment but less so in bed sediment. The petroleum inputs become clearly evident downstream of Prince George and Kamloops but increase considerably downstream of Chilliwack as the Fraser River enters the highly populated coastal plain. The influence of the Fraser River petroleum hydrocarbons can be detected in sediments well out into the Strait of Georgia. In particular, the tricyclic terpanes and pentacyclic hopanes appear to have good potential to identify petroleum inputs and, possibly, specific sources (e.g., the oil reservoir that produced the fuel). However, direct assignment of petroleum source proves to be a complex task because, as might be expected, the petroleum inputs are usually linked to obvious development (towns, roads, and railroads) which supplies multiple potential sources of hydrocarbons (crude oil, motor oil, asphalt, coal, etc.). At a number of locations, elevated concentrations of specific biomarkers, such as retene, suggest that some hydrocarbons derive directly from wood. Retene could be supplied directly to the river through pulp mill effluent or indirectly in disturbed watersheds (logging, road building) or through combustion of wood.

Within the Strait of Georgia, we see a strong influence of the Fraser River outside the delta. However, as we go northward and up into the industrialised and intensely populated vicinity of Vancouver Harbour, we see large inputs of combustion PAH. In general, the PAH burden in surface sediments of the Strait of Georgia is an order of magnitude higher than in older sediments from the Fraser River system, suggesting that a natural supply from the Fraser basin cannot account for the input, and that regional and local sources must also be important. Local sources to the Strait of Georgia have been identified as Point Roberts (coal dust; alkyl PAH) and municipal stormwater runoff and wastewater treatment plants (primarily flow through of street runoff containing elevated combustion and petroleum products; parent and alkyl PAHs). Overall the area exhibiting the greatest input of PAHs is Vancouver Harbour, while (based on more limited data) the lower Fraser River shows a greater input of petroleum alkanes. In the Greater

Vancouver urban region, direct and indirect inputs from the watershed clearly play a role in the supply of hydrocarbons to these areas. While petroleum and plant-derived hydrocarbons appear to be uniformly distributed in Strait of Georgia sediments, the combustion products are not. In particular, sediments from regions north of the Fraser River exhibit much higher loadings suggesting inputs from widespread combustion (vehicles, furnaces, wood burning, etc.) from urban areas.

Sommaire

Les hydrocarbures naturels et anthropogéniques qui pénètrent dans les eaux de surface, soit directement par l'intermédiaire des écoulements et des déversements soit indirectement par déposition et échanges atmosphériques, sont facilement adsorbés sur les particules en suspension et sur les sédiments. La quantité et la proportion relative de ces hydrocarbures permettent d'évaluer le degré de contamination des écosystèmes marins et dulcicoles. Afin d'effectuer une évaluation de ce type pour le bassin du Fraser, on a synthétisé un grand nombre de données recueillies dans le cadre de programmes d'échantillonnage des hydrocarbures mis en œuvre par des organismes fédéraux et municipaux au cours des dix dernières années dans le Fraser, dans six lacs à l'intérieur du bassin du Fraser et dans le détroit de Georgia. La grande base de données obtenue, très complexe, provient à la fois d'échantillons de sédiments de surface, de particules en suspension et de carottes de sédiments datées. On a mesuré dans tous ces échantillons une vaste gamme de produits qui font partie de la famille des hydrocarbures, notamment des hydrocarbures aromatiques polycycliques (HAP) non substitués, des HAP alkylés, des alcanes, des terpanes, des hopanes des stéranes.

Les données ont été interprétées en analysant les relations qui existent entre les produits et les classes d'hydrocarbures et en appliquant des techniques statistiques multivariées. À chaque fois que possible, des carottes sédimentaires datées à l'aide du ^{210}Pb ont été utilisées pour mettre en lumière l'évolution dans le temps de la répartition (et de la concentration) des hydrocarbures ainsi que des changements apportés par les activités humaines ou, dans certains cas, par les processus diagénétiques naturels. La large distribution spatiale des échantillons dans le bassin du Fraser et dans le détroit de Georgia a été un facteur clé qui a permis l'interprétation des processus géochimiques et des processus de diffusion des contaminants ainsi que la comparaison des impacts anthropogéniques d'une région à l'autre.

Dans l'ensemble, les données sur les hydrocarbures ont révélé que ce qui fut un jour un bassin vierge caractérisé par une géochimie faisant intervenir une variété d'hydrocarbures naturels subit maintenant l'influence de nombreuses activités humaines. Les sédiments provenant de zones vierges contiennent habituellement les traces de combustions passées (incendies naturels de forêts et de prairies), de l'érosion des sols (forte concentration de HAP provenant des plantes), de composants naturels du pétrole et de production d'algues. Au cours du siècle dernier, se sont ajoutées à cette composition naturelle des quantités variables d'hydrocarbures provenant de la combustion de combustibles liquides, de charbon et de bois, du déversement de produits dérivés du pétrole ainsi que de la transformation ou de la perturbation de matériaux ligneux terrestres. Les concentrations de HAP dépassent aujourd'hui les seuils fixés par les lignes directrices provinciales ou fédérales (intérimaires) sur la protection et la gestion des sédiments aquatiques dans la ville de Kamloops, dans la plupart des sections de carottes prélevées dans le lac Kamloops et postérieures à 1970, dans la plupart des échantillons prélevés sur les sites de l'estuaire du Fraser et du port de Vancouver et dans toutes les sections des deux carottes prélevées dans le détroit de Georgia. Quelques-uns de ces hydrocarbures ont pénétré les systèmes aquatiques directement par déposition atmosphérique mais il ne fait aucun doute que la plus grande partie d'entre eux provient des eaux de ruissellement, des stations d'épuration municipales et des déversements industriels.

Nous attribuons l'origine multiple des hydrocarbures aux activités humaines telles que la pétrochimie, la combustion du charbon, des combustibles liquides et du bois ainsi qu'aux perturbations infligées aux écosystèmes par les activités forestières, les aménagements routiers et, plus indirectement, par la fabrication de pâte à partir des matières ligneuses. Bien que l'on ait constaté une contamination tous azimuts par les produits pétroliers dans les profils d'alcane, la distribution des HAP, les mélanges complexes indéterminés de biomarqueurs et d'alcane ou autres, les signes les plus évidents de présence de contaminant se trouvent près des sources (p. ex. routes, stations d'épurations, zones urbaines, etc.), les sites éloignés restant relativement vierges. Les produits de combustion provenant des activités humaines peuvent être identifiés, bien que cela ne puisse se faire de manière aussi univoque que dans le cas des produits pétroliers. Dans l'ensemble de la région, c'est le port de Vancouver qui présente la plus forte contamination en HAP, certainement à cause des sources importantes et variées que l'on y rencontre et qui sont associées à sa forte population et à son industrie.

Résumé des résultats obtenus dans diverses zones de la région étudiée:

Dans les lacs Moose et Stuart, les pics de concentrations de certains HAP ou les changements de rapport de concentrations des HAP près de la surface des carottes reflètent des activités telles que la construction de routes ou l'exploitation forestière dans le bassin hydrographique en question. Le lac Stuart présente un intérêt supplémentaire parce que ses sédiments contiennent une proportion relativement élevée de HAP alkylés, ce qui suggère un apport de produits dérivés du pétrole. L'accumulation de ces produits ayant commencé avant l'aire industrielle, sans changement notable au cours du dernier siècle, on en déduit que la source de ces produits doit être naturelle (schistes, charbon, bitumes). Le lac Chilko ne semble avoir souffert d'aucun impact provenant de l'activité humaine. Les sédiments récents prélevés dans le lac Kamloops, révèlent par contre l'influence d'activités pétrochimiques et des usines de pâte à papier (niveau élevé de HAP alkylés, mélanges complexes indéterminés d'hydrocarbures, rétène). On trouve dans les sédiments des lacs situés à proximité des grands centres urbains de la côte (le lac Harrison et, dans une moindre mesure, le lac Nicola) des taux de HAP provenant de la combustion qui ont commencé à augmenter à partir du début des années 1900 et ont atteint un maximum au cours des années 1950s. Ces HAP reflètent probablement la déposition atmosphérique de produits de combustion provenant de la région urbaine de Vancouver, la diminution de la teneur en HAP correspondant au passage du charbon aux combustibles liquides après la Seconde Guerre mondiale.

On retrouve des traces de produits pétroliers dans tout le Fraser mais ces traces sont plus évidentes dans les sédiments en suspension que dans les matériaux du lit. Les apports de produits pétroliers deviennent évidents en aval de Prince George et de Kamloops et augmentent considérablement en aval de Chilliwack alors que le Fraser pénètre dans la vallée côtière densément peuplée. On retrouve les hydrocarbures transportés par le Fraser loin au large, dans le détroit de Georgia. En particulier, les terpanes tricycliques et les hopanes pentacycliques semblent pouvoir être utilisés pour caractériser les apports pétroliers et peut-être même pour identifier certaines sources (p. ex. le gisement de pétrole qui a produit le combustible). L'identification directe des sources de produits pétroliers s'avère néanmoins être une tâche complexe car, comme on s'y attend, les produits pétroliers sont habituellement liés à des développements évidents (villes, routes et voies ferrées) qui représentent autant de sources multiples d'hydrocarbures (pétrole brut, bitume, charbon, etc.). Dans un grand nombre de sites, des concentrations élevées de biomarqueurs spécifiques

tels que le rétène indiquent que certains hydrocarbures proviennent directement de matériaux ligneux. Le rétène trouvé dans les sédiments peut provenir directement des effluents des usines de pâtes à papier ou indirectement des activités entreprises dans les bassins hydrographiques (coupe d'arbres, construction de route ou combustion du bois).

On observe une forte influence du Fraser au-delà du delta, à l'intérieur du détroit de Georgia. Lorsqu'on se déplace vers le nord et qu'on pénètre à l'intérieur de la zone densément industrialisée et peuplée du port de Vancouver, on observe des apports importants de HAP. En général, la teneur en HAP dans les sédiments de surface prélevés dans le détroit de Georgia est 10 fois plus grande que celle des vieux sédiments trouvés dans le Fraser, ce qui suggère que les apports naturels du bassin du Fraser ne peuvent être suffisants pour alimenter le détroit en HAP et qu'il doit donc exister d'importantes sources régionales et locales. Parmi les sources locales, on a notamment identifié Point Roberts (poussière de charbon; HAP alkylés), les eaux de ruissellement municipales et les stations d'épuration (en particulier les écoulements de voiries qui contiennent des concentrations élevées de produits de combustion et de produits pétroliers; HAP non substitués et HAP alkylés). Dans l'ensemble, c'est le port de Vancouver qui présente les plus hautes teneurs en HAP tandis que le bas Fraser recèle les plus grosses concentrations d'alcanes. Dans la région urbaine de Vancouver, les apports directs et indirects provenant du bassin jouent un rôle indéniable dans l'accumulation des hydrocarbures dans ces régions. Contrairement aux produits de combustion, les hydrocarbures liés au pétrole et ceux dérivés des végétaux semblent être distribués de façon uniforme dans les sédiments du détroit de Georgia. Les sédiments trouvés dans les régions situées au nord du Fraser recèlent en particulier des teneurs importantes en produits de combustion, ce qui reflète des apports multiples en provenance de la zone urbaine (véhicules, chaudières, combustion de bois, etc.).

Abstract

Hydrocarbon data for surface sediments, suspended particulates and dated sediment cores from the Fraser River, from Fraser basin lakes and from the Strait of Georgia have been synthesised and interpreted. A pristine background is evident in sediments from pre-industrial times and from sediments far from modern sources. Within these “pristine” sediments are tracers of combustion (natural forest and prairie fires) and weathering of soils containing higher plant polycyclic aromatic hydrocarbons (PAHs), natural petroleum components and algal production. This natural background has been augmented over the past century by variable amounts of hydrocarbons derived from human activities. These contaminant hydrocarbons have been derived from petroleum, the combustion of liquid (oil, gasoline) and solid (coal, wood) fuels and from processing of wood either directly from disturbed land and slash burning or indirectly through pulp mill effluent. Although widespread petroleum contamination has been most evident in alkane profiles, PAH distributions, petroleum biomarkers and alkane unresolved complex mixtures (UCMs), the clearest evidence of contamination is associated with nearby activities (e.g., roads, wastewater treatment plants, urban areas), and remote areas have remained relatively pristine. Combustion products from human activities can also be identified, although not as unequivocally as the petroleum products. Within the entire region, Vancouver Harbour has exhibited the heaviest PAH contamination due to runoff from a highly urbanised watershed, discharges from chemical and wood production, atmospheric combustion emissions and a fairly low sedimentation rate.

Keywords: PAH and alkane hydrocarbons, hydrocarbon fluxes, higher plant PAH, PAH ratios, principal components analysis

Résumé

Des données concernant les hydrocarbures présents dans les sédiments de surface, les particules en suspension et les carottes de sédiments datées prélevés dans le Fraser, des lacs du bassin du Fraser et le détroit de Georgia ont été synthétisées et interprétées. Des teneurs correspondant à des matériaux vierges sont observées dans les sédiments remontant aux périodes préindustrielles et dans les sédiments prélevés dans des sites éloignés des sources modernes. Ces sédiments « vierges » contiennent des marqueurs caractéristiques de la combustion (incendies naturels de forêts ou de prairies), de l'érosion des sols contenant des teneurs élevées en hydrocarbures aromatiques polycycliques (HAP) provenant des végétaux et de la production d'algues. À ces teneurs naturelles de base sont venues s'ajouter au cours du dernier siècle des quantités variables d'hydrocarbures provenant des activités humaines. Ces contaminants proviennent de l'activité pétrochimique, de la combustion des combustibles liquides (pétrole, essence) et solides (charbon et bois) et du traitement du bois, soit directement (coupes et brûlis) soit indirectement (effluents des usines de pâtes à papier). Bien qu'on ait pu mettre en évidence une contamination générale provenant des produits pétroliers dans les profils d'alcane, la distribution des HAP, les biomarqueurs pétroliers et les mélanges complexes indéterminés d'alcane, les signes les plus évidents de contamination sont associés à des activités locales (routes, stations d'épuration, zones urbaines) tandis que les sites éloignés sont restés relativement vierges. Les produits de combustion provenant des activités humaines peuvent également être identifiés, bien qu'il soit plus difficile de leur attribuer une source unique comme il est possible de le faire dans le cas des produits pétroliers. Dans l'ensemble de la région, c'est le port de Vancouver qui présente les plus hautes teneurs en HAP à cause des ruissellements provenant d'un bassin hautement industrialisé, des déversements des usines chimiques et des usines de pâtes à papier, de la déposition des contaminants provenant de la combustion et d'un taux de sédimentation relativement faible.

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1. Introduction

The Fraser River, one of the major rivers of western North America, drains a 234,000 km² basin that encompasses a highly diverse geographical landscape of mountains (ca. 70% of the basin is over 900 m in altitude), coniferous and deciduous forests, semi-deserts, small urban areas and one large city (Dorcey, 1991; Encyclopædia Britannica, 1998). The tributaries of the river span southern British Columbia (B.C.) and have headwaters in the Rocky, Columbia and Coastal mountains and the Interior Plateau (Figure 1). The river flows through rich farming land in the extensive delta before passing through the highly urbanised municipalities of Greater Vancouver and finally draining into the Strait of Georgia, a large inland sea (6,900 km²) on Canada's west coast (Figure 2). During the past century, the delta and strait in particular have experienced escalating contaminant inputs to sediments due to increasing population and industry (Macdonald and Creclius, 1994). To date, published sediment contaminant work for the Fraser River basin and Strait of Georgia has been primarily related to organic (organochlorine, nonylphenol, alkane and polycyclic aromatic hydrocarbon, or PAH) contaminants (Yunker *et al.*, 1989; Macdonald *et al.*, 1992; 1998; Shang *et al.*, 1999; Yunker *et al.*, 1999), but metals (Macdonald *et al.*, 1991) and tributyltin compounds (Stewart and Thompson, 1994) have also been examined in the Strait of Georgia. A large body of additional, relevant PAH work has to date only been published in report format (Sekela *et al.*, 1995; Brewer *et al.*, 1998; Sylvestre *et al.*, 1998a; Sylvestre *et al.*, 1998b; Bertold and Stock, 1999).

From a larger suite of contaminants studied in the Fraser basin under Environment Canada's Fraser River Action Plan, PAHs have emerged as contaminants of concern because of documented exceedences above provincial and interim federal sediment quality guidelines for the protection of aquatic life (Brewer *et al.*, 1998). Moreover, studies in Puget Sound have revealed environmental effects associated with PAHs, especially on organisms living in close association with the sediments (Malins *et al.*, 1984). It is also well established that PAHs and other petroleum hydrocarbons can induce biological effects, including tumours (e.g., Lockhart *et al.*, 1992). A number of pioneering studies in organic geochemistry have investigated the sources of PAHs to Puget Sound (and Lake Washington, near Seattle) and the pathways affecting their distribution in sediments (Wakeham *et al.*, 1980a; 1980b; Bates *et al.*, 1984; Barrick and Prahl, 1987; Bates *et al.*, 1987). Despite the experience in Puget Sound and despite finding elevated PAH concentrations in surface sediments and biota from locations within the greater Strait of Georgia (Kay, 1989), PAH contaminant geochemistry is only recently being studied within this region (Yunker *et al.*, 1999).

Parent and alkyl PAHs have both natural (oil seeps, bitumens, plant debris, forest and prairie fires) and anthropogenic (fossil fuel and combustion) sources (e.g., Bouloubassi and Saliot, 1993; Yunker and Macdonald, 1995; Wakeham, 1996). Natural and anthropogenic sources overlap, particularly for the parent PAHs, and this has two important consequences. 1) The environmental fate and effects of anthropogenic PAH must be evaluated against a site-specific background of natural PAH. 2) It is difficult to distinguish sources based on parent PAH data alone and one must consider a broad range of hydrocarbon indicators to define inputs, transport and sedimentary persistence of PAHs. The use of a broad range of hydrocarbon indicators (including, but not limited to, trends in PAH concentrations and

ratios) together with the application of multivariate pattern recognition techniques is an efficient way to address both problems.

This study synthesises results from a number of programs conducted between 1987 and 1997 by the Departments of the Environment and Fisheries and Oceans and the Greater Vancouver Regional District (Yunker *et al.*, 1989; Sekela *et al.*, 1995; Brewer *et al.*, 1998; Sylvestre *et al.*, 1998a; Sylvestre *et al.*, 1998b; Bertold and Stock, 1999; Yunker *et al.*, 1999). A large number of parent and alkyl PAHs have been quantified in these studies, and additional PAHs and selected alkane biomarkers have been determined as part of this work. The data set encompasses a large number of sediment (grab and core) and suspended particulate matter (SPM) samples from the Fraser River basin and Strait of Georgia (Figure 1 and Figure 2). Additionally, the parent and alkyl PAHs have been determined in sediment cores from Vancouver Harbour and particulates obtained from treated effluent waste streams from the four major Greater Vancouver Regional District (GVRD) wastewater treatment plants (WWTPs).

To establish baseline PAH concentrations and distributions for the Fraser River basin we use pre-industrial core sections from ²¹⁰Pb-dated cores from six lakes. In most lakes a large proportion of this natural PAH input can be reasonably expected to be due to forest or prairie fires (Wakeham *et al.*, 1980a). Because PAHs in combustion-derived aerosol are associated with a refractory matrix of solid carbonaceous soot particles (black carbon; Miguel *et al.*, 1998), a recognisable PAH fingerprint of combustion can survive over geological time scales (Venkatesan and Dahl, 1989; Killips and Massoud, 1992; Jiang *et al.*, 1998). While the original distribution of combustion-derived PAHs can potentially be modified by alkylation of the less-stable PAHs in sedimentary environments (Jiang *et al.*, 1998), such diagenesis normally requires elevated temperatures (Alexander *et al.*, 1995; Smith *et al.*, 1995) or epochal time scales.

In this assessment an evaluation is made of alkane and PAH sources, sediment concentrations and trends with time for the region. Changes in PAH, hopane and sterane composition from the upper reaches of the river, through Greater Vancouver and into the Strait of Georgia are catalogued and interpreted. PAH ratios and principal component analysis (PCA) are used to compare PAH distributions between different regions of the basin and between the basin and the strait. Because samples of suspended particulate have been quantified from most sections of the river in 1996, we can also discuss the PAH fluxes and changes in composition from the upper reaches to the strait in terms of changes in PAH inventory.

2. Study area and Contaminant Sources

The Fraser River is the predominant source of freshwater (140 km³/yr) and sediments (12-30 x 10⁶ tons/yr) to the Strait of Georgia (Figure 2), with most of the sediment discharge occurring during the May - June freshet (Pharo and Barnes, 1976; Milliman, 1980). The North Arm of the river carries approximately 12% of the total flow, while the Main or South Arm carries the remaining 88% (Milliman, 1980)(Figure 2). The sediment transported by the river is about 20% sand; a large portion of this sand is deposited in the lower reaches where it is dredged from navigation channels to be used as construction material. The finer clay and silt fractions are discharged into the Strait of Georgia throughout the year (cf. Pharo and Barnes, 1976; Kostaschuk *et al.*, 1993), however, providing an important year-round transport vehicle for alkane and PAH hydrocarbons (Yunker *et al.*, 1999).

Much of the Fraser River drainage basin is sparsely inhabited and only lightly industrialised. Accordingly, direct inputs of anthropogenic hydrocarbons can be expected to be minimal near the headwaters of the Fraser River (north of Prince George) and in the more remote tributaries (Stuart, upper Nechako and Chilcotin Rivers; Figure 1). Hence pollutants (PAHs, pesticides, PCBs, etc.) that are transported atmospherically over long distances (Barrie *et al.*, 1997) are likely to be the major contaminant source to river sediments in these areas, as well as to Moose Lake, Stuart Lake and Chilko Lake.

Closer to major population centres petroleum products and by-products are much more prevalent and chronic discharges of anthropogenic hydrocarbons in stormwater and wastewater are expected at most locations (Volkman *et al.*, 1992; West *et al.*, 1994; Bieger *et al.*, 1996; Larkin and Hall, 1998). The numerous storm drains and small number of WWTPs collect and discharge water and wastewater that has received varying levels of contaminants (e.g., lubricating oils, muffler soot and road dust from streets or highways), but generally do not add hydrocarbon contaminants of their own. In the northern Fraser River potential direct sources specifically include secondary-treated wastewater that is discharged into the river by three pulp mills and a municipal WWTP near Prince George, and by two pulp mills and the municipal WWTP at Quesnel. Similarly on the Thompson system, secondary treated effluent from a single pulp mill and tertiary treated effluent from the municipal WWTP (discharge is suspended during the winter months) enter the river near the city of Kamloops. Hence locations that are directly downstream of major cities (such as Kamloops Lake and the eastern margin of the Strait of Georgia) are most likely to be impacted, but sites close to population centres such as Nicola Lake and Harrison Lake are also likely to be effected.

In the lower Fraser River, the number of potential direct and chronic sources of anthropogenic hydrocarbons increases dramatically. At the entrance to the Fraser valley, the town of Hope discharges primary-treated municipal wastewater to the Fraser River. Between Hope and Greater Vancouver, inputs are likely to be confined to agricultural runoff and discharges from moderate sized communities such as Abbotsford and Chilliwack. On the eastern side of Greater Vancouver the small Northwest Langley WWTP discharges secondary treated wastewater into the Fraser River (Bertold and Stock, 1999). At the time of sampling for this study, primary treated municipal wastewater was discharged directly through diffusers into the main arm of the Fraser River by the Annacis Island (8.4 m below lower low water) and Lulu Island (7.4-11.6 m depth) WWTPs. (Full secondary treatment commenced in late-1998 and early-1999, respectively.) The Iona Island and Lions Gate plants discharge primary treated wastewater through submarine outfall diffusers located in the Strait of Georgia off Sturgeon Bank (72-106 m depth) and in outer Burrard Inlet, west of the Lion's Gate bridge (17-23 m depth), respectively (Bertold and Stock, 1999). Of the four main WWTPs, Lulu Island and Lions Gate process domestic and industrial wastewater and sewage, while the Iona Island and Annacis Island plants are combined sewers that also process stormwater runoff from roads. During wet weather stormwater runoff can overload the Iona and Annacis Island systems, and excess wastewater is discharged through combined sewer overflows (CSOs) into Burrard Inlet and the North Arm of the Fraser River.

Within the Greater Vancouver vicinity (Figure 2), areas along the river in New Westminster and the North Arm also are heavily industrialised with steel and metal plants, sawmills, and food processing and creosote treatment plants. An additional potential source of petroleum hydrocarbons to the Fraser River, Burrard

Inlet and the Strait of Georgia is provided by the four oil refineries located on Burrard Inlet: Petrocan, Ioco, Shell and Chevron. Currently Chevron is the only refinery still processing crude oil, while the other three now handle only refined products. All petroleum products (including the crude oil) are shipped by pipeline from Alberta, and all refineries provide secondary treatment to stormwater (e.g., tank farm drainage) and process effluent. The Petrocan refinery discharges treated effluent into the wastewater system that feeds to the Annacis Island WWTP (with a number of CSOs along the way that discharge to the Fraser River). Prior to 1989 the Ioco refinery discharged treated stormwater and process effluent directly into Port Moody Arm, but now both effluents are diverted to the Annacis Island system. Shell and Chevron discharge treated effluent into another section of the system that crosses the city of Vancouver (with CSOs to Vancouver Harbour) and eventually ends up at the Iona Island WWTP.

3. Methods

3.1 Sampling

Suspended Particulate Sampling Locations. In the Fraser Basin samples of suspended particulate (Figure 1 and Table 1) were collected either at fall low flow or winter base flow. In the lower Fraser River in February 1987 samples were obtained mid-stream from the Main Arm at the Pattullo Bridge, just upstream of the limit of saline intrusion (Milliman, 1980), and within the zone of salt-wedge formation (Kostaschuk *et al.*, 1992) at the lower end of the river estuary near Steveston Island (Yunker *et al.*, 1989)(Figure 2). In late October/early November 1996 samples were obtained again approximately 400 m upstream of the Pattullo Bridge, in the initial dilution zone of the Annacis Island WWTP (~200 m directly downstream of the diffuser discharge) and from the North Arm 10 km downstream of the trifurcation of the river (Sylvestre *et al.*, 1998b; Sylvestre *et al.*, 1998a).

In the upper basin, the October 1992 and February and November 1993 samples were obtained near shore in the Fraser River at Shelley (18 km upstream of Prince George; Figure 1), Woodpecker (60 km downstream of Prince George), Marguerite (65 km downstream of Quesnel) and Yale (450 km downstream of Marguerite), and in the Thompson River system at McLure (on the North Thompson, 41 km upstream of Kamloops) and Savona (on the Thompson River 60 km downstream of Kamloops and 2 km downstream of Kamloops Lake)(Sekela *et al.*, 1995). In November 1994, the sampling was repeated at all sites except McLure and Savona. The October/November 1996 samples were collected on the Fraser River at McBride (200 km and 2 km upstream of Prince George and McBride, respectively), Woodpecker, Marguerite and Agassiz (in the Fraser valley 400 km downstream of Marguerite on the Fraser River and 250 km downstream of Savona on the Thompson River) and on the South Thompson River (35 km upstream of Kamloops) and the Thompson River at Savona (Sylvestre *et al.*, 1998b).

Effluent suspended solids were collected at four separate times between early October and early December 1997 from the effluent waste streams of the Annacis Island, Lulu Island, Iona Island and Lions Gate WWTPs (Figure 2). These samples were collected by Greater Vancouver Sewage and Drainage District staff (Bertold and Stock, 1999).

Suspended Particulate Sampling. The 1987 samples were obtained 100 m downstream the Pattullo Bridge (salinity 0.04; depth 7 m) by both direct filtration using precombusted GF/D and GF/F glass fibre filters (Whatman, 293 mm; nominal pore size 0.7 μm) and by integrated collection over 3.5 h using a continuous flow centrifuge and across the channel from Steveston Island (salinity 4.1-19.0; 5 m) using direct filtration (Figure 2). Sampling depths in the Fraser River were selected to sample the turbidity maximum. Suspended particulate matter (SPM) concentrations (mean \pm SD) were not significantly greater at the Pattullo Bridge (10.6 ± 2.2 mg/L, n=7) than at Steveston Island (8.9 ± 3.0 mg/L, n=9). All wetted surfaces were Teflon or stainless steel and were well cleaned with organic solvents (Yunker *et al.*, 1989).

The 1992-1996 suspended particulate samples were collected using as many as four continuous flow centrifuges (Westfalia Separator model KA-2-06-175) with as many as three submersible pumps (March model 5C-MD) used to deliver water from the river to the centrifuges. For all samples except the estuary samples (Pattullo Bridge, Annacis Island and North Arm; Figure 2), the pump intakes were suspended in the river approximately 3 m from shore and 1 m below the surface. For the estuary samples, the pump intakes were suspended from a research vessel and positioned at 1m, 3m and 5m depths from the surface. Teflon tubing was used to deliver the sample water from the pump to the centrifuges (Sylvestre *et al.*, 1998b). The flow rates of the centrifuges were maintained at approximately 4 L/min and the centrifuges were operated until approximately 300 g of sample was obtained (6 - 18 hours). Flow rates and total volumes were measured using an inline flow meter.

In 1997 an Alpha Laval centrifuge was used to obtain samples of effluent suspended solids from the four main GVRD WWTPs (all except the Northwest Langley plant). Each sample was based on an 8-h constant-flow integrated sample (Bertold and Stock, 1999).

Sediment Cores and Grabs. Samples of sediment (Table 2) were obtained in the Strait of Georgia at station A in November 1993 and station CM2 in the Saturna basin in February 1997 and from depositional areas in Vancouver Harbour (Burrard inlet) at stations CH-I and PM-V in October 1994 using a box corer (0.06 m², 50-55 cm deep) with a stainless steel liner (Yunker *et al.*, 1999)(Figure 2). The harbour cores were from the centre of the inner harbour (CH-I) and the eastern harbour (PM-V) in Port Moody Arm. Sediment cores were sectioned using stainless steel tools that were cleaned between samples (tap water, distilled water, and acetone). One wall of the removable stainless steel liner was lowered to allow subsampling of each core with minimal disturbance. Sediment from the outer 5 cm of the box was discarded. Subsamples (1-cm interval for the top 10 cm, 2-cm intervals from 10-30 cm and 5 cm intervals deeper) were split for organic determinations (glass Mason jars with Teflon-lined lids) and other determinations (Whirl-pak bags) and frozen. Mason jars were stringently precleaned (detergent rinse, 4-h soak in 2% RBS, distilled water rinse and baked overnight at 350 °C).

Sediment core samples (10 cm i.d.) were also obtained in November 1993 from Nicola Lake and Harrison Lake, June 1994 from Moose Lake, Chilko Lake, Kamloops Lake and Stuart Lake (Macdonald *et al.*, 1999), and February 1995 from two locations near the mouth of the North and Main Arms of the Fraser River (Figure 1 and Figure 2). From the North Arm, the MS-3 core was from McDonald Slough, a

backwater that has been used for log booming for decades. From the Main Arm, core GS-2 was from a small channel by Gunn Island, at the edge of a bird sanctuary.

Additional cores were obtained in July 1996 on Sturgeon and Roberts Banks at locations that coincide with those sampled by Gordon (1997)(Figure 2). Full cores were obtained at station AO adjacent to the Iona WWTP on the southern side of the Iona Jetty (where primary treated effluent was discharged into an open channel on Sturgeon Bank from 1963-1988), station A10 on Sturgeon Bank near the mouth of Middle Arm and from station BPt-1 on Roberts Bank near to the base of the causeway to the Westshore coal terminal. Surface samples (0-1 cm) were collected on southern Sturgeon Bank at station A12 and northern Roberts bank at station A14. Present day sediment transport on Sturgeon Bank is confined between the Iona and Steveston Jetties and on Roberts Bank between the Steveston Jetty and the causeway to the Westshore Coal Terminal.

Four sediment grab samples were collected in both 1994 and 1995 from eight Fraser River reaches: the upper Fraser River (McBride to Prince George), Nechako River, the sections of the Fraser River between Prince George and Quesnel, Quesnel and Lytton, and Lytton and Chilliwack, the North and the South Thompson Rivers and the Thompson River between Kamloops and Lytton (Table 2 and Figure 1). In 1995 and 1996 grab samples were also obtained from the Main and North Arms of the river between New Westminster and the mouth, and the section between Lytton and Chilliwack was also sampled again in 1996. In addition, grab samples were obtained from single sites in the Stuart, Chilcotin, Quesnel and Harrison Rivers. Locations and geographical co-ordinates are detailed in Brewer *et al.* (1998).

Fraser River sediment grabs were collected using an Eckman dredge (15 x 15 cm, 15 cm high) at a distance between 0.5 and 5 m from shore (Brewer *et al.*, 1998). The majority of samples were collected by wading into the river at a depth of 0.5 to 1.0 m, although the Fraser River North Arm and Main Arm samples and one of the Prince George locations had to be sampled by boat. All sampling equipment was made of stainless steel, and sample collection containers were made of Teflon. All jars and equipment contacting the sediment were washed with laboratory detergent, rinsed with tap water and deionized water and then pesticide grade acetone and hexane, and air-dried. A minimum of five bed sediment grabs was collected from each site. Sediment that came in contact with the sides of the dredge was discarded, and only the top layer (2-3 cm depth) of fine sediment from each grab was collected with a stainless steel spoon. Sediment from each of the grabs was homogenised in a stainless steel tray, subsamples for analytical splits and particle size determination were removed, and then samples were placed in Teflon sample containers and kept chilled until frozen. All samples for organic contaminant analysis were frozen within five hours of collection.

3.2 Carbon and particle size analysis

For the core samples and 1987 centrifuged suspended sediment samples, total carbon was measured by thermal conductivity in a Carlo-Erba 1106 CHN analyser following combustion in oxygen. Carbonate carbon was measured by coulometry following acid evolution of CO₂ in HCl. The method is fully described in Calvert *et al.* (1995).

For the Eckman dredge sediment grab samples and 1996 centrifuged suspended sediment samples, total organic carbon was determined by Cantest Ltd. in Vancouver, B.C., using a Leco Carbon analyser, and by the National Laboratory for Environmental Testing in Burlington, Ontario, using a PE2400 CHN analyser. Sediment particle size was determined by Geo-Sea Consultants in Cambridge, UK using a Malvern 2600L laser particle size analyser.

3.3 Hydrocarbon determinations

PAH (Table 3) and alkane analyses were performed by Axys Analytical Services Ltd. of Sidney, B.C. Details of the extraction and analysis methodology, calibration standards and determination of response factors have been recently provided in Yunker *et al.* (1999). Perdeuterated compounds were used for both surrogate (10 PAH standards from [²H₈]naphthalene to [²H₁₂]benzo[*ghi*]perylene; four alkanes from [²H₂₆]dodecane to [²H₇₄]hexatriacontane) and recovery standards (three PAH standards). The stated concentration was used for analytes reported by the laboratory as NDR (peak detected but confirming-ion ratios outside of the specified range).

PAH and alkane samples from Harrison Lake and Nicola Lake and PAH samples from station A in the Strait of Georgia were extracted using a base digest method (Yunker *et al.*, 1999). All other samples were extracted using column elution extraction. The latter method generally gives better surrogate recovery and fewer emulsions and usually performs better for samples with high fines content (Cretney, pers. commun.). Hydrocarbon data for samples extracted by the two methods can be combined without bias (Yunker *et al.*, 1999).

PAH and alkane data have been reported for 1992-1996 suspended particulate and bed sediment samples from the Fraser River and sediment cores from Nicola Lake, Harrison Lake, Moose Lake, Chilko Lake, Kamloops Lake, Stuart Lake, station A and Burrard Inlet (Axys Analytical Services Ltd., 1995a; Axys Analytical Services Ltd., 1995b; Sekela *et al.*, 1995; Boyd *et al.*, 1997; Brewer *et al.*, 1998; Sylvestre *et al.*, 1998a; Sylvestre *et al.*, 1998b). Additional alkane and PAH data for the 1987 Fraser River suspended particulate samples and sediments from Stuart Lake, Kamloops Lake, McDonald Slough, Gunn Island, Sturgeon Bank, Roberts Bank and station CM-2 have been formally reported by Axys but have not been presented in a data report.

For this work concentrations of acephenanthrylene, the mass 276 and 278 PAHs and the methylated tetra- and octahydrochrysenes and tetrahydropicenes (Table 3) were also determined for all samples using peak areas from the original laboratory chromatograms and relative retention times and response factors obtained according to Yunker *et al.* (1999). Consistent peak assignments and procedures for peak identification were applied to all samples. To further ensure data comparability concentrations of dibenz[*a,c/a,h*]anthracene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene were also recalculated as part of this quantification.

PAH concentrations for the full suite of PAHs shown in Table 3 have been reported for effluent suspended solids samples obtained in early October, 1997 from the Annacis Island, Lulu Island, Iona Island and Lions Gate WWTPs (Bertold and Stock, 1999). For the three subsequent samplings at each WWTP

data were only available for the standard series of parent and alkyl PAHs (i.e., not acephenanthrylene, or the additional mass 276 and 278 PAHs).

Concentrations of the hopane and sterane biomarkers were calculated with respect to [²H₅₀]tetracosane using response factors calculated from representative mass spectra using the abundance of the quantifying ion relative to the total ion current of each compound. Oleanane identifications have been based solely on retention time, and gas chromatography-mass spectroscopy-mass spectroscopy (GC-MS-MS) would be required to positively confirm assignments.

3.4 Quality assurance/quality control

Alkane and PAH samples were analysed in batches of usually 10 samples along with one sample blank, one sample duplicate and a sediment sample spiked with a known quantity of the even *n*-alkanes from *n*-C₁₂ to *n*-C₃₆ plus pristane or 17 parent PAHs from naphthalene to benzo[*ghi*]perylene (as appropriate). Recovery of each perdeuterated surrogate standard relative to the recovery standard added just before instrumental analysis was between 50-120% in almost all cases. Surrogate recoveries for both alkanes and PAHs were markedly better with the column elution method, particularly for [²H₇₄]hexatriacontane and [²H₁₄]dibenz[*a,h*]anthracene. Procedural blanks demonstrated non-detectable or low background levels of hydrocarbons. Agreement within each pair of sample duplicates was generally ± 20% of the concentration of each hydrocarbon. Recoveries of alkanes and PAHs from spiked samples were generally within the range of 70-130%.

To determine the variability among different sediment grabs taken from one site, five separate grabs were collected near the mouth of the North Arm of the Fraser River, and the individual samples and the homogenate from these grab samples were submitted separately for analysis. The coefficient of variation (CV) for the five individual grabs ranged from 7-36% with a median CV of 14.6% (Brewer *et al.*, 1998). The average concentrations of individual PAHs in the five separate grab samples also showed good agreement with the PAH concentrations measured in the composited sample (median CV = 10.7%). The low CV values between the individual grab samples and between the average of the five grab samples and the composite sample demonstrated good analytical precision and indicated that a composite of five grab samples provided a representative measure of sediment concentrations at a given sampling site.

Potential interferences and closeness to the limit of detection were also assessed for alkane and PAH measurements before data were used to interpret geochemical or environmental features.

3.5 Calculation of PAH relative stability

The relative stability of parent PAHs was calculated using two methods. The PAH Heat of Formation (H_f) was calculated with the AM1 method using *Hyperchem*, V4.5, [Hypercube, Inc., 419 Philip St., Waterloo, Ontario, N2L 3X2, Canada] and both H_f and the Strain Energy (SE) were calculated by the PCMODEL method using *PCMODEL*, V5.13, [Serena Software, Box 3076, Bloomington, Indiana, 47402-3076, USA].

In principle the values obtained by the AM1 and PCMODEL calculation methods should agree, but because the two methods used different parameters (e.g., PCMODEL allowed hydrocarbons to deform from planarity if they were strained, more than did AM1), in practice they did not (Table 4). However, the differences either in the Heat of Formation or Strain Energy by either method have provided a meaningful measurement of relative stability of different PAH isomers, even if the absolute values did not agree. The Heat of Formation calculation looked at all energy, both electronic (including π -energy, representing the differences in aromaticity) and steric (bond stretching, bending, twisting, etc.), while the Strain Energy only focused on steric differences. Hence, by examining the Strain Energy an estimate has been obtained of how much of the stability difference between isomers was due to steric considerations.

Mass 178. Both the AM1 and PCMODEL methods agreed that phenanthrene was more stable than anthracene by about 6 kcal/mole. Half of the difference was probably steric (the bay interaction) and half resonance energy. The relative stability of the phenanthrene/anthracene and pyrene/fluoranthene pairs has been discussed previously (Gschwend and Hites, 1981; Budzinski *et al.*, 1997).

Mass 202. With a structure entirely comprised of six-membered rings, pyrene was substantially more stable than either of the five-membered-ring-containing isomers, and fluoranthene was more stable than acephenanthrylene. Most of the difference in stability between pyrene and fluoranthene was steric (11.8 out of 13.2 kcal/mole), while steric and resonance energy differences were important for pyrene and acephenanthrylene.

Mass 228. The small difference in stability between the triphenylene and chrysene was probably not significant, and there was only a marginal difference between these two isomers and benz[*a*]anthracene. With this small energy separation, the two different calculation methods predicted a different order of isomer stability. Note also that triphenylene had the highest strain energy, but the larger resonance energy of this isomer relative to the others overcame this and overall triphenylene was the most stable molecule. Triphenylene and chrysene co-elute under normal GC conditions and a combined total has been reported here (Table 3).

Mass 252. All of the differences in stability between the molecular mass 252 isomers were significant. Both calculation methods led to the same isomer order, and both indicated that benzo[*e*]pyrene was the most stable isomer. Not surprisingly the “all six ring” isomers (benzo[*e*]pyrene, benzo[*a*]pyrene and perylene) were more stable than those containing a five membered ring (the benzofluoranthenes). While, the H_f differences between the three benzofluoranthenes were large enough to be significant, the three isomers have not been sufficiently separated under normal GC conditions to report individual concentrations (Table 3).

Mass 276. Again the differences between isomers were all significant and both methods gave the same stability order, with benzo[*ghi*]perylene the most stable and indeno[7,1,2,3-*cdef*]chrysene the least stable isomer.

Mass 278. The differences between dibenz[*a,h*]anthracene, picene and dibenz[*a,j*]anthracene were not significant, nor probably were the differences between dibenz[*a,c*]anthracene, benzo[*b*]chrysene and

pentaphene. However, both methods indicated that the first triad was a few kcal/mole more stable than the second triad. The interpretation of relative stability of the mass 278 PAHs has been complicated by the co-elution of dibenz[*a,h*]anthracene and dibenz[*a,c*]anthracene, PAHs that were in different triads.

3.6 Principal components analysis

The approach and methodology used for principal components analysis has been described in detail (Yunker and Macdonald, 1995; Yunker *et al.*, 1995). Briefly, unsupervised principal components analysis (PCA) was performed using the non-linear iterative partial least squares (NIPALS) algorithm in a program which allowed a detailed examination of both sample and variable projections (respectively scores and loadings; software was provided by the Chemometrics Clinic, Seattle, Washington). Undetected “zero-values” were replaced by a random value between zero and the detection limit. Each variable was evaluated for the percentage of undetectable (random value estimated) values before inclusion in the PCA data set (Yunker *et al.*, 1999). Because the outcome of PCA can be highly dependent on data scaling or pre-processing, careful consideration was given to choosing the most suitable pre-processing technique (Wold *et al.*, 1984; Kvalheim, 1985); several techniques (normalisation, log transformation, and variance and mean scaling) were evaluated before adopting the methods used.

Here the primary purpose of PCA modelling was to compare PAH distributions in different parts of the Fraser River basin to distributions in Greater Vancouver and the Strait of Georgia. Because concentrations differed by orders of magnitude in the different regimes being studied, normalisation of each sample before PCA was desirable. As in previous work (Yunker *et al.*, 1995), we found that the technique of mid-range normalisation was preferable to normalisation to the concentration total because there were fewer spurious effects in the normalised variables due to closure (Johansson *et al.*, 1984). This method employs a normalisation factor derived from a subset of variables with mid-range standard deviations and means (Johansson *et al.*, 1984). In the final model data were mid-range normalised and autoscaled (scaled to the mean and unit variance) before PCA. The PCA model had eigenvalues greater than 1.0 to PC4, indicating that the range of real (as opposed to random) variation in the data sets extended to the fourth PC (Meglen, 1992).

4. Hydrocarbon Parameters

To address questions of natural vs. anthropogenic PAH inputs, we utilise the relative proportions of different PAHs, PAH ratios and multivariate pattern recognition techniques as tools to interpret data for a wide range of parent, alkyl and higher plant PAHs (Table 3) in a large number of samples (Table 1 and Table 2). To further assess petroleum input we have quantified the resolved *n*-alkanes and isoprenoids plus the petroleum-derived unresolved complex mixture (UCM; a broad envelope that typically extends from phytane to *n*-C₃₃ and is usually centred near *n*-C₂₅). Additional biomarkers quantified in the alkane fraction of selected samples are the biogenic (bacterial) hopanes and the diagenetically modified (structurally rearranged) tricyclic terpanes, pentacyclic hopane triterpanes, regular steranes and diasteranes (e.g., Ourisson *et al.*, 1987; Volkman *et al.*, 1992; Peters and Moldowan, 1993)(see Table 5 for a list of compounds).

For parent PAH concentration comparisons, we use a total of the mass 178-278 constituents that is based on the common parent PAHs with three and more rings (Table 3). The smaller, more water soluble parent PAHs have been excluded from this group to restrict the discussion to PAHs that are likely to remain particle-bound during transport in the water column (McVeety and Hites, 1988; Yunker *et al.*, 1995). Note that perylene is also excluded from the Σ 178-278 PAH total (Table 3), because it is produced naturally in many sedimentary environments (Wakeham *et al.*, 1980b; Venkatesan, 1988; Yunker *et al.*, 1999).

To evaluate the input of plant detritus and plant degradation products we examine the concentrations and proportions of a two groups of stable, alkylated PAHs that have a source in higher plants (e.g., Wakeham *et al.*, 1980b; Simoneit and Mazurek, 1982; Yunker and Macdonald, 1995). The first group includes the two- and three-ring PAHs cadalene, simonellite and retene (Table 3). Simonellite has often been regarded as the principal natural precursor for retene (Wakeham *et al.*, 1980b; Simoneit and Mazurek, 1982). However, recently Jiang *et al.* (1998) have found that simonellite and retene have varied independently of one another with changes in climate, plant cover, etc. in a core dating back to the Triassic, and conclude that the two PAHs can be derived from different types of plants. Recently retene also has been implicated as a contributor to pulp mill effluent toxicity due to its strong induction of mixed function oxygenase in fish (Hodson, 1996). It is conceivable that other two- and three-ring higher-plant derived PAHs with similar structures (such as cadalene or simonellite) could also be contributing to the PAH contaminant burden.

The second group of higher plant PAHs is the characteristic series of four- and five-ring PAHs produced from the microbial breakdown of pentacyclic triterpenes present in plant waxes and woody tissues (Table 3). These compounds have also been used as markers of higher plant input in aquatic sediments (e.g., Wakeham *et al.*, 1980b; Tan and Heit, 1981; Bouloubassi and Saliot, 1993; Meyers and Ishiwatari, 1993; Yunker and Macdonald, 1995; Tan *et al.*, 1996), but (to our knowledge) their toxicity has not been evaluated. These PAHs are usually considered to arise from progressive aromatization of triterpenes such as α - and β -amyrin during early diagenesis, and normally two isomers of the five-ring tetrahydropicene derivatives and six isomers of the four-ring octahydro- or tetrahydrochrysene derivatives are observed (Table 3).

5. Depositional History in the Fraser River Basin and Strait of Georgia

5.1 Sediment core mixing and sedimentation rates

The ^{210}Pb sediment profiles have been interpreted using a steady-state two-layer advection-diffusion model for which there are analytical solutions to the differential equation (for methods see Robbins, 1978; Lavelle *et al.*, 1985). Sediment cores from the six lakes in the Fraser River basin exhibited little or no surface mixing and generally a well-defined depositional chronology (Figure 3 and Figure 4). (The sole exception was Chilko Lake, where the ^{210}Pb record may have been interrupted by sediment slumping.) In contrast, cores from the Fraser River estuary, Vancouver Harbour and the Strait of Georgia generally had a substantial surface mixed layer (SML), with in some cases evidence of episodic changes in

sedimentation, and only an approximate depositional history could be established (Yunker *et al.*, 1999). Particularly for the core locations in Vancouver Harbour and at the mouth of the North Arm, both dredging and the disposal of material dredged from other locations also could have interrupted the sediment record.

5.2 Biogenic components

In all six Fraser River basin lakes (Figure 1) perylene concentrations increase down core on both a ng/g and $\mu\text{g/g}$ OC basis, while in the Strait of Georgia the perylene increase is observed only at the base of the core from the Saturna basin (Figure 4)(Yunker *et al.*, 1999). The highest perylene value observed in a lake is 810 ng/g (170 $\mu\text{g/g}$ OC) from the bottom section of a core from Moose Lake. Perylene does not show this dramatic increase for the cores from Vancouver Harbour, but an increase has been observed in cores from McDonald Slough and Gunn Island, at the mouth of the Fraser River (Yunker *et al.*, 1999).

The magnitude of the perylene increase and the core depth/year of the onset vary from core to core in the lakes and Saturna basin. Natural, diagenetic production under anoxic conditions is the most likely explanation for these perylene increases (Wakeham *et al.*, 1980b; Venkatesan, 1988; Silliman *et al.*, 1998). Perylene covaries with the higher plant PAHs in samples from the lower Fraser River, Vancouver Harbour and Strait of Georgia, and likely has primarily a terrestrial source in southern B.C. (Yunker *et al.*, 1999).

Because of their low susceptibility to microbial degradation compared to other types of organic matter, alkanes can record many aspects of the depositional history of organic matter in lake sediments (Meyers and Ishiwatari, 1993). Two groups of odd-carbon biogenic alkanes are typically observed: the algal alkanes ($n\text{-C}_{17}$ with usually smaller amounts of $n\text{-C}_{19}$ or $n\text{-C}_{15}$) and the plant wax alkanes (odd carbon alkanes from $n\text{-C}_{23}$ to $n\text{-C}_{33}$, with a maximum at $n\text{-C}_{27}$ or $n\text{-C}_{29}$)(Eglinton and Hamilton, 1967; Meyers and Ishiwatari, 1993). Because organisms generally produce only the odd alkanes, changes in concentration for these alkanes and in the alkane odd-even predominance (OEP; Scalan and Smith, 1970) at $n\text{-C}_{17}$ or $n\text{-C}_{29}$ (see Figure 3 for definitions) can provide a valuable indication of the inputs and degradation of biogenic components over time in sediments.

Surface sediments from Moose Lake, Kamloops Lake, Nicola Lake and Harrison Lake all have markedly elevated concentrations and proportions of the algal biomarker $n\text{-C}_{17}$ (Figure 3). The $n\text{-C}_{17}$ concentration and the OEP at C_{17} both are highest in Nicola Lake (8590 ng/g and 33, respectively), but the lowest concentration is observed in Moose Lake (120 ng/g) and the lowest OEP in Kamloops Lake (5.2). The present day $n\text{-C}_{17}$ concentration in these four lakes varies between 4.1-times (Moose Lake) and 30-times (Nicola Lake) the pre-1940 levels (^{210}Pb dates). The $n\text{-C}_{17}$ OEP is increased 1.5- to 4.9-fold relative to pre-1940 levels in Moose Lake, Nicola Lake and Harrison Lake (with Moose Lake lowest, and Nicola Lake highest) and 1.9-fold relative to 1970-1990 in Kamloops Lake. Post-1970 in Kamloops Lake the $n\text{-C}_{17}$ OEP is depressed 4-fold relative to historical levels (see following), and the 1970-1990 average level provides a better benchmark to evaluate $n\text{-C}_{17}$ increases in recent sediments. In Chilko Lake surface sediments also have $n\text{-C}_{17}$ concentrations (91 ng/g) and an OEP (6.4) that are enhanced 2.3- and 1.9-fold, respectively, above ~1930 levels, but the pre-1870 bottom section of the core has a much higher $n\text{-C}_{17}$

concentration (440 ng/g) and OEP (18) than the surface section. In Stuart Lake the $n\text{-C}_{17}$ concentration (750 ng/g) and OEP (5.6) are both only two-thirds of pre-1940 levels, suggesting that significant algal inputs are absent.

In most lakes the $n\text{-C}_{17}$ alkane is comparable in concentration to the individual odd carbon, higher plant n -alkanes, but $n\text{-C}_{17}$ is particularly prominent in Nicola Lake, where its surface concentration is three times the plant alkane maximum. The algal alkanes are less protected from degradation than the plant wax alkanes (e.g., Meyers and Ishiwatari, 1993), and the proportion of $n\text{-C}_{17}$ (and of the lower alkanes) relative to the higher alkanes generally decreases downcore in all the lakes (not shown). In all lakes except Nicola Lake, the $n\text{-C}_{17}$ concentrations and OEP change little pre-1940 suggesting that a 50-60 year time span normally is sufficient to degrade the algal alkanes. $n\text{-C}_{17}$ is still markedly elevated in Nicola Lake (OEP C_{17} of 13.3) in ~1910, suggesting either a difference in phytoplankton species between lakes, or insufficient microbial capacity to degrade the large algal production in the lake. Surface sediments from the Strait of Georgia exhibit no enhancement of $n\text{-C}_{17}$. However, Strait of Georgia (particularly the Saturna Basin core CM2) and Puget Sound (Barrick *et al.*, 1980) surface sediments do contain a higher proportion of pristane (pristane/phytane ratios of 5-10), very likely from zooplankton (Blumer *et al.*, 1964; Prahl *et al.*, 1980). The lakes exhibit little or no pristane enhancement.

The remaining lower alkanes ($n\text{-C}_{13}\text{-C}_{22}$ plus isoprenoids; $n\text{-C}_{17}$ excluded) and higher plant derived n -alkanes ($n\text{-C}_{23}\text{-C}_{33}$) in most cases exhibit little change in concentration throughout the cores in Moose Lake, Stuart Lake, Chilko Lake, Nicola Lake and Harrison Lake and in Kamloops Lake pre-1970 (Figure 3). Concentrations of the lower alkanes are generally lower, and increase from Moose Lake (190 ± 48 ng/g; mean \pm SD), to Harrison Lake (320 ± 260 ng/g), to Chilko Lake (380 ± 160) and pre-1970 Kamloops Lake (380 ± 89 ng/g), to Nicola Lake (1450 ± 450) and then Stuart Lake (1540 ± 490). The higher alkanes follow a slightly different concentration order from Moose Lake (1080 ± 300 ng/g), to Chilko Lake (1110 ± 550), to Harrison Lake (1940 ± 540 ng/g), to Kamloops Lake (2940 ± 620 ng/g), to Stuart Lake (3890 ± 780) and then Nicola Lake (11700 ± 2300). The low alkane concentrations in Moose Lake and Chilko Lake are very likely a reflection of their remote locations and high altitude (1032 m and 1172 m, respectively).

The higher plant alkane OEP centred at $n\text{-C}_{29}$ also exhibits little change with core depth in Stuart Lake (6.8 ± 1.1), Chilko Lake (9.0 ± 1.2), Moose Lake (10.2 ± 1.4), and pre-1970 Kamloops Lake (10.8 ± 1.2 ; Figure 3). The $n\text{-C}_{29}$ OEP is higher and more variable in Nicola Lake (12.7 ± 3.9) and subsurface in Harrison Lake (16.9 ± 3.3). In Nicola Lake the OEP is comparable to the three northern lakes pre-1910 (9.5 ± 1.8), increases dramatically in the post-1910 to ~1974 period (17.5 ± 0.9) and decreases again to the present day (10.8 ± 2.3). Higher alkane concentrations also increase an average of 4000 ng/g in the lake post-1910 and decline again after ~1974. These OEP and concentration increases during the mid-century in Nicola Lake suggest a change in the composition of plant material being deposited in the lake, and likely reflect increased agricultural or forest-products inputs. A more gradual increase in higher plant n -alkane concentrations (from 2600 to 4300 ng/g) occurs in Kamloops Lake from ~1900 to ~1970 without a change in OEP. Post-1970 in Kamloops Lake a dramatic decline is observed for both the $n\text{-C}_{29}$ OEP (to 5.8 ± 1.5) and $n\text{-C}_{17}$ OEP (3.3 ± 1.1), and average alkane concentrations increase nearly ten-fold for the lower alkanes (to 3250 ± 2250 ng/g) and two-fold for the higher alkanes (5880 ± 1870 ng/g). An UCM also is present in all core sections post-1970 indicating that these increases are largely due to the input of

petroleum (Figure 3). (These sections of Kamloops Lake were the only lake samples that had a measurable UCM.) In Harrison Lake higher plant alkanes exhibit little change in concentration between ~1759 and ~1950 and then increase about two-fold to the present day without an appreciable change in the *n*-C₂₉ OEP. The *n*-C₂₉ OEP also declines markedly (to 4.1) in the surface section from Harrison Lake, suggesting either a reduction in higher plant input or the presence of small amounts of petroleum.

With the exception of a perylene increase downcore and the presence of algal alkanes in surface sediments and of higher plant alkanes throughout the core, the cores from the different lakes and the Strait of Georgia share few common features (Figure 3 and Figure 4).

5.3 Core-by-core comparison

5.3.1 Moose Lake

In Moose Lake the Σ 178-278 parent PAHs are essentially constant from ~1890 to the present in the two separate cores (Figure 4). The lower alkanes (*n*-C₁₃-C₂₂) remain constant in concentration until ~1970 and then increase twofold due to the presence of algal alkanes (Figure 3). The higher plant derived *n*-alkanes (*n*-C₂₃-C₃₃) and the plant PAHs retene and the methylated tetra- and octahydrochrysenes (THC and OHC, respectively) decline from ~1890 to approximately 1960-1970 and then increase again to ~1980. Around 1978 concentrations of the lower and higher alkanes, alkyl PAHs, perylene, retene and the THCs abruptly double in a “spike” that may reflect logging, road building or some other anthropogenic activity in the watershed. Concentrations of the plant alkanes and most PAHs decline after the “spike”, but the alkyl PAHs remain elevated above background to the present day.

5.3.2 Stuart Lake

Alkane and PAH concentrations in Stuart Lake are essentially the same in ~1580 as they are in ~1934 (Figure 3 and Figure 4). Σ 178-278 parent PAH concentrations are moderately elevated throughout the core (117-196 ng/g; 4.4-6.4 μ g/g OC), but the alkyl PAH concentrations are much higher than expected for a remote area (158-343 ng/g; 7.0-16 μ g/g OC; mean 11 μ g/g; see Section 7). Some of the highest alkyl PAH concentrations are found deeper in the core (343 ng/g in ~1948; 312 ng/g in ~1580), hence the elevated baseline of parent and alkyl PAHs likely reflects a natural petroleum PAH source in eroded bitumens, shales, coals, etc.

Alkane, OHC, THC and THP (tetrahydropicenes) and perylene concentrations increase in Stuart Lake about 1950. The PAHs remain elevated into the 1970s and then both alkanes and PAHs decline to below ~1934 levels in surface sediments. Retene remains at historical levels until ~1962 and then increases to the core surface. Again these increases over historical levels likely indicate some form of anthropogenic activity.

5.3.3 Chilko Lake

Chilko Lake is the most remote of the lakes studied (Figure 1). Parent and alkyl PAH concentrations are low and constant throughout the core (Figure 4), indicating negligible direct anthropogenic input. Alkane (Figure 3), perylene, OHC and THC concentrations are elevated in the lake in ~1870, but exhibit little change from ~1930 to the present day. The elevated concentrations of plant-related alkanes and PAHs suggest that the ~1870 core section contained unusually high amounts of plant debris.

5.3.4 Kamloops Lake

Alkane concentrations exhibit little change in Kamloops Lake between ~1859 and 1970, except for a gradual increase in higher plant *n*-alkane concentrations that began in ~1900 (Figure 3). OHC and THC concentrations increase from ~1859 to ~1893 and then decline gradually to about 1960 (Figure 4). Σ 178-278 parent PAHs lag slightly, increasing from ~1893 to ~1917, remaining constant to ~1941, and then declining to ~1969. Alkyls PAHs remain low throughout this period and these increases likely reflect the gradual industrialisation and development of forest products industries around the city of Kamloops.

After ~1970 alkane, UCM, Σ 178-278 parent and alkyl PAH, simonellite and retene concentrations increase dramatically in Kamloops Lake, maximise in the 1980s, and then decline in the 1990s (Figure 3 and Figure 4). OHC, THC and THP also exhibit some concentration increase after ~1970. These trends in petroleum components and the plant PAHs suggest new heavy industry or forest-products industry development post-1970, with improvements in pollution containment beginning in the late 1980s.

5.3.5 Nicola Lake

Higher plant alkane concentrations dip in ~1871, but otherwise remain almost unchanged in Nicola Lake from ~1828 to ~1974, and then decline slightly to the present (Figure 3). The Σ 178-278 parent PAHs gradually triple in concentration from ~1871 to the 1940s to 1950s and decline to slightly more than pre-1871 levels by 1980 (Figure 4). Alkyl PAHs remain low throughout this period, suggesting that atmospheric combustion is the principal parent-PAH source to the lake. OHC, THC and THP concentrations maximise in the core at different times: ~1910 for OHC, ~1943 for THC and ~1871 for THP, suggesting that the composition, and likely sources, of higher plant PAHs have changed over time near the lake.

5.3.6 Harrison Lake

In Harrison Lake higher plant alkanes exhibit little change in concentration between ~1759 and ~1950 and then increase about two-fold to the present day. Alkyl PAHs also increase approximately five-fold post-1950. Both increases suggest that anthropogenic activity has increased in the basin post-1950. The Σ 178-278 parent PAHs increase 10-fold between ~1835 and ~1873, maximise at 200 ng/g in ~1954 and then decline four-fold to the present day. Simonellite, retene and the OHCs and THPs all maximise in the late 1960s – early 1970s. The THCs also have a maximum around this time, but in older sediments they generally track the perylene concentration, with a concentration increase to the core bottom.

The alkyl PAH maximum concentration in Harrison Lake occurs later than the parent PAH maximum (~1974; Figure 3) and, at 28 ng/g, is low, and not much above the pre-industrial baseline (2-5 ng/g). The low amounts of petroleum PAHs, coupled with the absence of an alkane UCM, suggests that atmospheric combustion is the major PAH source to the lake (see further discussion in Sections 8 and 9). The parent PAH concentration profile in the lake also fits the historical pattern of combustion inputs in other industrialised areas (Hites *et al.*, 1980b; Gschwend and Hites, 1981; Readman *et al.*, 1987; Jones *et al.*, 1989).

5.3.7 Strait of Georgia

Concentration profiles for the alkanes and parent and alkyl PAHs exhibit little systematic change throughout the station A and Saturna Basin (station CM2) cores, although considerable variation is evident in the top 10 cm of both cores (post ~ 1980 and ~1995, respectively; Figure 3 and Figure 4). The UCM concentration increases more than three-fold throughout the station A core indicating that petroleum contamination has increased in the northern part of the Strait of Georgia since earlier in this century. (No UCM data are available for the Saturna core.) The OHC sum is elevated deeper in the core at both locations, while the THC sum and perylene are elevated at the core bottom in the Saturna basin.

5.4 Relationship between higher plant PAHs and other PAHs

In natural environments individual PAHs are created by one of three processes: 1) early diagenesis (biological, physical or chemical alteration) from biogenic precursors, 2) later diagenesis over long periods of geologic time, and 3) high-temperature processes that reconstitute organic matter into predictable (and often characteristic) series of PAHs (Meyers and Ishiwatari, 1993). Retene, the OHCs, THC_s and THP_s, and perylene are all formed during early diagenesis but, because they have different precursors, they usually vary independently of one another (e.g., Hites *et al.*, 1980b; Wakeham *et al.*, 1980b; Tan and Heit, 1981). Perylene generally increases in concentration downcore, suggesting a gradual production after burial in sediments (Wakeham *et al.*, 1980b; Venkatesan, 1988; Silliman *et al.*, 1998)(Figure 4). In contrast, concentrations of the plant-related PAHs vary little with core depth (this work and Hites *et al.*, 1980b; Wakeham *et al.*, 1980b; Tan and Heit, 1981), suggesting either that they are produced quickly in sediments, or they have been pre-formed either before (e.g., in leaf litter and soils) or during transport to rivers and lakes. Studies have also shown that perylene and the plant PAHs are generally unrelated to anthropogenic PAH inputs (Meyers and Ishiwatari, 1993).

In the Fraser basin retene is a minor constituent relative to the parent PAH total in all the lake cores (typically between 10 and 20% of the retene plus parent PAH total), with typically little change in concentration downcore (Figure 4). Retene and the plant related tetra- and octahydrochrysenes and tetrahydropicenes do show 5-10 fold concentration increases near the bottoms of both Moose Lake cores. These increases roughly coincide with the increase in perylene concentration, but, given the results of other studies (Meyers and Ishiwatari, 1993), this covariance is likely coincidental. In the other lakes, the perylene increase is accompanied by a 5-10 fold increase in the OHC and THC concentrations, with no evident pattern and little or no change in retene concentration. Given this constancy in higher plant content over time in the remote lakes, the retene “spikes” subsurface in Kamloops Lake and Harrison Lake, and

increases to the surface in Moose Lake and Stuart Lake (Figure 4) likely reflect recent inputs of wood waste from logging activity, sawmills, etc (see also Section 7).

6. Petroleum Biomarker Trends and Distributions

6.1 Hopane and sterane distributions

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. Well defined and characteristic series of the rearranged, diagenetic isomers of these hopane and sterane biomarkers are found in organic rich sediments and sedimentary rocks, petroleum source rocks, crude oils, coals, etc. (Peters and Moldowan, 1993)(Table 5). The diagenetic isomers are also present in petroleum products and by-products such as the lubricating oils, muffler soot and road dust that are chronic contaminants on streets and highways (Volkman *et al.*, 1992; Bieger *et al.*, 1996). Because these biomarkers are more stable than other petroleum components such as the resolved alkanes or the UCM, the hopanes and steranes can serve as conservative indicators (and tracers) of petroleum that has entered aquatic and marine environments (e.g., Volkman *et al.*, 1992; Yunker *et al.*, 1993; Prince *et al.*, 1994; Bieger *et al.*, 1996; Hostettler *et al.*, 1999).

Hopane and sterane distributions indicate that the natural petroleum background is low in the Fraser basin (cf., Barrick and Hedges, 1981). Biogenic (bacterial) hopanes (particularly neohop-13(18)-ene, 17 β (H),21 β (H)-norhopane, 17 β (H),21 β (H)-hopane and diploptene) generally make the largest contribution to sediment samples from the Chilcotin River, Chilko Lake, and the bottom (pre-1860) sections of the cores from Kamloops Lake, Harrison Lake and Stuart Lake (Table 6 and Figure 1). Diagenetically modified steranes are absent and tricyclic terpanes and hopanes are absent or present in only trace amounts in most of these samples. Diagenetic hopanes are present in noticeably higher concentration in the Stuart Lake core interval from ~1580, likely as a result of an enhanced background of natural petroleum (see above and Figure 4), but tricyclic terpanes are still largely absent. The Chilcotin River bed sediment sample is the only pre-industrial or remote location sediment sample that had detectable steranes, and these compounds all had the natural sterol substitution pattern indicative of early diagenesis (Mackenzie *et al.*, 1982). Accordingly petroleum inputs in the Chilcotin watershed are likely to be minimal or absent.

Biogenic hopanes also dominate and only small amounts of the diagenetic hopanes and tricyclic terpanes are present in surface sediments from Moose Lake, Stuart Lake, Nicola Lake and Harrison Lake and in Harrison Lake at the parent PAH maximum in ~1954 (Table 6). Biogenic hopanes are much less prominent in sediment from the upper Nechako River (the second sample from the west, obtained well upstream of the Stuart River confluence; Figure 1), but the diagenetic biomarkers are still only trace constituents. Rearranged steranes and diasteranes are only conclusively present in the samples from Moose Lake and Harrison Lake. None of these samples have a visible UCM, suggesting both that only

small amounts of anthropogenic petroleum have been introduced at these locations, and any petroleum present has been weathered or biodegraded (Bieger *et al.*, 1996).

Substantial amounts of tricyclic terpanes, and rearranged hopanes, steranes and diasteranes are present in samples from the core surface and 5-6 cm depth (~1985) from Kamloops Lake (Table 6). The presence of these diagenetic biomarkers reinforces the alkyl PAH and UCM data (Figure 3 and Figure 4) and confirms the presence of petroleum with an anthropogenic origin post-1970 in Kamloops Lake (Volkman *et al.*, 1992; Peters and Moldowan, 1993; Bence *et al.*, 1996). In these two core sections, the biogenic hopanes make the smallest contribution of any lake core sample examined.

Biomarker data also suggest that petroleum inputs are widespread in the Fraser and Thompson Rivers downstream of Prince George and Kamloops, respectively, as well as in the Strait of Georgia. Throughout the Fraser basin chronic petroleum inputs are much more evident in samples of suspended particulate than of bed sediment (Table 6 and Figure 1). All particulate samples collected in 1987 from the vicinity of Greater Vancouver (Yunker *et al.*, 1989) and in 1996 throughout the Fraser basin (Sylvestre *et al.*, 1998b) contain the diagenetic terpanes, hopanes and steranes indicative of petroleum contamination (Volkman *et al.*, 1992; Bieger *et al.*, 1996). Particulate samples from more remote locations in the upper Fraser and south Thompson River lack an UCM and have a predominance of biogenic hopanes (particularly diploptene), providing further evidence that petroleum inputs are relatively minor upstream of major population centres. However, all particulate samples obtained downstream of Prince George and Kamloops exhibit a pronounced UCM and have a dominance of the diagenetic hopanes and steranes. These diagenetic components and the UCM (Figure 3) are also evident in the Strait of Georgia in the surface and 45-50 cm sections from station A and the steranes are evident in the surface section from station CM2 (other data are unavailable). The station A sample cannot be dated precisely due to the substantial (14 cm) surface mixed layer (Yunker *et al.*, 1999), but the sedimentation rate (0.71 cm/year) suggests that petroleum inputs have occurred at this location for most of the past century.

The abundance of tricyclic terpanes relative to the diagenetic hopanes provides additional insight into the pattern of petroleum occurrence. The tricyclic terpanes are undetectable in sediments from remote locations (Chilko Lake, Chilcotin River) and in pre-industrial core sections from the lakes, indicating that they are not part of the natural background (Table 6). Small proportions of tricyclic terpanes are present in the upper Nechako River, modern sediments from Moose Lake, Stuart Lake, Nicola Lake and Harrison Lake, and in the 1996 suspended particulate samples from the upper Fraser and South Thompson River. The ratio of tricyclic terpanes (four C₂₃-C₂₅ compounds) to the tricyclics plus the principal diagenetic hopanes (C₂₇, C₂₉, C₃₀ 17 α (H)-hopanes) is low in these samples (0.19-0.39). Present day locations with a low tricyclic terpane content contain only minor amounts of alkyl PAHs (Figure 4 and Section 7) and have no alkane UCM. Hence, the low tricyclic content may reflect weathering (selective volatilisation or degradation of smaller molecules) of the small amounts of petroleum present.

Higher proportions of tricyclics (0.44-0.80) are found in sediment from station A, the surface sediment from Harrison Lake and Kamloops Lake, and the 1996 suspended particulate samples from Woodpecker, Marguerite, Agassiz, the Thompson River at Savona, Pattullo Bridge, and the North and Main Arms of the Fraser River in Greater Vancouver. The highest tricyclic content (0.83-0.90) is found in the Kamloops

Lake sediment sample from ~1985, and in suspended particulate samples from Steveston Island and the Pattullo Bridge in 1987. All of the samples in these two groups are from locations close to roads, railways and more industrialised locations where inputs of fresh petroleum are likely. Western Canada oils from different reservoirs can have different proportions of tricyclic terpanes (Creaney and Allan, 1992; Creaney *et al.*, 1994), hence the differences in tricyclic content particularly between the 1987 and 1996 suspended particulate samples is more likely to reflect differences in the original petroleum composition rather than a lack of weathering in the 1987 samples (see following).

The relative abundances of the C₂₇, C₂₈ and C₂₉ diagenetic steranes are one of the most specific tools that geochemists have to distinguish groups of petroleum from different sources (Moldowan *et al.*, 1985; Peters and Moldowan, 1993). Relationships are exclusive rather than inclusive: oils from different depositional environments can have the same sterane profiles, and therefore, identical profiles do not necessarily mean the same source. However, when samples have different sterane distributions it is very likely that oils with different sources, formed in different depositional environments, are involved. The relative proportions or abundances of the three, sterane carbon homologues are most commonly shown on a ternary diagram (Figure 5). The percentage of each component is shown along each side of the triangle, with the scale being read obliquely for the top and bottom components (27 and 29 in this case) and horizontally for the top component (28).

The ternary diagram for the C₂₇, C₂₈ and C₂₉ diagenetic steranes (Figure 5) provides the same sample separations as the tricyclics proportion data (Table 6). The right hand group of points has an elevated proportion of the C₂₉ steranes (>40% for some samples), and includes all 1996 suspended particulate samples from the Fraser River, sediments from Harrison Lake in ~1954 and 1993, Kamloops Lake in 1994, station A core surface and bottom and Saturna basin core surface. The left-hand group contains all suspended particulate samples from the lower Fraser (Pattullo Bridge and Steveston) in 1987 and the sediment sample from Kamloops Lake from ~1985. Together with the differences in tricyclic terpane content, these sterane data suggest that different oil reservoirs, containing oils with a different origin or maturity (e.g., Peters and Moldowan, 1993; Creaney *et al.*, 1994), may have supplied the oil used in B.C. in 1987 and 1996.

6.2 Petroleum sources

The pattern of occurrence of the petroleum biomarkers suggests, not unexpectedly, that petroleum discharges are primarily associated with human activity in transportation corridors along the rivers and major population centres. The tricyclics, hopanes and steranes are absent from refined products such as gasoline, but they are present in crude and heavy oils, motor oils, asphalt and coal (e.g., Barrick *et al.*, 1984; Peters and Moldowan, 1993; Bieger *et al.*, 1996). Because the bioavailability of contaminants such as the PAHs differs dramatically between these various matrices, the exact petroleum source(s) must be established to predict the impact of this petroleum on biota (e.g., Short *et al.*, 1999). Biomarker data for these specific endmembers (crude oils, coals, motor oils, etc.) are not yet available for the Fraser basin, but a preliminary assessment of petroleum origins in the river samples can be made using available published data.

Because large-scale pipeline breaks along the Fraser River or tanker spills in the Fraser estuary have not occurred, releases of crude oil are likely only to be locally significant near refineries and oil storage facilities (due to minor spills) or at stormwater or wastewater discharge points. Crude oil for the Greater Vancouver refineries currently all comes from Alberta, while Alaska North Slope crude brought in by tanker makes a major contribution to the oil coming into northern Washington State. Motor oils and asphalt particles could be introduced to the river by runoff from both highways and city streets. The motor oils could have either a North American source (most likely Alberta, but California or Midwestern U.S. would also be possible) or could be imported from abroad. Road asphalt in B.C. is likely (based on closeness of supply) to come from either the Athabasca deposits in Northern Alberta or the Californian Monterey deposits. Coal could be introduced from erosion of coal outcrops into rivers and streams in the Fraser basin or from spillage of coal or coal dust during railroad transport along the Fraser River from southeast B.C. to the Westshore coal terminal just south of the Fraser mouth (Figure 2). Multiple sources of biomarkers in a given sample are also likely, particularly close to urban centres.

Oils, bitumens, asphalts, etc. from different locations, geological periods, or maturities in the Western Canada sedimentary basin of Alberta contain different (and often characteristic) proportions of hopane and sterane biomarkers (Creaney and Allan, 1992; Creaney *et al.*, 1994). Also there are composition differences between many of these basins and oils from Alaska (Bence *et al.*, 1996). However, with the likelihood of mixed sources, none of these compositions are sufficiently unique to definitively correlate the present set of environmental samples from the Fraser River with any of the Alberta or Alaska North Slope petroleum basins. Part of the difficulty is that hopane distributions for both the Alberta and Alaska basins lack any characteristic triterpane biomarkers that can provide a definitive identification. Nevertheless, the presence or absence of given biomarkers in the river samples does provide some source information.

The structurally rearranged hopanes 25,28,30-trisnorhopane or 28,30-bisnorhopane (Rullkötter *et al.*, 1982; Volkman *et al.*, 1983) are not present in detectable amounts in any of the B.C. samples. The presence or absence of these hopanes can be useful for distinguishing oils from different sources (Peters and Moldowan, 1993). While the closest petroleum reservoir to B.C. that contains these compounds is in California, tars with a California origin have been found to be a significant component of the petroleum background in Prince William Sound, Alaska (Bence *et al.*, 1996), and California oils could also have been shipped to B.C. However, with the absence of these two hopanes, crude oils, motor oils or asphalts from California can be eliminated as a significant source for the petroleum in the Fraser River.

Another characteristic indicator is oleanane, an angiosperm (flowering plant) biomarker whose presence generally indicates Cretaceous or younger petroleum reservoirs (Peters and Moldowan, 1993; Moldowan *et al.*, 1994; Rullkötter *et al.*, 1994; Murray *et al.*, 1997). Oleanane is undetectable in most lake and river sediments, but is present in low proportions (undetectable to 14%; average 6%) relative to the oleanane plus 17 α (H),21 β (H)-hopane sum in Kamloops Lake (~1985 and 1994 sections), at station A, and in all 1987 and most 1996 suspended particulate samples from the river. The notable exception is the 1996 particulate sample from Agassiz, which has an oleanane proportion of 22-24% (for replicate determinations).

The generally low proportion of oleanane eliminates Gulf of Alaska (but not Cook Inlet) oils as a potential source (Bence *et al.*, 1996). Oleanane is absent from western Canada oils (Creaney and Allan, 1992; Creaney *et al.*, 1994)(Martin Fowler, pers. commun., 1999) and Alaska North Slope oils (Bence *et al.*, 1996) hence oils from either location may be contributing to the petroleum loading, but they can not be the source of oleanane in the Fraser basin samples.

The next possibility to consider is that the oleanane is a modern, diagenetic product derived directly from higher plants, rather than a fossil from petroleum (Murray *et al.*, 1997). In sedimentary environments the formation of oleanane from pentacyclic triterpene natural products tends to be a minor process relative to the partial aromatization of these triterpenes to the octahydrochrysenes, tetrahydrochrysenes and tetrahydropicenes (Table 3)(Murray *et al.*, 1997). Oleanane is a minor constituent (2-11%) relative to the oleanane + OHC + THC + THP concentration sum in most suspended particulate samples from the Fraser River and in the surface sediment from station A. Hence, these low concentrations could represent the background for the river. However, much higher proportions are found in the suspended particulate samples from the Thompson River (20%) and Agassiz (28%), in sediment from Kamloops Lake (surface 31%, ~1985 18%), and at the core bottom at station A (33%).

Further possibilities are that the oleanane is derived from coals or imported motor oils. Many B.C. coals, such as the economically important Hat Creek deposit in southeast B.C., are Tertiary age coals with high resin contents. No hopane data are available for this specific deposit, but bitumens and resinous coals of similar age from the Queen Charlotte Islands contain oleanane (Fowler *et al.*, 1988). Commonly traded oils that contain oleanane are those from Nigeria, southeast Asia (Indonesia, Philippines and Bangladesh) and possibly Australia/New Zealand although the latter countries may not produce enough from their coaly basins for export (Rullkötter *et al.*, 1994; Murray *et al.*, 1997)(Martin Fowler, pers. commun., 1999). However, because the oleanane proportion in the Fraser valley and delta is highest at Agassiz rather than near Greater Vancouver, it is more likely that the source of the excess oleanane is a local or transported coal, rather than an imported motor oil. Residents of Agassiz have complained of coal dust flying off the trains, making coal dust a very likely possibility.

Further biomarker data for specific crude oils, coals, motor oils, etc. are required to conclusively establish petroleum sources and processes for the Fraser basin.

7. Geographic Trends in Hydrocarbon Concentrations

7.1 Selection of a basis for comparison

In the Fraser basin and Strait of Georgia sediment properties have the potential to greatly influence hydrocarbon composition and are an important consideration for any assessment. Fraser River suspended particulate samples have all been collected during low flow periods and primarily contain silt (overall average 79.5%), with lesser amounts of clay (14.6%) and small amounts of sand (5.7%), although the sand content is 67.5% in one sample (Table 1). In contrast, bed sediments from the river generally contain sand and silt (average 46.5% and 50.5%, respectively), with only small amounts of clay (Table 2). The

lower amounts of sand and the large variations in sand content in the water column (Table 1) are both features of discontinuous sediment transport, in which the coarser material is only suspended during higher flows (Milliman, 1980). An important consequence of these large differences in sediment texture is that comparisons of PAH composition and sample-weight normalised concentrations between locations and between the water column and sediment can become problematic.

Weight-normalised parent PAH concentrations (ng/g) generally decrease with increasing sand content in remote areas of the Fraser basin. This suggests a direct link between PAH concentration and the organic matter content (Evans *et al.*, 1990), likely through association with organic-rich flocs (Droppo *et al.*, 1998; Leppard *et al.*, 1998). Sand-sized particles also have less surface area available for adsorption of hydrophobic, particle bound hydrocarbons such as the PAHs (e.g., Di Toro *et al.*, 1991; Budzinski *et al.*, 1997). The large sand content dilutes the PAH-containing fine fraction, resulting in greater sample heterogeneity, less fine material in a sample and a decreased likelihood of obtaining a representative sample. A likely result of the under-sampling of fine material is a reduced comparability of PAH compositions and sample-weight normalised concentrations between locations and between the water column and sediment. In practical terms, the presence of variable amounts of sand (and fine material) does not invalidate comparisons, but the resulting increase in scatter in the data makes patterns more difficult to discern and interpret. The prevalence of low density, higher plant debris and finer particulate in the suspended particulate phase can further exacerbate differences by elevating the ng/g concentrations of terrestrial hydrocarbons (e.g., retene and the plant wax alkanes) or pollution-related components (e.g., the petroleum alkanes) in the water column (Prahl and Carpenter, 1983; Bouloubassi and Saliot, 1991; Yunker *et al.*, 1993).

To minimise the “sand effect” on concentration comparisons between the water column and sediment and between the different sedimentary regimes of the basin, hydrocarbon concentrations have been normalised to the organic carbon (OC) content for the basin-wide comparisons (Table 7 and Table 8). This OC-normalisation minimises concentration artifacts due to the large variations in sand content, but it may be subject to minor perturbations due to oxidative removal of organic material during transport (Hedges and Keil, 1995; Keil *et al.*, 1997). However, because the sand content is lower in the lakes and carbon decreases downcore at all locations except station CM2, weight-normalised data has been more appropriate for the core profiles (Figure 3 and Figure 4). Due to the low sand content of most Fraser River suspended particulate samples, weight-normalised data are also used for the calculation of fluxes (Section 10). To minimise diagenetic artifacts from the *in situ* production of perylene (Figure 4), only surface sediments are used for perylene concentration comparisons (Table 8 and Figure 6).

The parent PAHs shown in Table 3 (except dibenzothiophene) have been quantified in all samples and provide the most comprehensive coverage for a discussion of PAH concentration trends in the Fraser basin. Dibenzothiophenes, alkyl PAH (Table 3) and retene concentration data are available for all core samples and the post-1995 samples from the Fraser River and good geographic and temporal comparisons can also be made for these PAHs. Data for other higher plant PAHs (cadalene, simonellite and the hydrochrysenes and hydropicenes) and the alkanes (both resolved alkanes and the UCM) are limited to the core samples and selected (mostly suspended particulate) samples from the Fraser River.

7.2 Establishing a pre-industrial PAH baseline

Using ^{210}Pb dates and the observed increases in alkane and PAH concentrations as a guide (Figure 3 and Figure 4), mean Σ 178-278 parent, alkyl PAH and retene concentrations have been calculated for sediment core intervals prior to the onset of significant industrialisation in the Fraser basin region (Table 9). To minimise artifacts from the downcore decrease in organic carbon content, surface-sediment carbon concentrations have been used for the ng/g to $\mu\text{g/g}$ OC conversions. With the exception of Stuart Lake for the Σ 178-278 parent and alkyl PAHs and Moose Lake for retene, the $\mu\text{g/g}$ OC totals fall within a narrow range. (The large increase in retene concentration that occurs at the bottom of the two Moose Lake cores is responsible for the elevated baseline for retene in Moose Lake; Figure 4.) Hence, a PAH concentration of about 1 $\mu\text{g/g}$ OC can be used as the pre-industrial baseline for both the parent and alkyl PAHs, and 0.5 $\mu\text{g/g}$ OC can be used for retene (Table 9). Present day sediment concentrations in the Strait of Georgia are more than an order of magnitude above this baseline level (except for station CM2 for retene).

For discussion purposes we can consider that a PAH concentration of 10 times the pre-industrial baseline (10 $\mu\text{g/g}$ OC for the parent and alkyl PAHs; 5 $\mu\text{g/g}$ for retene) indicates significant anthropogenic input. To facilitate concentration comparisons between different parts of the Fraser basin these levels are indicated by dashed lines on the PAH concentration plots in Figure 6. While the generation of perylene in most subsurface sediments precludes the calculation of a baseline, to aid interpretation a line indicating 10 $\mu\text{g/g}$ OC is also shown for perylene.

7.3 Nechako, Chilcotin and Quesnel tributaries, upstream of Kamloops in the Thompson system, upstream of Lytton in the Fraser River and Nicola Lake

In less-urbanised locations the mean (and in most cases maximum) Σ 178-278 parent PAH and alkyl PAH concentrations in suspended particulate and sediment samples are almost entirely greater than the 1 $\mu\text{g/g}$ pre-industrial baseline, but are still less than 10 $\mu\text{g/g}$ OC (Table 7, Table 8, Figure 4 and Figure 6a-b). Sediments from Moose Lake, Chilko Lake and Nicola Lake also fall below this 10 $\mu\text{g/g}$ threshold (Table 9), as do the sediment and suspended particulate samples from the vicinity of Prince George. In these areas there also are only a few instances where sediment PAH concentrations exceed either provincial or interim federal sediment quality guidelines for the protection of aquatic life, and in most cases these exceedences are only marginally above the guidelines (Table 10)(Brewer *et al.*, 1998).

The few exceptions where the Σ 178-278 parent PAHs are over 10 $\mu\text{g/g}$ OC include suspended particulate samples from Marguerite in November 1994 and Woodpecker in October 1996 (12-15 $\mu\text{g/g}$ OC), and single sediment samples from the Quesnel (11 $\mu\text{g/g}$ OC) and North and South Thompson Rivers (11 and 21 $\mu\text{g/g}$ OC, respectively) in 1994. Suspended particulate samples from the Woodpecker, Marguerite and South Thompson stations in 1996 have alkyl PAH concentrations (15-20 $\mu\text{g/g}$ OC) that are noticeably higher than in the corresponding bed sediments. Samples from the Quesnel (15 $\mu\text{g/g}$ OC) and South Thompson (11.3 $\mu\text{g/g}$ OC) Rivers in 1995 are also elevated. All locations with parent and alkyl PAH concentrations over 10 $\mu\text{g/g}$ OC are adjacent to highways except for the Woodpecker and Quesnel River stations. Hence it appears that in less-urbanised areas parent and alkyl PAH concentrations are most likely to be elevated adjacent to railroads and major highways, where runoff of asphalt particles,

motor oils, and vehicle combustion hydrocarbons can occur. One result is that the mean Σ 178-278 parent and alkyl PAH concentrations on suspended particulate are uniformly greater than the mean concentrations in bed sediment (Figure 6a-b).

Perylene concentrations in suspended particulate and surface sediments throughout the region are all below the 10 $\mu\text{g/g}$ OC level. With a few exceptions perylene generally makes a greater contribution to the parent PAH budget in the less-urbanised locations of the Fraser basin. Perylene also generally makes a greater contribution to bed sediments of the region than to the suspended particulate, with the result that perylene concentrations on suspended particulate are not always greater than the sediment concentrations (Figure 4 and Figure 6c).

The concentration of retene is greater than the Σ 178-278 parent PAH total in most samples of bed sediment from the upper Fraser River between McBride and Lytton, the Nechako River and the North and South Thompson Rivers, as well as in samples of suspended particulate from Woodpecker and Marguerite. Retene concentrations in sediment are notably elevated at locations on the Fraser River one-third of the way between McBride and Prince George (88 $\mu\text{g/g}$) and downstream of Marguerite (23 $\mu\text{g/g}$) and in a backwater on the upper South Thompson River (9.3-34 $\mu\text{g/g}$). The elevated retene upstream and downstream of Prince George is likely from old sawmill sites. Parent or alkyl PAH concentrations are not elevated at any of these locations.

7.4 Kamloops, the Thompson River, the Fraser River between Lytton and Chilliwack and Harrison Lake

In bed sediments from the vicinity of Kamloops, nine of the ten available Σ 178-278 parent PAH and two of the five alkyl PAH concentrations are over 10 $\mu\text{g/g}$ OC (Table 8 and Figure 6a-b). Maximum parent and alkyl PAH concentrations are well above this level (Table 8), indicating significant anthropogenic input of PAHs. Downstream of Kamloops parent and alkyl PAH concentrations decline in surface sediment from Kamloops Lake (7.2 and 3.7 $\mu\text{g/g}$ OC, respectively in the top 2 cm), and in suspended particulate and sediment samples from the Thompson River (Table 7). PAH concentrations exceed either provincial or interim federal sediment quality guidelines for the protection of aquatic life in the Thompson River (at and downstream of the city of Kamloops) and in most post-1970 core sections from Kamloops Lake (Table 10)(Brewer *et al.*, 1998).

Below Kamloops Lake on the Thompson River, the alkyl PAH concentration is 15 $\mu\text{g/g}$ OC in the one sample of bed sediment analysed, while Σ 178-278 parent PAH concentrations are less than 10 $\mu\text{g/g}$ OC. At Savona parent (5.0-10 $\mu\text{g/g}$ OC; mean 7.4 $\mu\text{g/g}$ OC, n=4) and alkyl (10 $\mu\text{g/g}$ OC; n=1) PAH concentrations on suspended particulate samples obtained between 1992 and 1996 are only slightly greater than parent PAH concentrations at McLure on the North Thompson (2.7-9.8 $\mu\text{g/g}$ OC; mean 5.1 $\mu\text{g/g}$ OC) over the 1992-1993 time period and are lower than at the South Thompson station sampled in 1996 (parent 10 $\mu\text{g/g}$ OC; alkyl 15 $\mu\text{g/g}$ OC). The weight-based parent PAH concentration is markedly elevated in a suspended particulate sample from Savona in February 1993 (1880 ng/g; nearly four times higher than the highest ng/g sediment concentration at Kamloops). However, due to the very high carbon

content (18.5 %) in this sample, the carbon normalised concentration is not exceptionally elevated (10.2 $\mu\text{g/g}$ OC).

PAH concentrations on suspended particulate also have been found to vary with river flow during the 1992-1993 period (Sekela *et al.*, 1995). The Thompson River flow in October 1992 is approximately double the February and November 1993 flows (Sekela *et al.*, 1995), and mean Σ 178-278 parent PAH concentrations at Savona during October 1992 (5.0 $\mu\text{g/g}$) are lower than in February and November 1993 (8.7 $\mu\text{g/g}$). This dependence of concentration on flow suggests that chronic PAH sources (e.g., municipal and industrial discharges) likely make a greater contribution than episodic sources (e.g., the introduction of atmospheric combustion particulate during spring runoff).

In bed sediment from the Fraser River and Fraser canyon between Lytton and Chilliwack parent (1.7-10 $\mu\text{g/g}$; mean 4.8 $\mu\text{g/g}$) and alkyl (2.6-11 $\mu\text{g/g}$; mean 4.6 $\mu\text{g/g}$) PAHs are typical of PAH concentrations further upstream in the Fraser River (Table 8) and in the surface section of Harrison Lake (3.9 $\mu\text{g/g}$). As in locations further upstream, suspended particulate concentrations for the parent PAHs at Yale in 1992-1994 and for parent and alkyl PAHs at Agassiz in 1996 (Table 7) are higher than the bed sediment concentrations by a factor of ca. 2-3 (shown under the Lytton to Chilliwack reach in Figure 6a-b).

Perylene concentrations in suspended particulate and surface sediments from Kamloops, surface sections from Kamloops Lake and Harrison Lake, the Thompson River and the Fraser canyon are all below the 10 $\mu\text{g/g}$ OC level except for a Kamloops bed sediment sample (87 $\mu\text{g/g}$).

Retene concentrations in bed sediment are well below 5 $\mu\text{g/g}$ OC and low relative to the Σ 178-278 parent PAH total in sediments from Kamloops Lake and Harrison Lake (Figure 4), the Thompson River and most Kamloops locations. The retene concentration is greater than the parent PAH concentration in most bed sediment samples from the Fraser River between Lytton and Chilliwack, although retene is only one-half the parent PAH concentration in suspended particulate from Agassiz in 1996. Retene concentrations in sediment are notably elevated at two locations in Kamloops (27 and 31 $\mu\text{g/g}$ OC) and one location near Chilliwack (17 $\mu\text{g/g}$), suggesting inputs from forest products activities.

7.5 The Fraser Estuary and Vancouver Harbour

Downstream of Chilliwack (Figure 2) the Σ 178-278 parent PAH and alkyl PAH concentrations increase considerably, indicating substantial anthropogenic PAH inputs (Table 7, Table 8, Figure 6a-b). All samples that have been analysed for alkanes from the vicinity of Greater Vancouver (1987 suspended particulate samples and sediment cores from mouth of the Fraser River and Vancouver Harbour) also have an appreciable UCM (Table 6)(Yunker *et al.*, 1999). There are many potential sources of these contaminant hydrocarbons, including combustion (Lee *et al.*, 1977), petroleum spills (Giger *et al.*, 1974; Barrick *et al.*, 1980), urban stormwater runoff and WWTP discharges (Eganhouse *et al.*, 1981; Hoffman *et al.*, 1984), and creosote (Merrill and Wade, 1985).

In the Fraser River estuary and Vancouver Harbour, almost all suspended particulate and sediment samples have parent and alkyl PAH concentrations over 10 $\mu\text{g/g}$ OC, with the suspended particulate

samples having the greater mean concentrations in the Main Arm (Table 7 and Table 8; Figure 6a-b). PAH concentrations also exceed either provincial or interim federal sediment quality guidelines in sediments from most locations sampled in the Fraser River estuary and Vancouver Harbour (Table 10)(Brewer *et al.*, 1998). Parent and alkyl PAH concentrations are less than 10 µg/g OC only in 1995 and 1996 sediment samples from a backwater near Gunn Island in the main channel (parent 5.8-8.3 µg/g; alkyl 5.0-6.4 µg/g), some subsurface sections of the Gunn Island core (parent 6.3-9.5 µg/g; alkyl 6.5-6.7 µg/g) and the pre-industrial section of the core from Port Moody Arm in Vancouver Harbour (parent 3.1-3.2 µg/g; alkyl 2.5-3.1 µg/g)(Brewer *et al.*, 1998; Yunker *et al.*, 1999).

The highest concentrations in the region for both parent and alkyl PAHs are found in the two sediment cores and in a number of grab samples from Vancouver Harbour (Table 8)(Yunker *et al.*, 1999). Averaged sediment PAH concentrations are lower (about one-quarter and one-third, respectively of the parent and alkyl concentrations in the harbour cores) in the industrialised areas around Annacis Island and along the North Arm, and decrease further in sediment samples collected downstream of Annacis Island (labelled Fraser Main Arm in Table 8). In contrast, average UCM concentrations in sediment cores are twice as high at the mouth of the Fraser River (McDonald Slough, 4800 µg/g OC; Gunn Island 0-1 cm, 4200 µg/g) as in Vancouver Harbour (Centre Harbour, 2300 µg/g OC; Port Moody Arm, 2000 µg/g). The data from these few cores suggest that inputs of parent and alkyl PAHs have been more important in Vancouver Harbour, while inputs of petroleum alkanes have been higher in the Fraser estuary.

Beyond the mouth of the river (Figure 2), PAH concentrations are elevated in the station AO core collected close to the pre-1988 (intertidal) outfall of the Iona WWTP treatment facility (Σ 178-278 PAHs are 24 µg/g OC in the surface section, 76 µg/g at 3-4 cm and 240 µg/g at 14-16 cm; alkyl PAHs 21 µg/g surface, 150 µg/g at 3-4 cm and 89 µg/g at 14-16 cm). PAH concentrations also exceed either provincial or interim federal sediment quality guidelines for the protection of aquatic life in the 3-4 cm and 14-16 cm sections of this core (Table 10). Concentrations are much lower (3.1 and 1.6 µg/g, respectively) at the core bottom (26-31 cm) and are close to or below 10 µg/g OC at stations A10 and A12 on Sturgeon bank. The alkane UCM (2100 µg/g OC surface, 11,000 µg/g at 3-4 cm and 3400 µg/g at 14-16 cm) has the same concentration trend as the alkyl PAHs in the upper part of the station AO core, but the UCM is undetectable at the core bottom and in other samples from Sturgeon Bank. These limited data suggest that prior to 1988 the Iona outfall had discharged significant amounts of PAHs and petroleum onto Sturgeon Bank. Conditions have improved since effluent was re-routed to the deep-sea Iona outfall, and the intertidal outfall appears to have had only a local impact on Sturgeon bank.

Adjacent to the causeway to the Westshore coal terminal on Roberts Bank (Figure 2), core BPt-1 has parent PAHs just above the 10 µg/g level (11-19 µg/g in the 0-1, 3-4, 14-16 and 31-36 cm sections), while alkyl PAHs are present in much higher concentrations (44-84 µg/g) except at the core bottom (16 µg/g at 31-36 cm). Closer to the mouth of the river at station A14, parent PAH concentrations are similar (14 µg/g) to BPt-1, but alkyl PAHs are present at much lower levels (11 µg/g). In contrast, UCM concentrations are much higher at station A14 (1500 µg/g OC) than at BPt-1 (770 µg/g surface, 260 at 3-4 cm and 69 µg/g at 14-16 cm; below detection at 31-36 cm). The presence of elevated alkyl PAHs with a lower UCM concentration at BPt-1 suggests that petroleum with different composition than in the river (such as coal dust) is making a greater contribution adjacent to the coal terminal (see Section 8.3).

Perylene is generally a minor constituent of suspended particulate and surface sediment samples from the vicinity of Greater Vancouver. Concentrations are all below 10 µg/g OC except for single samples of particulate and sediment from the North Arm in 1996 (13 µg/g OC for both; Figure 6c) and four samples from the Main Arm in 1987 (10-15 µg/g OC).

Perylene is present in unusually low amounts (0.1-0.2 µg/g: ca. 1% of the Σ 178-278 parent PAH concentration) in suspended particulate from the GVRD WWTPs (Table 7) and is low or undetectable (2.3 µg/g OC with a detection limit of 2 µg/g OC) in sediments adjacent to the Iona WWTP deep-sea outfall (Wilson *et al.*, 1999). Perylene is also low relative to other parent PAHs in asphalt (PAH chromatograms in Wakeham *et al.*, 1980a; Readman *et al.*, 1987) and in atmospheric particulate deposited by dry deposition in Chicago IL and over Lake Michigan (Franz *et al.*, 1998). Hence, it is likely that the unusually low perylene content in sediments near the Iona outfall reflects the presence of asphalt and combustion particles that have been washed from roads into storm sewers and discharged with the WWTP effluent. Accordingly, perylene depletion could accompany contaminants such as the nonylphenols (Shang *et al.*, 1999) as a tracer of the effluent in the sedimentary environment. Sedimentary PAH data with better detection limits from both pre- and post-discharge regimes are required to prove this hypothesis (Wilson *et al.*, 1999).

While retene is also a minor constituent relative to the parent PAHs, retene concentrations in suspended particulate samples from the estuary are all over 5 µg/g OC (maximum 24 µg/g). All of the North Arm sediment samples and one-third of the Main Arm samples have retene concentrations above 5 µg/g (maximum 28 µg/g; Figure 6d), while retene is below 5 µg/g in sediments from Vancouver Harbour (0.8-3.6 µg/g). The excess retene in the suspended particulate phase likely has a source in wood chip loading facilities and paper products manufacturing plants along the Fraser River in Greater Vancouver. Retene, OHC, THC and THP are minor constituents in WWTP particulate (Table 7), suggesting that only small inputs of fine plant detritus or wood debris have entered the sewers, at least during the time of sampling.

In sediment samples from the vicinity of Greater Vancouver, the Σ 178-278 PAH total is usually greater than the alkyl PAH total. The parent PAH total is also greater for suspended particulate samples collected by centrifuge (56-69 % of the parent plus alkyl total), but the balance shifts the other way for particulate samples collected by direct filtration (parent PAHs are only 37-46% of the total). This difference in alkyl PAH content has been observed previously (Yunker *et al.*, 1999), and is most likely due to the collection of greater amounts of finer particulate during filtration. Present day samples of effluent suspended solids obtained from the four GVRD WWTPs studied have an even smaller proportion of parent PAHs (14-40% of the total). Because the effluent suspended solids samples generally contain very fine particulates (Bertold and Stock, 1999), the high proportion of petroleum PAHs may be partially related to particle size, but the differences are more likely to reflect chronic petroleum inputs to wastewater collection systems (Eganhouse *et al.*, 1981; Hoffman *et al.*, 1984; Larkin and Hall, 1998).

7.6 Strait of Georgia

Parent and alkyl PAH concentrations at both core locations in the Strait of Georgia are substantially greater than in suspended particulate or sediment from the Fraser valley, upstream of Greater Vancouver

(between Lytton and Chilliwack), while retene concentrations are comparable at station A and in sediments obtained between Lytton and Chilliwack (Table 7 and Table 8; Figure 2). In both cores PAH concentrations exceed either provincial or federal sediment quality guidelines in all sections analyzed (Table 10).

In the Strait of Georgia, alkyl PAH concentrations are equivalent at station A ($49 \pm 11 \mu\text{g/g OC}$) and in the Saturna basin core ($44 \pm 2.9 \mu\text{g/g}$) but Σ 178-278 parent PAH concentrations are twice as high at station A ($38 \pm 6.7 \mu\text{g/g}$) as they are in the Saturna basin ($19 \pm 4.2 \mu\text{g/g}$; Table 8). Retene is also twice as high at station A as at station CM2, but simonellite is five times higher at station A (2.9 ± 1.4 vs. $0.63 \pm 0.19 \mu\text{g/g}$, respectively), while the OHC + THC +THP concentration total is equivalent at the two locations (Table 8). Data for these two cores suggest that petroleum-related alkyl PAHs and the four- and five-ring plant PAHs are evenly distributed in the Strait of Georgia, but combustion-derived parent PAHs and the smaller ring size plant PAHs are not.

In the aquatic environment petroleum-related compounds and the larger plant-derived PAHs are primarily transported on particles suspended in the water column, while combustion-derived compounds can be transported on particulate by both the atmosphere and water (e.g., Ramdahl, 1983; Prah *et al.*, 1984; Bouloubassi and Saliot, 1994). Hence, plant debris and petroleum from the Fraser River (or petroleum delivered by stormwater or the GVRD WWTPs) are likely to be uniformly distributed over large areas of the strait while combustion inputs are likely to be greater near to Greater Vancouver. Accordingly, the elevated parent PAH, retene and possibly simonellite concentrations found at station A likely reflect additional atmospheric input of combustion products from sources such as vehicles, furnaces and wood burning.

8. PAH Distributions

8.1 Parent PAH composition

Diagrams showing the relative proportions of parent PAHs of different molecular masses (Table 3) can provide a valuable overview of PAH composition in different parts of the Fraser basin as well as an effective probe of potential PAH sources (e.g., Gschwend and Hites, 1981; Lipiatou and Saliot, 1991; Yunker *et al.*, 1993). While the rapid decrease in PAH solubility with increasing molecular weight would be predicted to distort the distributions by solubility fractionation (e.g., May *et al.*, 1978), in practice environmental samples often show no evidence of this skewing, particularly when the PAHs have a combustion origin (Lake *et al.*, 1979; Readman *et al.*, 1987). Evidence provided from core studies in the Tamar estuary of the U.K. (Readman *et al.*, 1987) suggests that once deposited, PAHs as small as phenanthrene appear to be irreversibly bound and unavailable for desorptive depuration into the water column. Hence, any equilibrium partitioning of PAHs with the water column would normally have to have been achieved before burial, and PAH compositions from different sediment depths and times can be compared without bias.

In Figure 7 and Figure 8 the principal PAHs of molecular mass 178 (phenanthrene and anthracene), 202 (fluoranthene and pyrene), 252 (benzo[*b/j/k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene) and 276 (indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene) are compared in two sets of ternary diagrams. This comparison employs only the most prevalent three-and-larger-ring PAH constituents (e.g., acephenanthrylene and indeno[7,1,2,3-*cdef*]chrysene have been omitted). Perylene has also been excluded to avoid complications due to downcore increases in perylene concentration.

To facilitate interpretation of the PAH distribution and ratio diagrams suspended particulate and sediment samples have been divided into different groups by geographic region. The designation “Remote” is used for suspended particulate and most sediment samples collected upstream of Lytton on the Fraser (including Moose Lake and Stuart Lake), and of Kamloops in the Thompson system, and in the Nechako and Chilcotin Rivers and Chilko Lake (Figure 1). Pre-1940 core intervals from Kamloops Lake, Nicola Lake and Harrison Lake and the pristine sections below 10 cm in the core from Gunn Island at the mouth of the Fraser River and below 45 cm in Port Moody Arm have also been included in the “Remote” sediment group (Figure 2). The designation “Semi-urban” is used for sediment samples obtained near Prince George and between Kamloops and Chilliwack, and for the post-1940 sections from Kamloops Lake, Nicola Lake and Harrison Lake. “Vancouver” is used to indicate sediment samples from Vancouver Harbour, the Fraser River from vicinity of Greater Vancouver and the 10 cm and above sections of the core from Sturgeon Bank, adjacent to the old Iona WWTP outfall. “Strait of Georgia” is used for all other sediment samples from Sturgeon and Roberts Banks, and for sediment cores from Stations A and CM2. Finally, “Urban Particulate” is used for suspended particulate samples collected downstream of Kamloops and Lytton, while “WWTP Particulate” is used for effluent particulate samples from the four main GVRD WWTPs.

Suspended particulate samples from locations downstream of Kamloops Lake and Lytton in the Thompson and Fraser Rivers and sediment samples from the vicinity of Greater Vancouver generally have very consistent proportions of the principal PAH molecular mass constituents (roughly outlined areas in Figure 7a and Figure 8a). The outlined area in Figure 8a extends further to the right side of the main cluster due to a few particulate samples from locations upstream of Greater Vancouver that have higher proportions of the mass 178 PAHs than most urban samples. Sediments from the vicinity of Prince George, Kamloops, post-1970 Kamloops Lake, post-1940 Nicola Lake, the Fraser River downstream of Lytton, Sturgeon and Roberts Banks, and the Strait of Georgia also usually fall within the outlined areas (Figure 7 and Figure 8). These urban-influenced samples have a parent PAH profile with a predominance of PAHs with mass 202 and 252, with in most cases mass 202 as the major constituent. This profile is commonly observed in sediments from industrialised areas (Lake *et al.*, 1979; Hites *et al.*, 1980a; Bates *et al.*, 1984; Lipiatou and Saliot, 1991; Yunker *et al.*, 1996) and, particularly where mass 202 is the highest molecular mass constituent, a predominance of pyrolytic PAHs is likely (Grimmer *et al.*, 1983; Li and Kamens, 1993; Khalili *et al.*, 1995).

In contrast, in most sediments from the upper Fraser, Nechako, Chilcotin and Quesnel Rivers, upstream of Kamloops in the Thompson system, upstream of Lytton in the Fraser River and Moose Lake and Chilko Lake the parent PAHs of molecular mass 178 and 202 dominate PAH profiles (scatter of points to the right of the outlined area in Figure 8b). Pre-industrial sections of cores from Moose Lake, Chilko Lake,

Nicola Lake and Harrison Lake and pristine sections from the core bottom at Gunn Is at the mouth of the Fraser River (Yunker *et al.*, 1999) have the same dominance of molecular masses 178 and 202 and also plot to the right of the outlined area. PAHs of mass 228 (benz[*a*]anthracene and chrysene), 252 and 276 are also present in most of these samples, but are minor constituents. One result of the low mass 252 concentrations is that benzo[*a*]pyrene is undetectable in most sediments from these areas.

In the Stuart River and Stuart Lake the mass 178 and 202 PAHs are also major constituents, but mass 252 is more prominent than 202. This mass 178 and 252 dominance is present in Stuart Lake core sections dating back to ~ 1580 (cluster of points above the areas outlined in Figure 7b and Figure 8b). The PAH maxima at 178 and 252 in Stuart River and Lake are reminiscent of the Mackenzie River, where natural petroleum makes a significant contribution to the PAH budget (Yunker *et al.*, 1993; Yunker *et al.*, 1996).

Molecular masses 252 and 276 predominate in post-1870 sections from Harrison Lake, ~1941 and earlier sections from Kamloops Lake, the ~1918 and ~1945 sections from Moose Lake and the ~1962 section from Chilko Lake (points to the right of the area outlined in Figure 7b). Masses 252 and 276 also become elevated (but 178 and 202 still predominate) between ~1870 and ~1910 in the core at Nicola Lake and also are prominent at the bottom of the core from Port Moody Arm in Vancouver Harbour (not datable but likely pre-industrial; Yunker *et al.*, 1999). Harrison Lake, Kamloops Lake and Nicola Lake all have mass 252 and 276 concentration maxima in the 1940s or 1950s, and while much higher PAH concentrations are subsequently present in Kamloops Lake, mass 202 only becomes the major PAH constituent with the large alkane and PAH concentration increases post-1970 (Figure 3 and Figure 4). A predominance of molecular masses 252 and 276 has also been observed in surficial sediment from Lake Superior collected in 1986 and in a sediment core from Woods Lake in the Adirondack Mountains in the northeastern U.S. obtained in 1978 (Tan and Heit, 1981; Baker *et al.*, 1991; Yunker *et al.*, 1996).

Alkyl PAHs are largely absent from Kamloops Lake, Nicola Lake and Harrison Lake pre-1950 (Figure 4), hence a combustion-related process must be responsible for the change in PAH composition in these areas in the late 1800s (Wakeham *et al.*, 1980b; Sporstøl *et al.*, 1983). This change in PAH composition generally coincides with the start of large-scale clearing of forests in southern B.C., and the slash burning that accompanied this logging activity could be of sufficient magnitude to account for the PAH increase. Harrison Lake is also downwind of Greater Vancouver, and coal combustion may have contributed to the ~1870 PAH increase. The molecular mass 252 and 276 PAHs are normally present as minor constituents in wood and coal combustion emissions (Freeman and Cattell, 1990; Li and Kamens, 1993; Khalili *et al.*, 1995), but the lower molecular weight PAHs tend to be lost during atmospheric transport and passage through the water column of a lake (McVeety and Hites, 1988; Baker *et al.*, 1991; Simcik *et al.*, 1996; Simo *et al.*, 1997), and the resulting sediment composition would likely have a much lower proportion of volatile PAHs than the original combustion sources. The elevated proportions of molecular mass 276 PAHs that are observed in a few sections from Moose and Chilko also are liable to have a combustion origin.

The predominance of the lower molecular mass PAHs in less-industrialised areas of the basin and pre-industrial sections of cores suggests that the majority of these PAHs are most likely contained in refractory matrices such as bitumen, coal or soot, and hence protected from dissolution in water or

bacterial degradation (Readman *et al.*, 1987; Yunker and Macdonald, 1995; Gustafsson *et al.*, 1997). A lower toxicity would be expected for these strongly associated or encapsulated PAHs, because their reduced dissolution in water will result in a decreased availability for bioaccumulation by invertebrates and fish.

Masses 178 and 202 (with 202 most often the maximum) are major constituents in all suspended particulate samples from the Fraser basin (Figure 8). Mass 202 is most prominent in the GVRD WWTP effluent samples, and these samples plot on the lower left side of the outlined areas in Figure 7a and Figure 8a. Particulate samples also generally have elevated dibenzothiophene concentrations (see Section 9.4) and fresh petroleum is likely to be contributing to the samples (Section 6). Mass 252 becomes more prominent in particulate downstream of Kamloops at Savona and Yale (upper right of the outlined area in Figure 8a), and generally declines in importance closer to Greater Vancouver.

8.2 Parent PAH PCA model

Composition differences for individual parent PAHs can be examined in more detail using a PCA model based on riverine and effluent suspended particulate and surface sediment samples (both grabs and core surface sections; replicates averaged) collected throughout the Fraser basin. The PCA model separates the parent PAH variables roughly into three groups (Figure 9a), while suspended particulate and sediment samples classify into two major groups (Figure 9b-c). In these PCA plots the distance and direction from the axis centre has the same meaning for both samples and PAH variables. For example, fluoranthene and pyrene project on the upper right side of Figure 9a, and samples that project on the upper right in Figure 9 b and c will have high proportions of these PAHs.

The first PC defines the first variable group by clearly separating three of the lower molecular weight PAHs (naphthalene, fluorene and phenanthrene) from all other PAH variables (left and right sides, respectively in Figure 9a). The second PC then separates most of the remaining PAHs into two groups: fluoranthene, pyrene, benz[*a*]anthracene and benzo[*a*]pyrene on the upper right and benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, benzo[*e*]pyrene, benzo[*b/j/k*]fluoranthene and indeno[7,1,2,3-*cdef*]chrysene on the lower right in Figure 9a. Chrysene and anthracene project close to the origin in the first two PCs (Figure 9a), while chrysene has the highest loadings in the third PC (not shown).

The PCA model separates suspended particulate (Figure 9b) and sediment (Figure 9c) samples in different ways. For sediments, samples from more remote locations project on the left side of the y-axis while samples from urban-influenced locations project on the right. The samples from remote locations generally have higher proportions of the lower molecular weight PAHs (particularly naphthalene, fluorene and phenanthrene), while the urban samples have more of the higher mass PAHs (Figure 9a). Samples from the shallow banks at the margins of the Strait of Georgia straddle the two groups: the Sturgeon bank samples project to the right of centre with the urban samples (suggesting greater urban influence at this location), while the Roberts bank sediments project to the left of centre with samples from more remote areas (Figure 9c).

Riverine suspended particulate samples project to the right of axis centre in a much tighter cluster than the sediment samples (Figure 9b-c). This indicates 1) that particulate samples from different parts of the basin are more homogeneous in PAH composition than sediment samples, and 2) particulate samples contain a greater proportion of the higher molecular weight PAHs than sediments from remote areas. The particulate samples from urbanised areas generally project above the *x*-axis and samples from more remote areas project below (Figure 9b). The greater predominance of fluoranthene and pyrene in most urban suspended particulate samples is the primary reason for this distinction (Figure 9a).

Samples of effluent suspended particulate from the four main GVRD WWTPs exhibit much larger variations in PAH composition than the Greater Vancouver particulate samples (Figure 9a). The three samples on the upper right are samples of Annacis Island secondary effluent particulate. (The Oct. 30, 1997 Annacis sample had very high detection limits and could not be included in the PCA model.) These samples have particularly high amounts of fluoranthene and pyrene with low amounts of both the volatile and lower molecular weight PAHs. Three Lion's Gate and two Iona primary effluent particulate samples project on the left side of the *y*-axis (the Lion's Gate samples are furthest left), indicating high proportions of naphthalene, fluorene and phenanthrene. The other Lion's Gate sample and the six remaining primary effluent particulate samples from the Lulu and Iona Island WWTPs project to the right of centre, indicating PAH compositions more typical of suspended particulate samples from the North and Main Arms of the Fraser River.

While the PCA results support the classification of samples into roughly two groups based on parent PAH composition, the PCA model also clearly demonstrates that the PAH composition is sufficiently variable that the PCA projections for different areas of the Fraser basin frequently overlap (Figure 9). This melding of PAH compositions is indicative of multiple PAH sources and variable amounts of anthropogenic PAH inputs. Sample heterogeneity due to the high sand content of bed sediments could also be an important factor in this variability.

8.3 Alkyl PAH content and composition

In almost all suspended particulate and most modern sediment samples from the Fraser River basin and the Strait of Georgia, the maximum for the alkyl naphthalene (N) homologous series is at C₂ or C₃ and the alkyl phenanthrene/anthracene (P/A) series maximises between C₁ and C₃ (usually C₂). In samples from all areas the C₄ compounds usually dominate the P/A series, but C₄ isomers other than retene are only present in a few of the samples from the vicinity of Kamloops and Greater Vancouver (particularly in sediments from along the North Arm of the Fraser River). The increases in parent and alkyl PAH concentrations in Kamloops Lake post-1970 (with maxima at ~1982 and ~1988; Figure 4) also produce well-defined N and P/A alkyl PAH series with maxima typically at C₂, or less frequently C₃.

Particularly where alkyl PAH concentrations are elevated above background (Section 7), these maxima at C₁ 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.*, 1980b; Sporstøl *et al.*, 1983). Combustion processes that use low to moderate temperatures (e.g., a wood stove or the combustion of coal) will also contribute alkyl PAHs (Laflamme and Hites, 1978), but high

temperature processes (e.g., petroleum fuels in a furnace) will not (Lee *et al.*, 1977; Lake *et al.*, 1979). Larger amounts of alkyl PAHs are produced by the combustion of coal, than of wood, while soot from kerosene/fuel oil is almost devoid of alkyl PAH (Lee *et al.*, 1977). Alkyl PAHs also are produced at lower engine and exhaust temperatures in diesel engines (Jensen and Hites, 1983). Hence, near urban locations diesel engines, wood stoves and (particularly in the past) coal furnaces will contribute to the alkyl PAH budget. Given that petroleum-derived PAHs can be rapidly biodegraded in sediments, while the combustion-derived PAHs are relatively resistant to degradation (Gschwend and Hites, 1981; Jones *et al.*, 1986), combustion-related alkyl PAH may also form a larger fraction of the alkyl PAH total as the petroleum fraction degrades.

The alkyl PAH maxima are usually at C₀, but alkyl PAHs are generally still detectable, in sediments from the upper Fraser and Chilcotin Rivers, pre-1970 in Kamloops Lake, and Moose Lake, Chilko Lake, Nicola Lake and Harrison Lake. PAH concentrations are near background in these remote locations and pristine sediments (Section 7). At these low concentrations large scale forest or prairie fires would likely contribute sufficient alkyl PAH to account for the small amounts of alkyl PAHs present, even though the production of alkyl PAHs during wood combustion is a minor process (Lee *et al.*, 1977).

In Stuart Lake, however, alkyl PAH concentrations are elevated and exhibit little change in core sections dating back to ~1580. The alkyl PAH maxima are at C₁ or higher (N at C₂, P/A at C₁ or C₂) throughout the core, suggesting relatively constant inputs of natural petroleum PAHs.

The sediment and 1996 suspended particulate samples from the vicinity of Greater Vancouver have a very consistent parent vs. alkyl PAH composition where parent PAHs dominate, P/A series PAHs are secondary, and only small amounts of alkyl naphthalenes are present (outlined area in Figure 10a). Particulate and sediment samples from the vicinity of Kamloops also fall within this outlined area. The 1996 suspended particulate sample from Agassiz and the 1987 samples from Greater Vancouver have higher amounts of N series PAHs and plot to the right of the outlined area (Figure 10a). The shift in N content in the lower Fraser between 1987 and 1996 could reflect either a change in petroleum composition (as with the hopane and sterane results discussed in Section 6) or a reduction in the discharge of lower molecular weight hydrocarbons into the river.

Alkyl PAH concentrations in effluent suspended solids are much higher than parent PAH concentrations at three out of the four GVRD WWTPs, with the Iona plant having the highest alkyl PAH concentrations. Primary-treated effluent suspended particulate samples from Iona, Lulu and Lion's Gate WWTPs have a dominance of alkyl N, lesser amounts of P/A plus only small amounts of parent PAHs and plot on the centre-right of the ternary plot (Figure 10a). In contrast, the secondary-treated effluent samples from Annacis Island WWTP contain parent and P/A PAHs with only small amounts of alkyl Ns, and plot on the other side, to the left and below the outlined area. The Annacis plant also has the greatest proportion of the alkyl fluoranthene/pyrenes (three-quarters of the P/A concentration) of any WWTP. At the GVRD WWTPs surveyed influent (water plus solids) obtained concurrent with the particulate sampling (Bertold and Stock, 1999) contains even higher proportions of the alkyl Ns than in the effluent particulate (Figure 10a). The two Annacis Island samples plot on the left side of the influent group and have a somewhat lower alkyl N content than the other WWTPs, but parent PAHs are still minor constituents. Hence,

selective removal of the smaller ring size alkyl PAHs during secondary treatment is the most likely explanation for the difference in composition of the Annacis particulate.

Sediment samples from Sturgeon Bank, northern Roberts Bank and station A fall within the outlined area of the Greater Vancouver sediment samples (Figure 2 and Figure 10a). However, upper sections of the core at the base of the Westshore coal terminal and from station CM2 in Saturna basin have much higher proportions of alkyl PAHs, and plot well to the right of the outlined area, likely reflecting the input of coal dust (see Sections 7.5 and 7.6). N, P/A and D (alkyl dibenzothiophene) concentrations are similar at stations A and CM2, but parent PAH concentrations are two-fold higher at station A (Table 8), and this shifts the station CM2 samples to the right in the ternary diagram.

Sediment samples from remote locations in the Fraser basin (Figure 10b) exhibit more variation in composition both within a given area and between tributaries than samples from urban-influenced locations (Figure 10a). The Σ 178-278 parent PAHs predominate over alkyl PAHs in most sediments from the upper Fraser, and most sections from Moose Lake, Chilko Lake, Kamloops Lake, Nicola Lake and Harrison Lake (Table 7, Table 8; Figure 3 and Figure 6a-b). Samples from these locations generally plot on the lower edge and lower left side of the outlined area in Figure 10b. Alkyl PAHs predominate in Stuart Lake, the Nechako and North and South Thompson rivers, and in most river sediments between Prince George and Chilliwack. These samples generally plot in the centre of the ternary diagram, to the right of the outlined area.

8.4 Comparison of abiogenic and higher plant PAHs

With the potential that higher plant PAHs such as retene may be contributing to the PAH contaminant burden (Hodson, 1996; Yunker *et al.*, 1999), it is important to know if any relationship exists between plant-related and anthropogenic PAHs in the Fraser basin. In Figure 11 a comparison is made between the relative proportions of the abiogenic parent PAHs and the higher-plant-derived PAHs simonellite and retene and the methylated hydrochrysenes and hydropicenes. (Cadalene is a minor constituent in all but a few samples and has been omitted from the totals.) The comparison shown in Figure 11 should be regarded as preliminary because data for plant PAHs other than retene are available only for core samples, 1987 and 1996 suspended particulate samples and a few grab samples.

Since few comparisons have been performed between the abiogenic and higher plant PAHs, consideration must first be given to the suitability of the parameters chosen. Similar sample distributions to those shown in Figure 11 are obtained if the alkyl PAHs are used instead of the parent PAHs in constructing the ternary diagram (not shown). Simonellite is a minor constituent relative to retene except in suspended particulate samples from Agassiz and the Main and North arms of the Fraser River and sediment core samples from the vicinity of Greater Vancouver at Gunn Island and McDonald Slough, and very similar results are also obtained just with retene.

Like retene (Figure 6d), concentrations of the methylated tetra- and octahydrochrysenes (THC and OHC, respectively) and tetrahydropicenes (THP) are generally higher near Greater Vancouver. The hydrochrysenes and hydropicenes concentration sum is under 10 $\mu\text{g/g}$ OC in sediment samples from most

remote locations but over 10 µg/g in most samples from Greater Vancouver and the highest suspended particulate concentrations are found in the Vancouver area (Table 7 and Table 8). However, large increases or concentration “spikes” do not occur simultaneously for the simonellite + retene sum and the hydrochrysenes and hydropicenes and concentrations of the two groups generally do not covary. Substantial increases in the OHC + THC + THP concentration also are observed in large parts of the Nicola and Harrison Lake cores without any change in the concentrations of simonellite or retene (Figure 3). Furthermore, simonellite and retene do not covary with the hydrochrysenes and hydropicenes in PCA models that include samples from Greater Vancouver and the Strait of Georgia (Yunker *et al.*, 1999). Hence, there is value in keeping the two groups separate in any discussion of higher plant PAHs.

For the Greater Vancouver area parent PAH concentrations exhibit much more variation than the higher plant PAHs, and the parent PAH content is the main determinant of the sample position in Figure 11a. Sediment samples from Vancouver Harbour and particulate samples from the four WWTPs contain high proportions of parent PAHs (Table 7 and Table 8), and plot in the extreme lower left corner of Figure 11a. In contrast, sediments from Gunn Island, McDonald Slough and Sturgeon and Roberts Banks plot in the centre left of the plot indicating a higher proportion of plant PAH content. While the composition does vary, most of these latter samples have low proportions of simonellite + retene, and in a few cases the hydrochrysenes + hydropicenes sum is the major constituent. Urban particulate samples from the Fraser River near Greater Vancouver are equally variable in composition, but the parent PAHs alternate with the simonellite + retene as the major constituents, and the hydrochrysenes and hydropicenes are generally only minor components. In the Strait of Georgia, cores CM2 and A have only small amounts of simonellite and retene, and plot as two separate clusters on the lower left of Figure 11a, with the station A samples closer to the Vancouver Harbour samples due to their higher parent PAH content (Table 8).

In contrast, in the Fraser basin both the parent and the higher plant PAHs vary in concentration, and both have an influence on sample positions in Figure 11b. The 1996 suspended particulate samples from Marguerite and Woodpecker have a dominance of simonellite and retene (right of centre in Figure 11b), but the samples from McBride and the South Thompson River have the hydrochrysenes and hydropicenes as the major constituents (upper centre in Figure 11b). Sediment samples from remote and semi-urban locations are even more variable in composition. Parent PAHs are the dominant constituents in Moose Lake, most sections of Chilko Lake, and core sections that are post-1900 in Harrison Lake and post-1970 in Kamloops Lake, and plot on lower left in Figure 11b. In contrast, the hydrochrysenes and hydropicenes dominate in Stuart Lake, Nicola Lake, older sections of Chilko Lake, Harrison Lake and Kamloops Lake and in pristine sections of Gunn Island core, and these samples plot towards upper left and centre in Figure 11b. Simonellite and retene are not the dominant components in any of these sediment samples.

Overall, the PAHs that exhibit the largest concentration increases in urban regions for both sediment and suspended particulate samples are the parent and alkyl PAHs. In more remote regions other factors such as the amount of forest cover and the timing of forest disturbance by logging in each area will be important controls on the proportion of higher plant PAHs in suspended particulate and sediment samples (e.g., Wakeham *et al.*, 1980b).

9. PAH Ratios as Source Indicators

9.1 Parent PAH relative stability

PAH ratios have been used to determine PAH sources, classify samples by location and estimate the importance of combustion-derived PAH (Blumer, 1976; Simoneit, 1985; Lipiatou and Saliot, 1991; Yunker *et al.*, 1996; Budzinski *et al.*, 1997). 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, complications due to differences in volatility, water solubility, adsorption characteristics, etc. are minimised (Readman *et al.*, 1987; McVeety and Hites, 1988). While differences in PAH solubility amongst isomers can be appreciable (e.g., fluoranthene is 1.5 times more soluble in water than pyrene, May *et al.*, 1978) it is likely that only the strongly bound PAHs remain after transport through the atmosphere or water column (Lake *et al.*, 1979; Readman *et al.*, 1987; McVeety and Hites, 1988). Typical values of the ratios vary between different groups of PAHs and a more robust interpretation is obtained if a number of PAH ratios are used in concert (Yunker *et al.*, 1996; Budzinski *et al.*, 1997; Yunker *et al.*, 1999).

To date the application of PAH ratios to environmental samples has been somewhat qualitative since, to our knowledge, the calculated stability of PAH isomers has only been used to interpret results for the smaller PAHs (Budzinski *et al.*, 1997, and references therein). Calculations of the most stable PAH isomers have been performed (e.g., Stein and Fahr, 1985), but comprehensive examinations of full suites of PAHs are lacking. To rectify this situation we have used molecular modelling software (see Section 3.5) to calculate the relative stability of all of the parent PAHs quantified in this study where more than one isomer is present (Table 4). In Table 4 the PAH isomers with the higher Heat of Formation (H_f) or Strain Energy (SE) values have lower stability. The calculated results are valid for comparisons of H_f or SE between PAH isomers (e.g., phenanthrene and anthracene), or for comparisons of H_f differences between masses, but they are not valid for the comparison of absolute values of H_f or SE between PAHs with different masses (e.g., phenanthrene and pyrene).

For the major (commonly quantified) PAHs, the greatest difference in stability is observed for the mass 276 PAHs (indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene differ by 17-25 kcal/mole depending on the model used; Table 4). A slightly smaller difference (about 13-21 kcal/mole) is found between fluoranthene and pyrene (mass 202), and the benzofluoranthenes and benzo[*e*]- and benzo[*a*]pyrene (mass 252). Phenanthrene and anthracene (mass 178) are next in order of stability difference (6 kcal/mole), followed by the PAHs of mass 228 and 278 (only a few kcal/mole of energy difference between isomers).

9.2 Application of parent PAH ratios

In using PAH ratios as indicators, it is valuable to examine both PAHs with large differences in thermodynamic stability between isomers (as petroleum vs. combustion indicators) and PAHs with large differences in composition throughout a study area (as indicators of a variety of PAH inputs or sources).

The PAHs of mass 202 and 276 have some of the largest differences in thermodynamic stability between isomers (Table 4) and merit close examination even if the covariance of fluoranthene and pyrene and to a lesser extent benzo[ghi]perylene, indeno[7,1,2,3-cdef]chrysene and indeno[1,2,3-cd]pyrene in PCA models (Figure 9a) would suggest little change in composition in the Fraser basin. The PAH pairs phenanthrene and anthracene, chrysene and benz[a]anthracene, benzo[e]pyrene and benzo[a]pyrene have less difference in thermodynamic stability between isomers (Table 4) but exhibit larger differences in their PCA projections and are likely to be more useful for tracking changes in overall PAH composition. Most of the PAHs included in the PCA model are detectable in samples from all parts of the Fraser basin and are good candidates for ratio comparisons. Indeno[7,1,2,3-cdef]chrysene and benzo[a]pyrene have more limited applicability for ratios because they are undetectable in about 30 % of the samples from remote areas (although their presence or absence can provide information on PAH sources).

Benzo[b/j/k]fluoranthene and benzo[e]pyrene have also been considered as ratio candidates (Yunker *et al.*, 1996), but these PAHs both covary in PCA models (Figure 9a) and show little or no ratio difference with region in the Fraser basin.

In the Fraser basin ratios of anthracene, fluoranthene, benz[a]anthracene and indeno[1,2,3-cd]pyrene to their respective major isomers exhibit the greatest differences amongst regions and sample types. Ratios of these PAHs are presented as cross plots (Figure 12 to Figure 14) along with the downcore profiles for the proportions of fluoranthene and indeno[1,2,3-cd]pyrene in the six Fraser basin lakes (Figure 15). (Anthracene and benz[a]anthracene are only marginally detectable in most lake core samples and their ratios exhibit considerable scatter.)

PAHs of molecular mass 178 and 202 have probably been employed most frequently to distinguish combustion and petroleum inputs (Gschwend and Hites, 1981; Sicre *et al.*, 1987; Budzinski *et al.*, 1997). These PAHs are also present in the highest concentration in remote regions of the Fraser basin (Figure 8b), and hence should provide the most reliable ratio data for the locations where parent PAH concentrations are the lowest (Figure 6a). To interpret these ratios for molecular mass 178, an anthracene to anthracene plus phenanthrene (An/178) ratio less than approximately 0.10 usually is taken as an indication of petroleum input while a ratio over 0.10 indicates a dominance of pyrolytic or combustion sources (Budzinski *et al.*, 1997). For mass 202 a fluoranthene to fluoranthene plus pyrene (Fl/Fl + Py) ratio over 0.50 can usually be taken as an indication of combustion, while a lower ratio suggests a petrogenic origin. The boundaries of these ratios are not precise and exceptions do occur (Budzinski *et al.*, 1997). For example, anthracene can be elevated relative to phenanthrene in coal or coal tar (Wise *et al.*, 1988; Radke *et al.*, 1990), and fluoranthene is depleted relative to pyrene in emissions from cars (Fl/Fl + Py = 0.45-0.49) and diesel trucks (0.41-0.43)(Miguel *et al.*, 1998). PAHs of molecular mass 228 and 276 are used much less frequently as indicators (Yunker *et al.*, 1996; Yunker *et al.*, 1999) and (to our knowledge), no empirical rules are available to interpret the clear differences in the ratios of these PAHs.

9.2.1 Remote and semi-urbanised Locations

In the Fraser basin, anthracene is undetectable in most sediments from the upper Fraser, Stuart/Nechako, Chilcotin and North and South Thompson above Kamloops, and where anthracene is detectable, the An/178 ratio is usually less than 0.10 (left side of Figure 12a). Pre-1970 sections of Kamloops Lake have

ratios of 0.07-0.11, and also fall into this group. The low An/178 ratio in most samples coupled with the presence of alkyl PAHs in sediments from these locations (including pre-industrial sections of cores; Table 9 and Figure 6b) suggests that the mass 178 PAHs originate in mature organic matter (or petroleum) that is primarily natural in origin. The principal exceptions for these remote areas are recent sections from Moose Lake and Chilko Lake, where An/178 generally ranges between 0.17-0.25.

Anthracene is detectable more frequently and the An/178 ratio is usually greater than 0.10 in suspended particulate samples from the upper Fraser and Thompson basins and in most semi-urban sediment samples from locations near Prince George, between Kamloops and Chilliwack, and in Nicola Lake and Harrison Lake (Figure 12a). This suggests that combustion processes make a more significant contribution than natural petroleum to the mass 178 PAHs in most suspended particulate and semi-urban sediment samples from the Fraser basin. One suspended particulate sample from Marguerite in February 1993 has an An/178 ratio of 0.60 (off the scale in Figure 12a), indicating anthropogenic input, possibly from a municipal WWTP upstream, or from a nearby wood combustion source (e.g., beehive burners).

Sediments from the upper Fraser, Stuart/Nechako, Chilcotin and North and South Thompson have Fl/Fl + Py ratios over 0.50 in most cases (top side of Figure 12a), and hence, likely a combustion source for the molecular mass 202 PAHs. The Fl/Fl + Py ratio is also greater than 0.50 in all but two of the suspended particulate samples from the upper Fraser and Thompson basins and in most semi-urban sediment samples from locations near Prince George, between Kamloops and Chilliwack, in Nicola Lake and Harrison Lake, and in pre-1970 Kamloops Lake.

Comparable concentrations and ratios of the mass 202 PAHs are present in both modern and in pre-industrial sections of cores from Moose Lake, Stuart Lake and Chilko Lake (Figure 15a). This suggests that combustion inputs from fossil fuel or biomass burning in this century have not appreciably augmented the natural PAH background from forest or prairie fires at these locations (e.g., Hites *et al.*, 1980b; Wakeham *et al.*, 1980a; Gschwend and Hites, 1981). Regions with the lowest mass 202 concentrations generally exhibit the largest variation in Fl/Fl + Py ratios. At these low concentrations, small additions of mature organic matter or combustion debris would produce marked shifts in the observed ratios, and this is likely the source of the wide variation.

The benz[*a*]anthracene to benz[*a*]anthracene plus chrysene/triphenylene (BaA/228) ratio is generally below 0.35 in less-urbanised areas and in samples from Prince George, the Fraser River upstream of Chilliwack, most sections from Nicola Lake and pre-1970 Kamloops Lake and a number of samples from the Thompson River below Kamloops (lower half of Figure 13a). The main exceptions for these remote and semi-urbanised locations are recent sections from Moose Lake (0.43) and Chilko Lake (0.40-0.50), a few locations in the North and South Thompson Rivers (0.38-0.50) and suspended particulate samples from Shelley, Woodpecker and Marguerite in 1992-1993 (BaA/228 > 0.35 in four cases).

Ratios of indeno[1,2,3-*cd*]pyrene to indeno[1,2,3-*cd*]pyrene plus benzo[*ghi*]perylene (IP/IP + Bghi) are generally less than 0.45 in the Fraser River upstream of Chilliwack, in Moose Lake, Stuart/Nechako and Chilcotin Rivers (Figure 14a and Figure 15a). Ratios are over 0.45 in the upper Nechako River, in the Fraser River at a few locations downstream of Prince George and the Thompson system (including the

city of Kamloops, pre-1970 Kamloops Lake and Nicola Lake and Harrison Lake). Most suspended particulate samples from the Fraser River above Lytton have ratios below 0.45, while particulate samples from the Thompson system are above 0.45.

9.2.2 Urbanised locations

Where PAH concentrations are elevated in both suspended particulate and sediment samples (Kamloops, Kamloops Lake/Thompson River, the North and Main Arms of the Fraser River near Greater Vancouver, and Vancouver Harbour; Figure 6), there are only a few instances where anthracene is undetectable, and there is much less scatter in both the An/178 and Fl/Fl + Py ratios (Figure 12b). At these locations the An/178 and Fl/Fl + Py ratios are almost all over 0.10 and 0.50, respectively, the BaA/228 ratio is usually greater than 0.35 and the IP/IP + Bghi ratio is over 0.45 (Figure 13b). These elevated ratios suggest that combustion is likely the principal PAH source for these samples.

Recent sediments deposited in Kamloops Lake and Vancouver Harbour are notable exceptions for urban-influenced locations. Coincident with the input of substantial amounts of petroleum alkanes and PAHs to the Kamloops Lake (Figure 3 and Figure 4), ratios of FP/FP + Py and IP/IP + Bghi decline below 0.50 and 0.45, respectively, in most post-1970 core sections (Figure 15b). Ratios of An/178 and BaA/228 also decline below 0.10 and 0.35, respectively, in most sections (not shown). These ratio value decreases are consistent with the recent shift from combustion to petroleum sources in the lake (Figure 15). Fl/Fl + Py is also depleted in most Vancouver Harbour core sections (0.27-0.47), again likely due to the input of petroleum (Yunker *et al.*, 1999).

The consistent elevation of PAH ratios in sediment samples from urban-influenced locations (Figure 13 and Figure 14), suggests that ratios of 0.35 and 0.45 for BaA/228 and IP/IP + Bghi, respectively, evidently can accompany An/178 and Fl/Fl + Py ratios of 0.10 and 0.50 as indicators of combustion. However, because most (if not all) environmental samples have mixed PAH sources, it does not necessarily follow that the entire sample is combustion-derived. Conversely, ratios below these levels do not mean that petroleum is the only source to a sample. One result of this diversity is that the Σ 178-278/Alkyl + Σ 178-278 ratio is only poorly correlated with the An/178, Fl/Fl + Py, BaA/228 and IP/IP + Bghi ratios ($r^2 = 0.0004, 0.04, 0.03$ and 0.001 , respectively; $n = 212$) in the Fraser River – Strait of Georgia data set. (Only the correlations with Fl/Fl + Py and BaA/228 are significant at $p < 0.05$.) Hence, no simple relationship will hold in all cases and the designations of “combustion” and “petroleum” on Figure 12 to Figure 14 should be regarded as guidelines only.

One further caveat applies to the interpretation of the IP/IP + Bghi ratio. Because the higher mass PAHs (five and more rings) are present only in trace amounts in refined products such as diesel fuel (e.g., Wang *et al.*, 1999), the presence of a less volatile fraction than diesel (e.g., coal, coal tar, bitumen) would be necessary to introduce significant amounts of petroleum-derived higher mass PAHs (e.g., Yunker *et al.*, 1993). Hence, a low IP/IP + Bghi ratio may at times indicate a different combustion process (see following section), rather than the presence of “petroleum”.

9.2.3 Greater Vancouver Regional District WWTPs

Elevated An/178 ratios are found in effluent particulate samples from the GVRD WWTPs (0.11-0.24) and the sediment core sample adjacent to the old Iona outfall on Sturgeon Bank (the ratio is 0.48 in a subsurface section of the core; off the scale in Figure 12b). In contrast, the Fl/Fl + Py ratios are below 0.50 and petroleum inputs are evident in effluent suspended particulate samples from the Iona (0.47-0.49), Annacis (0.30-0.40) and Lulu Island (0.45-0.50) WWTPs. Fl/Fl + Py ratios are over 0.50 in effluent suspended particulate samples from Lion's Gate WWTP (0.52-0.61), however. By comparison, urban suspended particulate samples from the Fraser River near Greater Vancouver are elevated for both An/178 (0.10-0.15) and Fl/Fl + Py (0.52-0.55; Figure 12b).

For both BaA/228 and IP/IP + Bghi the most elevated ratios observed are found in effluent particulate samples from the four main GVRD WWTPs, and the lowest ratios are found in urban suspended particulate samples from the Fraser River (Figure 13b). The highest ratios for both are found at the Lion's Gate and Annacis Island WWTPs, although the maximum for BaA/278 is at Annacis Island (0.57) and IP/IP + Bghi is at Lion's Gate (0.89). The suspended particulate samples from the WWTPs have provided significant interferences during quantification, with the result that most of the five-ring and larger PAHs (mass 252 and above) have been reported by the analytical laboratory as NDR. On PAH chromatograms for the WWTP samples, the indeno[1,2,3-*cd*]pyrene peak in particular is broad, poorly resolved and generally maximises 1-2 sec later than in the authentic standard. While these interferences will affect the precision (and magnitude) of the IP/IP + Bghi ratios, it is still likely that most of the WWTP samples have a predominance of indeno[1,2,3-*cd*]pyrene over benzo[*ghi*]perylene.

Overall, samples of effluent suspended particulate from the GVRD WWTPs and sediment from Vancouver Harbour are elevated in anthracene, benz[*a*]anthracene and indeno[1,2,3-*cd*]pyrene but with the exception of Lion's Gate, are generally depleted in fluoranthene (Figure 12 to Figure 14). Fluoranthene proportions are low in emissions from cars (Fl/Fl + Py = 0.42-0.49) and diesel trucks (0.41-0.44), benz[*a*]anthracene is elevated in cars (BaA/228 = 0.39-0.51) and particularly diesel trucks (0.53-0.60), but indeno[1,2,3-*cd*]pyrene is low in both cars (IP/IP + Bghi = 0.24-0.35) and trucks (0.26-0.40) (Benner *et al.*, 1989; Miguel *et al.*, 1998; Marr *et al.*, 1999). Hence, the introduction of combustion aerosol from vehicles into the sewers and waterways either directly by atmospheric transport or indirectly by roadway stormwater runoff would account for the observed fluoranthene and benz[*a*]anthracene ratios in WWTP effluents, but not the indeno[1,2,3-*cd*]pyrene ratio. Heavy-duty diesel trucks emit much more of the lower molecular weight, mass 202 and 228 PAHs than light-duty vehicles, and their emissions dominate pollutant PAH profiles even when they are a small percentage of the total traffic (Miguel *et al.*, 1998). Hence, it is likely that trucks are the major source of these lower mass PAHs.

The high indeno[1,2,3-*cd*]pyrene ratios indicate that the higher mass PAHs must have a major source other than combustion particulate from vehicles (cf. Yunker *et al.*, 1999). Indeno[1,2,3-*cd*]pyrene is elevated over benzo[*ghi*]perylene in PAH chromatograms for asphalt given by both Wakeham *et al.* (1980a) and Readman *et al.* (1987). Asphalt has been found to make a larger contribution to street dust washed from roads into Swiss lakes than exhaust emissions or particles from tire wear (Wakeham *et al.*, 1980a), hence asphalt particles could be the source of the elevated indeno[1,2,3-*cd*]pyrene.

Roadways are potentially a significant source of PAHs for both the Iona and Annacis Island WWTPs. However, because the Lulu Island and Lion's Gate WWTPs are closed systems that do not process stormwater runoff from roads (Bertold and Stock, 1999), asphalt particles, motor oils, and vehicle emissions can not make a direct contribution, and other PAH sources must be present. Motor oil can be expected to contain abundant alkyl PAHs and (due to its petroleum source) be depleted in fluoranthene, hence the dumping of waste oil into sewers could make a significant contribution for all WWTPs. However, without more information on PAH inputs to the sewers the similarity in PAH composition and ratios between WWTPs that receive stormwater (Iona and Annacis) and those that do not (Lion's Gate and Lulu Island) is difficult to fully explain.

Nevertheless, because the PAH ratio pattern for urban suspended particulate samples from the Fraser River — elevated in anthracene and fluoranthene, but depleted in benz[*a*]anthracene and indeno[1,2,3-*cd*]pyrene — is substantially different than the pattern in the WWTPs effluents, it is unlikely that the Annacis or Lulu Island WWTP discharges are having a major effect on the river PAH budget (see also Section 10).

9.2.4 Strait of Georgia

An/178 ratios are higher in Vancouver Harbour (0.22-0.27) than in the Fraser River near Greater Vancouver (sediment and particulate, 0.08-0.25), and higher at station A (0.16-0.21) and on Sturgeon and Roberts Banks (0.13-0.20) than at station CM2 in the Saturna basin (0.13-0.16). For Fl/Fl + Py, ratios are lower in Vancouver Harbour (0.38-0.47) than in the Fraser River near Vancouver (0.50-0.56), but station A (0.50-0.53), is more comparable to Vancouver Harbour than to Sturgeon and Roberts Banks (0.50-0.71) or the Saturna basin (0.53-0.68). BaA/228 ratios are higher in Vancouver Harbour (0.43-0.51) than in the Fraser River near Greater Vancouver (0.31-0.37), and higher at station A (0.40-0.45) than on Sturgeon and Roberts Banks or in the Saturna basin (0.32-0.40). For IP/IP + Bghi, ratios are also higher in Vancouver Harbour (0.50-0.57) than in the Fraser River near Greater Vancouver (0.31-0.53), but station A (0.43-0.49), is more comparable to Sturgeon and Roberts Banks (0.36-0.48) than to the Saturna basin (0.50-0.55).

Together the ratio data for An/178; Fl/Fl + Py and BaA/228 suggest that sediments from station A are most similar to Vancouver Harbour, while the Saturna basin is most similar to the Fraser River and (except for An/178) Sturgeon and Roberts Banks (Figure 2). The IP/IP + Bghi ratio data still suggest that the Fraser River is directly influencing the Saturna basin, but the linkage between Vancouver Harbour and station A is less evident. In general, locations that are remote from the Fraser River but close to urban areas of Greater Vancouver (e.g., station A) have the highest PAH ratios, suggesting that urban atmospheric combustion particulate is the main PAH source. Locations that are closer to the mouth of the Fraser River than to urban locations (e.g., station CM2) reflect the river PAH composition, and riverine particulate is likely to be the main PAH source.

9.2.5 Combustion inputs to Fraser basin lakes

Some of the highest IP/IP + Bghi and Fl/Fl + Py values are found in samples from the North and South Thompson Rivers and Nicola Lake and Harrison Lake (Figure 15). These are all locations where alkyl PAH concentrations are low and combustion is the primary PAH source (Table 8 and Figure 3). Equally elevated ratios have been observed for Fl/Fl + Py (0.61 ± 0.04 ; $n=8$) and IP/IP + Bghi (0.55 ± 0.02) in a study of remote European lakes at high altitude sites (1680-2799 m) and on Spitzbergen (Fernández *et al.*, 1996). Both the fluoranthene (0.60 ± 0.08) and indeno[1,2,3-*cd*]pyrene (0.56 ± 0.06) ratios were unchanged in deep sections of these European cores. The authors concluded that both wood and coal combustion have contributed to surface sediments, with wood combustion becoming more important downcore (Fernández *et al.*, 1996).

In contrast to the remote European lakes (Fernández *et al.*, 1996), Moose Lake and Chilko Lake — the most isolated B.C. lakes (Figure 1) — have high proportions of fluoranthene (Fl/Fl + Py >0.60, except for 0.55 in the ~1978 section of Moose Lake with elevated alkyl PAHs; Figure 3), but are depleted in indeno[1,2,3-*cd*]pyrene (IP/IP + Bghi consistently <0.45; Figure 15). Most samples from the upper Fraser, Stuart/Nechako and Chilcotin also have this pattern of excess fluoranthene with low indeno[1,2,3-*cd*]pyrene (Figure 14). However, much closer to population centres in southern B.C., Nicola Lake and Harrison Lake have proportions of both fluoranthene and indeno[1,2,3-*cd*]pyrene that are elevated throughout the core (Figure 15).

The reasons for this shift in composition in the Fraser basin and differences from the European lakes are not entirely clear. The predominance of fluoranthene in Moose Lake and Chilko Lake may represent combustion input that is less weathered (Freeman and Cattell, 1990; Li and Kamens, 1993; Khalili *et al.*, 1995), or it could also indicate combustion particulate that has been transported some distance (e.g., atmospheric samples from Alert in the Canadian Arctic have a similar predominance of fluoranthene)(Patton *et al.*, 1991; Halsall *et al.*, 1997) or to a higher altitude (Moose and Chilko lake are at 1032 m and 1172 m, respectively, and have alpine areas in their drainage basins). In contrast, the high indeno[1,2,3-*cd*]pyrene in the southern lakes likely suggests a more local combustion source. The higher altitude is most likely to be the determining factor, as alpine areas and high altitude lakes have been shown to be subject to greater amounts of deposition from long range atmospheric transport (Blais *et al.*, 1998).

9.3 Non-standard parent PAHs

A number of the lower concentration, rarely studied, mass 276 and 278 parent PAHs have been quantified as part of this study (Table 3 and Figure 16). These PAHs, along with the mass 202 PAH acephenanthrylene, exhibit marked differences in composition between urban and remote locations (plus some differences between tributaries) and show promise as indicators (and tracers) of anthropogenic input. These components are not detectable in all samples (particularly in remote regions of the Fraser basin), hence plots of individual PAH ratios are presented rather than cross plots (Figure 17).

Concentrations of these minor PAHs for the GVRD WWTP samples have been modified from the originally reported NDR data (Bertold and Stock, 1999) based on re-examination of sample

chromatograms using different retention time criteria derived from a more complete set of authentic standards (Yunker *et al.*, 1999). The resulting PAH concentrations and ratios are reasonable in light of other urban samples from this study but, given the significant interferences experienced with the analysis of the WWTP samples, it is likely that the concentrations have not been precisely determined. However, these WWTP results still should be sufficient for a preliminary assessment.

9.3.1 Acephenanthrylene

Acephenanthrylene is a minor isomer of fluoranthene and pyrene that can be formed in appreciable amounts during the combustion of coal, wood or kerosene (Lee *et al.*, 1977). In the Fraser basin the highest proportions of acephenanthrylene (as a ratio to the molecular mass 202 total) are observed in remote areas (Figure 17a). The acephenanthrylene proportion also is generally higher for suspended particulate samples than sediment samples. Ratios greater than 0.04 (the highest value for the Vancouver region) occur in sediments from the upper Fraser and Stuart/Nechako (including Moose Lake dating from ~1918 and Stuart Lake from ~1580), North and South Thompson, Nicola Lake, and a few samples from the Thompson River below Kamloops and the Fraser River below Lytton. Acephenanthrylene is undetectable in most of the Chilcotin River and Chilko Lake samples. The acephenanthrylene ratio in suspended particulate samples is over 0.04 at Woodpecker, Marguerite, McLure, Savona and Yale, with the highest concentrations and proportions observed at Marguerite in 1994. Acephenanthrylene occurs in low proportion (0.01) in the effluent particulate of three of the Vancouver WWTPs, but its ratio is much higher (0.08) in the sample from the Lulu Island WWTP. The spatial pattern of occurrence for acephenanthrylene, coupled with its presence in pre-industrial sediments, suggests that the primary source for acephenanthrylene in the Fraser basin is wood combustion (cf. Lee *et al.*, 1977).

9.3.2 Mass 276 and 278 PAHs

The “non-standard” PAHs of molecular mass 276 (indeno[7,1,2,3-*cdef*]chrysene and anthanthrene) and 278 (dibenz[*a,j*]anthracene, pentaphene, benzo[*b*]chrysene and picene; Figure 16) occur in coal tar (from coke ovens) and the combustion products of brown coal along with the more commonly quantified mass 276 (indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene) and 278 (dibenz[*a,c/a,h*]anthracene) isomers (Grimmer *et al.*, 1983; Wise *et al.*, 1988). Indeno[7,1,2,3-*cdef*]chrysene and anthanthrene are also produced during the combustion of diesel fuel (chromatograms given in Wang *et al.*, 1999) and anthanthrene has been reported in wood and coal combustion products (Lee *et al.*, 1977). The presence of the full suite of mass 276 and 278 PAHs recently has been reported in sediments from Vancouver Harbour and the Strait of Georgia, where these PAHs generally covary with other high molecular weight parent PAHs (Yunker *et al.*, 1999). Anthanthrene has been reported in sediments from Lake Michigan, where coal combustion (particularly from coke and steel production) is likely the major PAH source (Simcik *et al.*, 1996), and indeno[7,1,2,3-*cdef*]chrysene and benzo[*b*]chrysene have been reported in sediments from the NW Mediterranean Sea, where they covary with PAHs with an anthropogenic origin (Salau *et al.*, 1997).

Concentrations of indeno[7,1,2,3-*cdef*]chrysene, anthanthrene, dibenz[*a,j*]anthracene, dibenz[*a,c/a,h*]anthracene, pentaphene, benzo[*b*]chrysene and picene are highest in urban regions (as with

the Σ 178-278 parent PAHs; Figure 6a), but their distributions in the Fraser basin suggest that they should be considered as three separate groups.

9.3.3 *Indeno[7,1,2,3-cdef]chrysene, dibenz[a,j]anthracene, dibenz[a,c/a,h]anthracene and picene*

PAHs in the first group are found in sediments from all parts of the Fraser basin and Strait of Georgia, although their presence (or detection) can be intermittent in remote regions (Figure 17b-e). Indeno[7,1,2,3-cdef]chrysene and dibenz[a,c/a,h]anthracene are detectable with about the same frequency, although the presence/absence of the two PAHs does not appear to be correlated. After indeno[1,2,3-cd]pyrene and benzo[ghi]perylene these two PAHs are usually present in the highest concentrations and they are present more often than dibenz[a,j]anthracene or picene in sediments from remote areas. Indeno[7,1,2,3-cdef]chrysene and dibenz[a,c/a,h]anthracene are also present in most suspended particulate and GVRD WWTP samples, while dibenz[a,j]anthracene and picene are intermittent everywhere except in river and WWTP particulate samples from the vicinity of Greater Vancouver. Particularly for picene it is also possible that some year-to-year variation may be occurring: for example, in the main arm of the Fraser River picene is undetectable in all four 1995 sediment samples but is present in all four 1996 samples.

All four of the PAHs in the first group are present in pre-industrial sections of the cores from Stuart Lake and Kamloops Lake (dating to ~1580 and ~1859, respectively) and pristine sections from the core bottom in Port Moody Arm of Vancouver Harbour (Yunker *et al.*, 1999). Dibenz[a,j]anthracene data are not available for most core sections from Nicola Lake and Harrison Lake, but in Harrison Lake the three other PAHs are present in all sections dating back to ~1873, while in Nicola Lake indeno[7,1,2,3-cdef]chrysene and dibenz[a,c/a,h]anthracene are present to ~1828, and picene to ~1910. In Nicola Lake and Harrison Lake the appearance of picene in the sediment record coincides with the increase in parent PAH concentrations above baseline (~1910 and ~1873, respectively; Figure 3).

Proportions of indeno[7,1,2,3-cdef]chrysene and dibenz[a,j]anthracene relative to their molecular mass totals exhibit little difference in sediments from the Fraser River near Greater Vancouver, Vancouver Harbour and stations A and CM2 in the Strait of Georgia (Figure 2 and Figure 17c-d), although the indeno[7,1,2,3-cdef]chrysene (and possibly dibenz[a,j]anthracene) content appears to increase between station A and CM2. (Dibenz[a,j]anthracene peak area data are only available for the core surface at station A, so trends for this PAH can not be established for certain.) The dibenz[a,c/a,h]anthracene content is lower in Vancouver Harbour than in most Fraser River samples, and the proportion increases from the Harbour to station A and then to station CM2 (Figure 17b). Proportions of indeno[7,1,2,3-cdef]chrysene, dibenz[a,j]anthracene and dibenz[a,c/a,h]anthracene in many sediment and suspended particulate samples from the Fraser River near Greater Vancouver are substantially higher than in Vancouver Harbour, suggesting that the increases at station CM2 may reflect a greater influence of particulate from the Fraser River. In contrast, picene has the same proportion in the lower Fraser River, Vancouver Harbour and station A, and then declines at station CM2 (Figure 17e). Picene is not elevated to the same extent as the other PAHs in suspended particulate from the lower Fraser River, and may be associated with denser material that does not transport easily in the suspended particulate phase.

9.3.4 Benzo[b]chrysene and anthanthrene

In the second group benzo[b]chrysene and anthanthrene are undetectable in most surficial sediment samples from the Stuart/Nechako, upper Fraser River, Chilcotin River, the Fraser River through to the mouth of the Harrison River, the Thompson River upstream of Kamloops and the Fraser Canyon (Figure 17f-g). The two PAHs are also absent from the cores from Moose Lake, Stuart Lake and Chilko Lake. These compounds are present in most sediments from the vicinity of Kamloops and the Thompson River, the Harrison River and most samples from the vicinity of Greater Vancouver (particularly from the North Arm and Vancouver Harbour). Benzo[b]chrysene is absent from Nicola Lake, present in one section from Harrison Lake (~1954; the PAH maximum) and is found in Kamloops Lake from ~1941-1985. Anthanthrene appears in Kamloops Lake, Nicola Lake and Harrison Lake at the same time as picene (see above). Anthanthrene is undetectable in Harrison Lake after 1967, but occurs to the present day in the cores from the other two lakes. In suspended particulate samples, benzo[b]chrysene and anthanthrene are only consistently present at Marguerite, and in river and WWTP samples from the vicinity of the Greater Vancouver urban region.

Proportions of benzo[b]chrysene decline from the Fraser River estuary to Vancouver Harbour to the Strait of Georgia, and are the same at station A and in the Saturna basin (Figure 17f). Proportions of anthanthrene are higher in Vancouver Harbour than in the Fraser River near Greater Vancouver, and decline at stations A and CM2 (Figure 17g). As with picene, these decreases in the Strait of Georgia suggest that benzo[b]chrysene and anthanthrene may be associated with material that does not transport easily on suspended particulate.

9.3.5 Pentaphene

Pentaphene, the final molecular mass 278 PAH measured (Figure 16)(Yunker *et al.*, 1999), is intermittently detectable in sediments from Harrison Lake (~1910, ~1954), the North and Main Arms of the Fraser River (both suspended particulate and sediment) and is present in both cores from Vancouver Harbour, the core adjacent to the old Iona intertidal outfall, and the cores from station A (all sections) and the Saturna basin (one-half of the core; Figure 17h). Pentaphene is not detectable elsewhere. Pentaphene proportions increase from the Fraser River estuary to Vancouver Harbour. The range of pentaphene proportions in the two Strait of Georgia cores is greater than in the lower river and harbour combined (Figure 17h).

9.3.6 Sources of the non-standard mass 276 and 278 PAHs

The distribution evidence suggests that dibenz[*a,j*]anthracene, dibenz[*a,c/a,h*]anthracene, indeno[7,1,2,3-*cdef*]chrysene and picene are PAHs with natural, likely combustion-related sources in the Fraser basin, while benzo[b]chrysene, anthanthrene and pentaphene primarily have an anthropogenic origin. Dibenz[*a,j*]anthracene, dibenz[*a,c/a,h*]anthracene, indeno[7,1,2,3-*cdef*]chrysene and picene are present in Arctic Ocean basin sediments dating back to glacial times (Yunker *et al.*, in preparation) when only natural sources in combustion or re-worked organic matter are possible. Pentaphene is undetectable in all

Arctic samples, while benzo[*b*]chrysene and anthanthrene are only present at very low levels in a few samples.

A full suite of mass 278 PAHs (dibenz[*a,j*]anthracene, dibenz[*a,c/a,h*]anthracene, pentaphene, benzo[*b*]chrysene, and picene with the dibenzanthracenes and picene as major constituents; Figure 16) is only observed in sediment samples from the vicinity of Greater Vancouver and in the Strait of Georgia. Concentrations of these PAHs in the Fraser River are highest near Annacis Island and along the North Arm, demonstrating that all of these PAHs can also have an anthropogenic source(s). Similar mass 278 and 276 profiles to those of the Greater Vancouver samples are also found in sediments adjacent to the Alcan smelter in Kitimat (Cretney, pers. commun.). Hence, a coal or “coal tar” type combustion source is suggested for this profile. It is not certain whether the major source(s) are along the North Arm or whether discharges from New Westminster (north side of the Fraser River just before the split into the North and Main arms) could also contribute. These PAHs could enter the river through direct discharge or stormwater run-off from road surfaces, but leachate from creosote treatment plants (e.g., the Domtar/Stella Jones site) would be another possible source.

9.4 Dibenzothiophenes

Dibenzothiophenes (DBT) are sulphur-containing PAHs that are present in oil and coal (Barrick *et al.*, 1984; Hughes *et al.*, 1995), coal products such as creosote and coal tar (Merrill and Wade, 1985; Wise *et al.*, 1988) and the combustion products from the burning of oil and coal (Grimmer *et al.*, 1983; Tong and Karasek, 1984). Coal soot in particular can contain significant amounts of sulphur-containing compounds, while these are absent in wood or kerosene/fuel oil combustion products (Lee *et al.*, 1977). The DBT content of crude oils varies from trace levels to more than 30 % of the alkyl PAH total (Requejo *et al.*, 1996) and is not always correlated with the sulphur content (Hughes *et al.*, 1995). It also is not always possible to use the DBT alkyl homologue series to univocally assign whether the DBTs have a direct source in petroleum (e.g., oil, coal) or in the combustion of petroleum products such as diesel or coal (Sporstøl *et al.*, 1983). However, elevated levels of dibenzothiophenes usually indicate enhanced anthropogenic input (Tolosa *et al.*, 1996).

DBT homologue distributions maximise at C₂ in all suspended particulate samples from the Fraser River and most sediment samples from Kamloops, Kamloops Lake and the vicinity of Greater Vancouver. The DBT maximum is at C₁ in sediment samples from the Nechako and Stuart Rivers and in the ~1580 section from Stuart Lake. DBTs are undetectable in sediments from the upper Fraser River, (except for a few recent sections from Moose Lake) and but are present in the Fraser River just downstream of Prince George.

In the Fraser basin the C₀ to C₂ DBT totals (Figure 18a) exhibit the same concentration trends as the alkyl PAH totals (Figure 6b): sediment concentrations are low (undetectable to 0.2-0.3 µg/g OC) in sediments from less-industrialised areas, elevated in the vicinity of Kamloops and in post-1977 sections from Kamloops Lake (maximum 1.3 µg/g) and are much higher in Fraser River sediments close to Greater Vancouver (max. 5.3 µg/g) and in Vancouver Harbour (max. 12 µg/g; Table 8). However, in all areas of the Fraser basin the DBT concentrations on suspended particulate are elevated over the corresponding

sediment concentrations by a factor that is much higher than for the alkyl PAHs as a whole (Figure 6b and Figure 18a). This suggests either that petroleum sources differ between the water column and the sediment or, more likely, that the DBTs are associated with a particulate fraction that tends to remain resuspended in the river.

It has recently been established that the ratio of the dibenzothiophenes to the phenanthrenes is characteristic of the depositional environment where a crude oil was formed (Hughes *et al.*, 1995; Requejo *et al.*, 1996) and can be used to distinguish petroleum sources in the environment (Bence *et al.*, 1996; Douglas *et al.*, 1996). Ratios can be based either on the totals for all homologues (e.g., C₀ - C₂ sum), and thereby improve the detectability of the ratio (Requejo *et al.*, 1996), or on the ratios of specific homologues (e.g., C₂), and reduce the sensitivity of the ratio to petroleum weathering (Douglas *et al.*, 1996).

The proportions of the C₀ - C₂ DBT sum relative to the C₀ - C₂ P/A sum are higher and the C₂ DBTs are more prevalent in sediments from urbanised areas of the Fraser basin (Figure 18b-c). The C₀ - C₂ DBT and C₂ DBT proportions are both low and relatively constant (0.01-0.05 and 0.02-0.06, respectively) in the Stuart/Nechako, Quesnel/Chilcotin and North and South Thompson Rivers and ratios remain within these ranges back to ~1580 in Stuart Lake. This suggests that the mature organic matter or petroleum background of dibenzothiophenes in the Fraser basin is low, and that the elevated DBT proportions at Kamloops, in the Thompson River, Harrison River/Lake, Vancouver vicinity and stations A and CM2 are due to anthropogenic petroleum inputs.

Both the C₀ - C₂ DBT and C₂ DBT proportions indicate that the DBT content of suspended particulate samples is dramatically higher and exhibits less change with location in the basin than the sediments (Figure 18b-c). Because the two ratios show similar trends, and because C₂ DBT and C₂ P/A are homologues with almost identical weathering characteristics (Douglas *et al.*, 1996), PAH degradation can be ruled out as a significant cause for the differences in DBT content between suspended particulate and sediment. This suggests that the primary source for DBTs in suspended particulates in the Fraser basin is large-scale atmospheric input of anthropogenic aerosols or more local petroleum input from roads. However, the differences in DBT concentrations and ratios between the suspended particulate and sediment samples also suggest that this anthropogenic DBT input has had little impact on sediments in the less-urbanised areas.

The shift in the DBT maximum and the localized presence of dibenzothiophenes in the Fraser River near Prince George are consistent with a local petroleum source from the city. In Moose Lake the same parent PAH concentrations and parent PAH distributions occur in the 1990s and ~1918 (Figure 3). Alkyl PAH concentrations are more than 10-fold lower in ~1918, hence a different alkyl PAH source (e.g., petroleum from the nearby highway) is likely to be contributing to recent sediments in Moose Lake. Similar inputs of petroleum from nearby highways to other Fraser and Thompson River samples are also likely to have occurred.

10. PAH Fluxes

10.1 Comparison of particulate fluxes in the Fraser River to the Greater Vancouver Regional District WWTPs

The suspended particulate PAH flux in different parts of the Fraser River (Figure 1 and Figure 2) has been estimated by using the SPM to convert ng/g PAH concentrations to volume-based concentrations and then multiplying by river flow (Figure 19). SPM and river flow can vary from hour-to-hour with weather conditions and (in the lower Fraser) with the tidal height and flow (Kostaschuk *et al.*, 1992). To minimise tidal effects, modelled river flows in the lower Fraser (calculated at 15 min. intervals; Woollard, pers. commun., 1999) have been averaged over the two tidal cycles (25 h, from lowest tide to lowest tide) that bracket each sampling time. The resulting averaged flows for the Pattullo Bridge in 1987 and 1996 differ by only 12% and 1%, respectively, from the predicted freshwater inflow for the Fraser plus all significant tributaries between Hope and the Pitt River (~10 km upstream of the bridge). While the tidal component has been largely removed from the flows used for flux calculations, the flux estimates given in Figure 19 and Table 11 should only be used to probe large-scale changes in PAH inventory.

The 1996 suspended particulate PAH fluxes in the Fraser River are lowest at McBride on the upper Fraser, and increase substantially downstream of Prince George at Woodpecker and Marguerite (Figure 19). PAH fluxes downstream of Kamloops Lake at Savona are lower than at the South Thompson location upstream of Kamloops. The settling out of particulate-associated contaminants in Kamloops Lake would account for part of this difference in fluxes. However, Savona also had a very low concentration of total suspended solids during sampling (2.6 mg/L), while the South Thompson had a very high suspended solids concentration (32.2 mg/L) as the result of a storm (Sylvestre *et al.*, 1998b). Overall it is likely more significant that the PAH flux at Agassiz — reflecting the combined PAH inputs of the Fraser and Thompson Rivers — is larger than the flux at Woodpecker and Marguerite.

The 1996 flux of parent and alkyl PAHs increases dramatically between Agassiz and New Westminster (the Pattullo bridge), then decreases somewhat after the bifurcation of the river into the North and Main arms (Figure 19). Alkyl PAH fluxes at the Pattullo Bridge are comparable in 1987 and 1996, while the flux of parent PAHs is higher in 1987. Fluxes of the higher plant PAHs (particularly simonellite) are very much higher at the Pattullo Bridge in 1996 than 1987. A storm with heavy rainfall occurred during the 1996 sampling, and debris (e.g., sawdust, wood particles, etc.) washed from wood processing facilities may have augmented the normal PAH profile.

Effluent suspended particulate fluxes of parent and alkyl PAHs are substantially below the river flux for three of the four GVRD WWTPs surveyed (Figure 19). (The calculated WWTP fluxes are based on the average of the four samplings for the parent and alkyl PAHs but only a single sampling for the higher plant PAHs.) For the Iona WWTP, however, mean alkyl PAH fluxes (0.71 kg/day) are equivalent to the flux at the Pattullo Bridge (0.74 kg/day), while parent PAH fluxes (0.22 kg/day) are only one-fifth of flux at the Pattullo Bridge (1.03 kg/day; Table 11). Because the Iona WWTP receives urban stormwater runoff an important component of the alkyl PAHs in the Iona discharge is likely from chronic petroleum inputs from roads, etc. (Eganhouse *et al.*, 1981; Hoffman *et al.*, 1984; Larkin and Hall, 1998). The Lulu and Lion's

Gate WWTPs only receive inputs from sanitary sewers (i.e., not from storm drains or street run-off) and a lower PAH flux at these two locations would be expected.

PAH fluxes for the Annacis Island WWTP are even lower than for the Lulu and Lion's Gate WWTPs (Table 11), even though the Annacis plant also receives input from stormwater. Bertold and Stock (1999) have observed that an increase in the treatment efficiency (from primary to secondary) can produce substantial reductions in the amounts of particle-associated contaminants (such as the PAHs), and this is the likely cause of the low PAH fluxes. The previously mentioned composition differences for the effluent particulate samples from Annacis Island WWTP (parent and P/A PAHs with only small amounts of alkyl Ns; Figure 10a) is also consistent with selective removal of the smaller ring size alkyl PAHs during secondary treatment.

The PAH composition data for Annacis Island WWTP and the fluxes shown in Table 11 are somewhat misleading, however, because only about 44% of the flow was receiving secondary treatment during the 1997 sampling (Bertold and Stock, 1999). Effluent from the Annacis WWTP was also receiving only primary treatment at the time of the particulate sampling in 1996 (Sylvestre *et al.*, 1998b). Because only secondary effluent was sampled at Annacis WWTP during the fall 1997 sampling, a full comparison of the effluent to the river is not possible. Nevertheless, Annacis Island WWTP and Iona WWTP both receive stormwater inputs, and the primary treated effluent particulate composition at Annacis Island is likely similar to Iona in having a marked prominence of alkyl PAHs (Figure 19). Because the particulate sample obtained 100 m below the Annacis outfall has a higher proportion of parent PAHs than the sample collected upstream at the Pattullo Bridge, and still contains substantial amounts of plant PAHs, it is likely that the effluent has not had a major effect on the PAH composition at this site.

10.2 Significance of WWTP inputs

The flux calculations given in Table 11 suggest that in late fall the Iona WWTP delivers a point source loading of petroleum PAHs (average of 0.71 kg/day) that is comparable to the Fraser River before the bifurcation (0.74 kg/day). Late fall is both the low flow period for the Fraser River and a time of typically heavy rainfall on the B.C. coast. Hence, petroleum inputs could be making their highest relative contribution to either the river or the outfall at this time, with the result that the alkyl PAH concentrations and fluxes indicated could be unrepresentative of annual loadings.

By comparison, data from sediment trap arrays and dated sediment cores (Bates *et al.*, 1987; Murphy *et al.*, 1988) collected in Puget Sound in the early 1980s suggest that the transport of particulate-associated parent PAHs (a slightly smaller group than used here) north out of Puget Sound through Admiralty Inlet was about 0.38 kg/day (Murphy *et al.*, 1988). Although these flux estimates have a large uncertainty, they illustrate that the Fraser River, Iona WWTP and Puget Sound outflow are about the same size, and that no source is likely to dominate beyond its own region.

The suspended particulate carbon content of the Iona effluent (26-33%) is much higher than the carbon content of either the river particulate (0.72-0.87%; Table 1 and Table 11) or sediments from the Strait of Georgia (1.37-1.73%; Table 2). Sediments in the Strait of Georgia also are depleted in petroleum

components (alkanes and some PAHs) and other volatile and biodegradable compounds, relative to suspended particulate material from the Fraser River (Sylvestre *et al.*, 1998b; Sylvestre *et al.*, 1998a; Yunker *et al.*, 1999) and the WWTPs (see Section 8). This “ephemeral” material includes compounds such as the petroleum PAHs that are present in high concentrations in the WWTP discharge, but which are apparently biodegraded in the water column or at the sediment-water interface. While this suggests that dispersal, and likely biodegradation (Prahl *et al.*, 1980; Bence *et al.*, 1996; Douglas *et al.*, 1996), substantially reduces the actual carbon and PAH loadings to sediments of the strait, further study would be required to establish what happens to these contaminants between the discharge pipe and the sediments. Here the key question is which components are degraded or volatilized quickly in seawater, and which are persistent enough to be available for ingestion by epibenthic and benthic organisms?

11. Conclusions

In this work we have assessed the relative contribution of natural vs. anthropogenic polycyclic aromatic hydrocarbons (PAHs) in different parts of the Fraser River basin and Strait of Georgia. Significant observations and conclusions from this interpretative synthesis are as follows:

1. Bed sediments from the Fraser River generally contain sand and silt, with only small amounts of clay, while suspended particulate samples primarily contain silt, with lesser amounts of clay and small amounts of sand (Table 1 and Table 2). The lower amounts of sand and the large variations in sand content in the water column are both features of discontinuous sediment transport, in which the coarser material is only suspended during higher flows. The large sand content of bed sediments dilutes the PAH-containing fine fraction, resulting in greater sample heterogeneity and increased likelihood of samples being unrepresentative. As a result comparisons of PAH composition and sample-weight normalised concentrations between locations and between the water column and sediment can become problematic.
2. Sediment cores from the six lakes in the Fraser River basin exhibited little or no surface mixing and a well-defined depositional chronology (Figure 3 and Figure 4). In contrast, cores from the Fraser River estuary, Vancouver Harbour and the Strait of Georgia generally had a substantial surface mixed layer (SML), with in some cases evidence of episodic changes in sedimentation, and only an approximate depositional history could be established.
3. In all six Fraser River basin lakes (Figure 1) perylene concentrations increase down core on both a ng/g and µg/g organic carbon (OC) basis, while in the Strait of Georgia the perylene increase is observed only in the core from the Saturna basin (Figure 3). The magnitude of the perylene increase and the core depth/year of the onset vary from core to core.
4. Surface sediments from all lakes also contain high proportions of the algal biomarker *n*-C₁₇ (odd-even predominance or OEP C₁₇ from 3.3 in Stuart Lake to 33 in Nicola Lake). The decreases in OEP C₁₇ and *n*-C₁₇ concentration with core depth are most pronounced in the three southern lakes (Kamloops Lake, Nicola Lake and Harrison Lake).

5. In Moose Lake and Stuart Lake the alkanes and Σ 178-278 parent PAHs are essentially constant from ~1890 and ~1580, respectively, to the present. Several PAH and higher plant parameters exhibit concentration “spikes” in recent sediments from the two lakes that likely reflect logging, road building or some other anthropogenic activity in the two watersheds. In Stuart Lake the presence of elevated alkyl PAHs and diagenetic hopanes in pre-industrial core sections points to natural petroleum PAH source(s) in eroded materials such as bitumens, shales or coals.
6. Alkane, perylene, OHC and THC concentrations change little to the present day in Chilko Lake (Figure 3 and Figure 4). This observation of negligible direct anthropogenic input is consistent with Chilko Lake being the most remote of the lakes studied (Figure 1).
7. Alkane and PAH concentrations exhibit little change in Kamloops Lake between ~1859 and 1970. After ~1970 alkane, UCM, Σ 178-278 parent and alkyl PAH, simonellite and retene concentrations increase dramatically in Kamloops Lake, maximise in the 1980s, and then decline in the 1990s (Figure 3 and Figure 4). These trends in petroleum components and the plant PAHs suggest new heavy industry or forest-products industry development post-1970, with improvements in pollution containment beginning in the late 1980s.
8. In Nicola Lake and Harrison Lake the Σ 178-278 parent PAHs begin increasing in the late 1800s, maximise in the 1940s and 1950s and decline to the present day. The low amounts of alkyl PAHs, coupled with the absence of an alkane UCM, suggests that atmospheric combustion products from the burning of wood or coal are the major PAH source(s) to the lakes.
9. Hopane and sterane biomarker data suggest that petroleum inputs are widespread in the Fraser and Thompson Rivers downstream of Prince George and Kamloops, respectively, as well as in the Strait of Georgia. Throughout the Fraser basin chronic petroleum inputs are much more evident in samples of suspended particulate than of bed sediment (Table 6).
10. The pattern of occurrence of the petroleum biomarkers suggests, not unexpectedly, that petroleum discharges are primarily associated with human activity in transportation corridors and major population centres. None of the hopane or sterane biomarker compositions are sufficiently unique to definitively correlate the present set of environmental samples from the Fraser River with any of the Alberta or Alaska North Slope petroleum basins. Further biomarker data for specific endmembers (crude oils, coals, motor oils, etc.) are required to conclusively establish petroleum sources and processes for the Fraser basin.
11. A PAH concentration of about 1 $\mu\text{g/g}$ OC can be used as the pre-industrial baseline for both the parent and alkyl PAHs, and 0.5 $\mu\text{g/g}$ OC can be used for retene (Table 9). Present day sediment concentrations in the Strait of Georgia are more than an order of magnitude above these baseline levels (except for station CM2 in the Saturna basin for retene).
12. In less-urbanised locations the mean (and in most cases maximum) Σ 178-278 parent PAH and alkyl PAH concentrations in suspended particulate and sediment samples are almost entirely greater than

the 1 µg/g pre-industrial baseline, but are still less than 10 µg/g OC (Table 7, Table 8, Figure 3 and Figure 6a-b). All locations with parent and alkyl PAH concentrations over 10 µg/g OC are adjacent to highways except for the Woodpecker and Quesnel River stations. The concentration of retene is greater than the Σ 178-278 parent PAH total in most samples of bed sediment from the upper Fraser River between McBride and Quesnel, the Nechako River and the North and South Thompson Rivers, as well as in samples of suspended particulate from Woodpecker and Marguerite.

13. In the vicinity of Kamloops and downstream of Chilliwack, the Σ 178-278 parent PAH and alkyl PAH concentrations increase considerably, indicating significant anthropogenic input of PAHs. All samples that have been analysed for alkanes from the vicinity of Greater Vancouver (1987 suspended particulate samples and sediment cores from mouth of the Fraser River and Vancouver Harbour) also have an appreciable unresolved complex mixture (UCM). In the Fraser River estuary and Vancouver Harbour, almost all suspended particulate and sediment samples have concentrations over 10 µg/g OC, with the suspended particulate samples having the greater mean concentrations in the Main Arm. There are many potential sources of these contaminant PAHs, including combustion, petroleum spills, urban stormwater runoff and WWTP discharges, and creosote.
14. The highest concentrations in the lower Fraser River for both parent and alkyl PAHs are found in the two sediment cores and in a number of grab samples from Vancouver Harbour (Table 8). Averaged sediment concentrations are much lower in the industrialised areas around Annacis Island and along the North Arm, and decrease further in sediment samples collected downstream of Annacis Island. In contrast, average UCM concentrations in sediment cores from the mouth of the Fraser River are twice as high as those of Vancouver Harbour. The data from these few cores suggest that inputs of parent and alkyl PAHs have been more important in Vancouver Harbour, while inputs of petroleum alkanes have been higher in the Fraser estuary.
15. Beyond the mouth of the river (Figure 2), PAH concentrations are elevated in the station AO core collected close to the previous (intertidal) outfall of the Iona WWTP treatment facility. Concentrations are much lower at the core bottom (26-31 cm) and are close to or below 10 µg/g OC at stations A10 and A12 on Sturgeon bank. The alkane UCM has the same concentration trend as the alkyl PAHs in the upper part of the station AO core, but the UCM is undetectable at the core bottom (26-31 cm depth) and in other samples from Sturgeon Bank. These limited data suggest that prior to 1988 the Iona outfall had discharged significant amounts of PAHs and petroleum into the Fraser estuary. Conditions have improved since effluent was re-routed to the deep-sea Iona outfall, and the intertidal outfall appears to have had only a local impact on Sturgeon bank.
16. Adjacent to the causeway to the Westshore coal terminal on Roberts Bank (Figure 2), core BPt-1 has parent PAHs just above the 10 µg/g level, while alkyl PAHs are present in much higher concentrations except at the core bottom. Closer to the mouth of the river at station A14, parent PAH concentrations are similar to BPt-1, but alkyl PAHs are present at much lower levels. In contrast, UCM concentrations are much higher at station A14 than at BPt-1. The presence of elevated alkyl PAHs with a lower UCM concentration at BPt-1 suggests that mature organic matter with a different

composition than petroleum in the river (such as coal dust) is making a greater contribution adjacent to the coal terminal.

17. While retene is a minor constituent relative to the parent PAHs, retene concentrations in suspended particulate samples from Agassiz and the Fraser estuary are all over 5 µg/g OC (maximum 22 µg/g). All of the North Arm and one-third of Main Arm sediment samples have retene concentrations above 5 µg/g (maximum 28 µg/g; Figure 6d), while retene is below 5 µg/g in sediments from Vancouver Harbour (0.8-3.6 µg/g). The excess retene in the suspended particulate phase in the vicinity of Vancouver likely has a source in wood chip loading facilities and paper products manufacturing plants along the Fraser River in Greater Vancouver. Retene and other higher plant PAHs are minor constituents in WWTP particulate (Table 7), suggesting that only small inputs of fine plant detritus or wood debris have entered the sewers, at least at the time of sampling.
18. Strait of Georgia data suggest that plant debris and petroleum from the Fraser River (or petroleum delivered by stormwater or the GVRD WWTPs) are uniformly distributed over large areas of the strait. The elevated parent PAH, retene and possibly simonellite concentrations found at station A likely reflect additional atmospheric input of combustion products from vehicles, furnaces, wood burning, etc. due to the closer proximity to Greater Vancouver urban locations.
19. Suspended particulate samples from locations downstream of Kamloops Lake and Lytton in the Thompson and Fraser Rivers and sediment samples from urban-influenced areas have a parent PAH profile with a predominance of PAHs with mass 202 and 252, with in most cases mass 202 as the major constituent. This profile is commonly observed in sediments from industrialised areas and, particularly where mass 202 is the highest molecular mass constituent, a predominance of pyrolytic (heat formed) PAHs is likely.
20. In most sediments from remote areas and pre-industrial sections of cores from Moose Lake, Chilko Lake, Nicola Lake and Harrison Lake the parent PAHs of molecular mass 178 and 202 dominate PAH profiles. Sediments from the Stuart River and Stuart Lake have a different profile with a dominance of mass 178 and 252 PAHs. This same profile prevails in Stuart Lake back to ~ 1580 and it is inferred that natural petroleum makes a significant contribution to the PAH budget in the Stuart River watershed.
21. The predominance of the lower molecular mass PAHs 178 and 202 in less-industrialised areas of the basin and pre-industrial sections of cores suggests that the majority of these PAHs are most likely contained in refractory matrices such as bitumen, coal or soot, and hence protected from dissolution in water or bacterial degradation.
22. Alkyl PAHs are largely absent from Kamloops Lake, Nicola Lake and Harrison Lake pre-1950 (Figure 3), hence an anthropogenic combustion-related process(s) must be responsible for the change in PAH composition from a predominance of masses 178 and 202 to 252 and 276 that commenced in the late 1800s. This shift to a predominance of molecular masses 252 and 276 is likely due to wood or coal combustion.

23. Masses 178 and 202 PAHs (with 202 most often the maximum) are major constituents in all suspended particulate samples from the Fraser basin, likely reflecting inputs of fresh petroleum.
24. Principal components analysis (PCA) illustrates that samples from remote locations generally have higher proportions of the lower molecular weight PAHs (particularly naphthalene, fluorene and phenanthrene), while the urban samples have more of the higher mass PAHs. Samples from the shallow banks at the margins of the Strait of Georgia straddle the two groups: the Sturgeon bank samples project with the urban samples (suggesting greater urban influence at this location), while the Roberts bank sediments project with samples from more remote areas.
25. Riverine suspended particulate samples from different parts of the basin are more homogeneous in PAH composition than sediment samples and contain a greater proportion of the higher molecular weight PAHs than sediments from remote areas. In addition, most urban suspended particulate samples have a greater predominance of fluoranthene and pyrene, indicating combustion sources, than samples from remote areas.
26. While PCA results support the classification of samples into roughly two groups based on parent PAH composition, the PCA model also clearly demonstrates that the PAH composition is sufficiently variable that the PCA projections for different areas of the Fraser basin frequently overlap (Figure 9). This melding of PAH compositions is indicative of multiple PAH sources and variable amounts of anthropogenic PAH inputs. Sample heterogeneity due to the high sand content also could be an important factor in this variability.
27. In almost all suspended particulate and most modern sediment samples from the Fraser River basin and the Strait of Georgia (including Kamloops Lake post-1970), the maximum for the alkyl naphthalene (N) homologous series is at C₂ or C₃ and the alkyl phenanthrene/anthracene (P/A) series maximises between C₁ and C₃ (usually C₂). Where alkyl PAH concentrations are elevated above background, these maxima at C₁ and higher for the PAH alkyl homologue series establish a source in mature organic matter or petroleum for the majority of the alkyl PAHs.
28. The N or P/A maximum is at C₀ (i.e., combustion PAHs predominate) in the upper Fraser and Chilcotin Rivers, and for most sections of the cores from Moose Lake, Chilko Lake, Nicola Lake and Harrison Lake, and in Kamloops Lake pre-1970. These samples still contain small amounts of alkyl PAHs, likely from low-temperature combustion in forest and prairie fires. In contrast, the Stuart Lake alkyl PAH concentrations exhibit little change and the alkyl PAH maxima are at C₁ or higher (N at C₂, P/A at C₁ or C₂) in core sections dating back to ~1580, suggesting relatively constant inputs of natural petroleum PAHs.
29. The sediment and 1996 suspended particulate samples from the vicinity of Kamloops and Greater Vancouver have a very consistent parent vs. alkyl PAH composition where parent PAHs dominate, P/A series PAHs are secondary, and only small amounts of alkyl naphthalenes are present. The 1996 suspended particulate sample from Agassiz and the 1987 samples from Greater Vancouver have higher amounts of N series PAHs. The shift in N content in the lower Fraser between 1987 and 1996

could reflect either a change in petroleum composition (as with the hopane and sterane results) or a reduction in the discharge of lower molecular weight hydrocarbons into the river.

30. Alkyl PAH concentrations in effluent suspended solids are much higher than parent PAH concentrations at three out of the four GVRD WWTPs, with the Iona plant having the highest alkyl PAH concentrations. Primary-treated effluent suspended particulate samples from Iona, Lulu and Lion's Gate WWTPs have a dominance of alkyl N plus only small amounts of parent PAHs, while the secondary-treated effluent samples from Annacis Island WWTP contain parent and P/A PAHs with only small amounts of alkyl Ns. At GVRD WWTPs surveyed influent (water plus solids) contains even higher proportions of the alkyl Ns than in the effluent particulate, hence, selective removal of the smaller ring size alkyl PAHs during secondary treatment is the most likely explanation for the difference in composition of the Annacis particulate.
31. Like retene (Figure 6d), concentrations of the methylated tetra- and octahydrochrysenes (THC and OHC, respectively) and tetrahydropicenes (THP) are generally higher near Greater Vancouver. However, large increases or concentration "spikes" do not occur simultaneously for the simonellite + retene sum and the hydrochrysenes and hydropicenes and concentrations of the two groups generally do not covary. Nevertheless, the PAHs that exhibit the largest concentration increases in urban regions for both sediment and suspended particulate samples are the parent and alkyl PAHs. In more remote regions other factors such as the amount of forest cover and the timing of forest disturbance by logging in each area will be important controls on the proportion of higher plant PAHs in suspended particulate and sediment samples.
32. In urbanised locations, where PAH concentrations are elevated in both suspended particulate and sediment samples, the anthracene (An)/178 and fluoranthene to fluoranthene plus pyrene (Fl/Fl + Py) ratios are almost all over 0.10 and 0.50, respectively, the benz[*a*]anthracene (BaA)/228 ratio is usually greater than 0.35 and the indeno[1,2,3-*cd*]pyrene/indeno[1,2,3-*cd*]pyrene plus benzo[*ghi*]perylene (IP/IP + Bghi) ratio is over 0.45. These elevated ratios suggest that combustion is likely the principal PAH source for these samples. Recent sediments deposited in Kamloops Lake and Vancouver Harbour are notable exceptions for urban-influenced locations. Coincident with the input of substantial amounts of petroleum alkanes and PAHs to the Kamloops Lake, PAH ratios decline in most sediment core sections.
33. The consistent elevation of PAH ratios in sediment samples from urban-influenced locations, suggests that ratios of 0.35 and 0.45 for BaA/228 and IP/IP + Bghi, respectively, evidently can accompany An/178 and Fl/Fl + Py ratios of 0.10 and 0.50 as indicators of combustion. However, because most (if not all) environmental samples have mixed PAH sources, it does not necessarily follow that the entire sample is combustion-derived. In addition, because the higher mass PAHs (five and more rings) are present only in trace amounts in refined products such as diesel fuel, the presence of a less volatile fraction than diesel (e.g., coal, coal tar, bitumen) would be necessary to introduce significant amounts of petroleum-derived higher mass PAHs. Hence, a low IP/IP + Bghi ratio may at times indicate a different combustion process, rather than the presence of "petroleum".

34. Samples of effluent suspended particulate from the GVRD WWTPs and sediment from Vancouver Harbour are elevated in anthracene, benz[*a*]anthracene and indeno[1,2,3-*cd*]pyrene but with the exception of Lion's Gate, are generally depleted in fluoranthene. Based on literature values for these PAHs in vehicle emissions, combustion aerosol from vehicles would account for the observed fluoranthene and benz[*a*]anthracene ratios in WWTP effluents, but not the indeno[1,2,3-*cd*]pyrene ratio. Hence, it is likely that the high indeno[1,2,3-*cd*]pyrene ratio is indicating that the major source of higher mass PAHs is not combustion particulate from vehicles, but likely asphalt particles in road runoff.
35. Because the PAH ratio pattern for urban suspended particulate samples from the Fraser River — elevated in anthracene and fluoranthene, but depleted in benz[*a*]anthracene and indeno[1,2,3-*cd*]pyrene — is substantially different than the pattern in the WWTPs effluents, it is unlikely that the Annacis or Lulu Island WWTP discharges are having a major effect on the river PAH budget.
36. Ratio data for An/178, Fl/Fl + Py and BaA/228 suggest that sediments from station A are most similar to Vancouver Harbour, while the Saturna basin is most similar to the Fraser River and (except for An/178) Sturgeon and Roberts Banks. IP/IP + Bghi ratio data also suggest that the Fraser River is directly influencing the Saturna basin, but the linkage between Vancouver Harbour and station A is less evident. In general, locations that are remote from the Fraser River but close to Greater Vancouver (e.g., station A) have the highest PAH ratios, suggesting that urban atmospheric combustion particulate is the main PAH source. Locations that are closer to the mouth of the Fraser River than to urban locations (e.g., station CM2) reflect the river PAH composition, and riverine particulate is likely to be the main PAH source.
37. Some of the highest IP/IP + Bghi and Fl/Fl + Py values are found in samples from the North and South Thompson Rivers and Nicola Lake and Harrison Lake. In contrast, Moose Lake and Chilko Lake (the most isolated B.C. lakes) have high proportions of fluoranthene (Fl/Fl + Py >0.60), but are depleted in indeno[1,2,3-*cd*]pyrene (IP/IP + Bghi consistently <0.45). The higher altitude of Moose Lake and Chilko Lake is most likely to be the determining factor, as alpine areas and high altitude lakes have been shown to be subject to greater amounts of deposition from long range atmospheric transport, while the high indeno[1,2,3-*cd*]pyrene in the southern lakes likely suggests a more local combustion source.
38. A number of the lower concentration, rarely studied, mass 202, 276 and 278 parent PAHs have been quantified as part of this study. The spatial pattern of occurrence for acephenanthrylene, coupled with its presence in pre-industrial sediments, suggests that the primary source for acephenanthrylene in the Fraser basin is wood combustion. The distribution evidence suggests that dibenz[*a,j*]anthracene, dibenz[*a,c/a,h*]anthracene, indeno[7,1,2,3-*cdef*]chrysene and picene are PAHs with natural, likely combustion-related sources in the Fraser basin, while benzo[*b*]chrysene, anthanthrene and pentaphene primarily have an anthropogenic origin.
39. A full suite of mass 278 PAHs (dibenz[*a,j*]anthracene, dibenz[*a,c/a,h*]anthracene, pentaphene, benzo[*b*]chrysene, and picene with the dibenzanthracenes and picene as major constituents) is only

observed in sediment samples from the vicinity of Greater Vancouver and in the Strait of Georgia. A coal or “coal tar” type combustion source is suggested for this profile.

40. Dibenzothiophene to phenanthrene proportions suggest that the mature organic matter or petroleum background of dibenzothiophenes in the Fraser basin is low, and that the elevated DBT proportions at Kamloops, in the Thompson River, Harrison River/Lake, Vancouver vicinity and stations A and CM2 are due to anthropogenic petroleum inputs.
41. Both the C₀ - C₂ dibenzothiophene (DBT) and C₂ DBT proportions indicate that the dibenzothiophene content of the suspended particulate samples is dramatically different from the sediments and exhibits little change with location in the basin. This suggests that the primary source for DBTs in suspended particulates in the Fraser basin is anthropogenic — *via* either atmospheric input or local petroleum input from roads. However, the differences in DBT concentrations and ratios between the suspended particulate and sediment samples also suggest that this anthropogenic DBT input has had little impact on sediments in the less-urbanised areas.
42. The 1996 suspended particulate PAH fluxes in the Fraser River are lowest at McBride on the upper Fraser, and increase substantially downstream of Prince George at Woodpecker and Marguerite (Figure 19). PAH fluxes downstream of Kamloops Lake at Savona are lower than at the South Thompson location upstream of Kamloops, likely due to the combined effects of the settling out of particulate-associated contaminants in Kamloops Lake and a very high suspended solids concentration during sampling at the South Thompson location. The PAH flux at Agassiz — reflecting the combined PAH inputs of the Fraser and Thompson Rivers — is larger than the flux at Woodpecker and Marguerite.
43. The 1996 flux of parent and alkyl PAHs increases dramatically between Agassiz and New Westminster (the Pattullo bridge), then decreases somewhat after the bifurcation of the river into the North and Main arms (Figure 19). Alkyl PAH fluxes at the Pattullo Bridge are comparable in 1987 and 1996, while the flux of parent PAHs is higher in 1987.
44. Effluent suspended particulate fluxes of parent and alkyl PAHs are substantially below the river flux for three of the four GVRD WWTPs surveyed. For the Iona WWTP, however, mean alkyl PAH fluxes are equivalent to the flux at the Pattullo Bridge, while parent PAH fluxes are only one-fifth of flux at the Pattullo Bridge. Annacis Island WWTP PAH fluxes are even lower than for the Lulu and Lion’s Gate WWTPs, even though both the Annacis and Iona plants receive stormwater inputs. The secondary treatment used at the Annacis WWTP is the likely cause of the low PAH fluxes.
45. The PAH composition data for Annacis Island WWTP and the fluxes shown in Table 11 are somewhat misleading, however, because only about 44% of the flow was receiving secondary treatment during the 1997 sampling. Nevertheless, because the particulate sample collected 100 m below the Annacis outfall contains substantial amounts of plant PAHs and has a higher proportion of parent PAHs than the particulate sample collected upstream at the Pattullo Bridge, it is likely that the effluent has not had a major effect on the PAH composition at this site.

46. The flux calculations given in Table 11 suggest that in late fall the Iona WWTP delivers a point source loading of petroleum PAHs (average of 0.71 kg/day) that is comparable to the Fraser River before the bifurcation (0.74 kg/day; Figure 19). Late fall is both the low flow period for the Fraser River and a time of typically heavy rainfall on the B.C. coast. Hence, petroleum inputs could be making their highest relative contribution to either the river or the outfall at this time, with the result that the alkyl PAH concentrations and fluxes indicated could be unrepresentative of annual loadings.
47. The suspended particulate carbon content of the Iona effluent (26-33%) is much higher than the carbon content of either the river particulate (0.72-0.87%; Table 1 and Table 11) or sediments from the Strait of Georgia (1.37-1.73%; Table 2). Sediments in the Strait of Georgia also are depleted in petroleum components (alkanes and some PAHs) and other volatile and biodegradable compounds, relative to suspended particulate material from the Fraser River and the WWTPs (see Section 8). This “ephemeral” material includes compounds such as the petroleum PAHs that are present in high concentrations in the WWTP discharge, but which are apparently biodegraded or volatilized in the water column or at the sediment-water interface.
48. While these data suggest that dispersal, and likely biodegradation, substantially reduces the actual carbon and PAH loadings to sediments of the strait, further study would be required to establish what happens to these contaminants between the discharge pipe and the sediments. Here the key question is which components are degraded or volatilized quickly in seawater, and which are persistent enough to be available for ingestion by epibenthic and benthic organisms?

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14. Tables and Figures

Table 1. Carbon and particle size percentages (mean \pm SD) and ranges for suspended particulate samples.

Geographic Region (Location)	Sites/ Times ¹	Organic Carbon %	% Sand (0.062-2 mm)	% Silt (0.004-0.062 mm)	% Clay (< 0.004 mm)
Upper Fraser R. (McBride)	1	0.66	1.5	86	13
Prince George (Shelley)	4	1.28 \pm 0.68 0.57-1.92	7.2 \pm 1.0 5.8-8.2	79 \pm 3.9 74-82	14 \pm 3.6 9.8-18
Prince George–Quesnel (Woodpecker)	4	1.69 \pm 1.42 0.56-3.59	21 \pm 32 0.0-67	65 \pm 23 30-81	14 \pm 9.1 2.2-24
Quesnel–Lytton (Marguerite)	5	2.02 \pm 0.95 0.98-3.34	5.1 \pm 8.6 0.0-20	78 \pm 3.6 72-82	15 \pm 6.1 7.4-22
North Thompson (McLure)	3	2.50 \pm 1.13 1.39-3.64	16 \pm 6.1 10-22	80 \pm 5.5 75-85	3.6 \pm 0.7 3.2-4.5
South Thompson	1	0.90	0.0	92	8.1
Thompson R. (Savona)	4	6.72 \pm 8.02 1.43-18.5	2.7 \pm 4.2 0.0-8.8	83 \pm 3.9 77.7-87.0	14 \pm 6.1 7.5-22.3
Lytton–Chilliwack (Yale and Agassiz)	5	1.30 \pm 0.66 0.69-2.29	6.2 \pm 4.9 1.4-12	77 \pm 3.2 74-82	17 \pm 3.3 14-22
Fraser and North Arm (Pattullo and North Arm)	5	0.90 ² 0.72-1.13	0.0 0.0-0.0	76.5 76-77	23.5 23-24
Fraser Main Arm (Annacis and Steveston)	4	0.87 ²	2.3	77	21
WWTP Effluent (Annacis, Iona, Lions Gate and Lulu Island)	16	31 \pm 3.0 26-36	-	-	-

¹ The number given is the total number of locations and times sampled in each geographic region. Replicates and field splits have been averaged before calculation of regional averages.

² Carbon data are only available for the single 1987 suspended particulate sample obtained by centrifuge.

Table 2. Carbon and particle size percentages (mean \pm SD) and ranges for sediment samples.

Geographic Region (Lake Core Locations)	Sites/ (Cores) ¹	Organic Carbon %	% Sand (0.062-2 mm)	% Silt (0.004-0.062 mm)	% Clay (< 0.004 mm)
Upper Fraser R. (Moose L.)	8 (2)	0.49 \pm 0.15 0.29-0.94	54 \pm 17 35-79	45 \pm 16 21-62	1.4 \pm 1.5 0.0-2.9
Nechako/Stuart R. (Stuart L.)	12 (2)	1.10 \pm 0.95 0.25-3.23	55 \pm 18 26-73	43 \pm 17 25-72	1.8 \pm 1.3 0.0-4.1
Prince George	6	0.84 \pm 0.72 0.47-2.31	41 \pm 17 22-57	57 \pm 15 42-74	2.8 \pm 1.7 1.0-4.6
Prince George–Quesnel	4	0.44 \pm 0.08 0.35-0.53	37 \pm 17 27-62	59 \pm 15 37-68	3.8 \pm 1.7 1.3-4.8
Quesnel–Lytton	8	0.50 \pm 0.13 0.35-0.66	40 \pm 11 24-60	57 \pm 11 39-73	4.0 \pm 1.2 1.4-5.0
Quesnel/Chilcotin R. (Chilko L.)	6 (2)	0.69 \pm 0.41 0.29-1.25	40 \pm 9 28-48	55 \pm 7 49-66	4.6 \pm 2.0 2.8-7
North Thompson	8	0.50 \pm 0.30 0.14-0.88	74 \pm 14 56-99	25 \pm 14 1.4-44	0.6 \pm 0.6 0.0-1.4
South Thompson	6	0.60 \pm 0.27 0.25-0.98	53 \pm 21 29-79	46 \pm 21 19-70	0.8 \pm 0.7 0.0-1.7
Kamloops	9	0.59 \pm 0.40 0.07-1.20	54 \pm 15 25-76	45 \pm 15 23-74	1.0 \pm 0.6 0.0-1.5
Thompson R. (Kamloops L.)	4 (2)	1.29 \pm 0.58 0.46-1.93	55 \pm 4.0 52-57	43 \pm 2.6 41-45	2.2 \pm 1.3 1.2-3.1
Nicola (Nicola L.)	1 (1)	3.76 \pm 0.62 2.83-4.58	- -	- -	- -
Harrison (Harrison L.)	3 (1)	1.23 \pm 0.68 0.60-1.99	55	45	0.0
Lytton–Chilliwack	12	0.48 \pm 0.22 0.16-0.83	62 \pm 19 41.6-92	36 \pm 17 7.9-54	1.9 \pm 1.8 0.0-4.6
Fraser Main Stem and North Arm (McDonald Slough)	13 (1)	1.09 \pm 0.47 0.54-2.20	10 \pm 11 0.0-27	82 \pm 8.6 69-91	8.2 \pm 2.8 3.5-14
Fraser Main Arm (Gunn Is.)	5 (1)	0.77 \pm 0.28 0.40-1.15	18 \pm 21 0.0-38	73 \pm 19 57-92	8.8 \pm 3.9 5.0-14
Pre-1988 Iona Outfall (Iona)	1 (1)	0.68 \pm 0.25 0.39-0.86	Clay (Gordon, 1997)		
Vancouver Harbour (Centre, Port Moody)	2 (2)	2.98 \pm 1.60 1.22-4.38	-		
Sturgeon and Roberts Banks	5 (2)	0.30 \pm 0.23 0.10-0.73	Variable from medium sand to silt or clay (Gordon, 1997)		
Station A (core)	1 (1)	1.61 \pm 0.10 1.39-1.73	Silt (Pharo and Barnes, 1976)		
Station CM2 (core) Saturna Basin	1 (1)	1.48 \pm 0.13 1.37-1.63	Muddy sand (Pharo and Barnes, 1976)		

¹ The number of locations/times sampled in each geographic region with the number of core samples shown in brackets. Replicates, field splits and upper sections of cores (representing approximately the last 20 years of deposition) have been averaged before calculation of regional averages.

Table 3. PAH parameters and abbreviations.

Compound	Molecular Mass	Abbreviation	Σ 178-278 PAH	Compound	Abbreviation
<i>Parent PAHs</i>				<i>Higher Plant PAHs</i>	
Naphthalene	128	Na		Cadalene (4-isopropyl-1,6-dimethylnaphthalene)	Cd
Acenaphthylene	152	Ayl		Simonellite (1,1-dimethyl-1,2,3,4-tetrahydro-7-isopropyl phenanthrene)	Sim
Acenaphthene	154	Aen		Retene (1-methyl-7-isopropylphenanthrene)	Ret
Fluorene	166	F		3,3,7,12a-Tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene	gOH
Phenanthrene	178	Pn	✓	3,4,7,12a-Tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene	vOH
Anthracene	178	An	✓	Tetramethyl octahydrochrysene isomer	oOH
Fluoranthene	202	Fl	✓	1-Methylisopropyl-7,8-cyclopentenophenanthrene	iPrP
Acephenanthrylene	202	ApA		3,4,7-Trimethyl-1,2,3,4-tetrahydrochrysene	vTC
Pyrene	202	Py	✓	3,3,7-Trimethyl-1,2,3,4-tetrahydrochrysene	gTC
Benz[a]anthracene	228	BaA	✓	1,2,9-Trimethyl-1,2,3,4-tetrahydropicene	vTP
Chrysene/triphenylene	228	Ch	✓	2,2,9-Trimethyl-1,2,3,4-tetrahydropicene	gTP
Benzo[b/j/k]fluoranthene	252	BF	✓	<i>Alkyl PAHs</i> ¹	
Benzo[e]pyrene	252	BeP	✓	C ₁ -C ₄ Naphthalenes	N1-N4
Benzo[a]pyrene	252	BaP	✓	C ₁ -C ₂ Dibenzothiophenes	D1, D2
Perylene	252	Per		C ₁ -C ₃ Phenanthrene/anthracenes	P1-P3
Dibenz[a,j]anthracene	278	DjA		C ₁ -C ₃ Fluoranthene/pyrenes	F1-F3
Dibenz[a,c/a,h]anthracene	278	DhA	✓		
Pentaphene	278	Pt			
Benzo[b]chrysene	278	BbC			
Picene	278	Pi			
Indeno[7,1,2,3-cdef]chrysene	276	IC			
Indeno[1,2,3-cd]pyrene	276	IP	✓		
Benzo[ghi]perylene	276	Bghi	✓		
Anthanthrene	276	AA			
Dibenzothiophene	184	DBT			

¹ Alkyl substituted naphthalenes, phenanthrene/anthracenes, dibenzothiophenes and fluoranthene/pyrenes with 1 to 4 alkyl carbons.

Table 4. Relative stability calculation results for parent PAH isomers.

Compound	AM1 Calculation		PCMODEL Calculation		
	AM1 (H _f)	H _f Difference kcal/mole	PCM (H _f)	H _f Difference kcal/mole	PCM-SE
<i>Mass 178</i>					
Phenanthrene	57.13	0	49.7	0	29.3
Anthracene	62.61	5.48	56.1	6.4	26.6
<i>Mass 202</i>					
Pyrene	67.00	0	57.8	0	34.1
Fluoranthene	87.58	20.58	71.0	13.2	45.9
Acephenanthrylene	95.55	28.55	77.6	19.8	45.5
<i>Mass 228</i>					
Triphenylene	75.10	0	67.8	1.1	46.7
Chrysene	75.82	0.72	66.6	0	41.7
Benz[<i>a</i>]anthracene	77.85	2.75	68.6	2.0	38.4
<i>Mass 252</i>					
Benzo[<i>e</i>]pyrene	83.57	0	73.5	0	50.1
Benzo[<i>a</i>]pyrene	87.09	3.52	76.3	2.8	46.3
Perylene	88.88	5.31	80.0	6.5	49.9
Benzo[<i>b</i>]fluoranthene	102.82	19.25	83.7	10.2	56.6
Benzo[<i>j</i>]fluoranthene	104.65	21.08	86.6	13.1	54.8
Benzo[<i>k</i>]fluoranthene	108.65	25.08	89.7	16.2	57.9
<i>Mass 276</i>					
Benzo[<i>ghi</i>]perylene	90.87	0	77.9	0	54.1
Anthanthrene	98.97	8.10	87.0	9.1	51.1
Indeno[1,2,3- <i>cd</i>]pyrene	115.89	25.02	94.5	16.6	63.7
Indeno[7,1,2,3- <i>cdef</i>]chrysene	131.15	40.28	104.1	26.2	74.1
<i>Mass 278</i>					
Dibenz[<i>a,h</i>]anthracene	93.72	0	81.9	0	50.1
Picene	93.87	0.15	82.8	0.9	54.1
Dibenz[<i>a,j</i>]anthracene	93.91	0.19	82.3	0.4	50.4
Dibenz[<i>a,c</i>]anthracene	95.09	1.37	86.2	4.3	56.1
Benzo[<i>b</i>]chrysene	97.22	3.50	86.5	4.6	54.8
Pentaphene	97.88	4.16	86.9	5.0	47.7

Note: H_f denotes Heat of Formation and SE denotes Strain Energy. The H_f difference is the energy difference for each PAH isomer relative to most stable isomer for each mass.

Table 5. Tricyclic terpanes, pentacyclic hopanes, and steranes used for concentration totals.

Terpanes	Steranes and Diasteranes
<i>Tricyclic Terpanes</i>	<i>Steranes</i> ¹
C ₂₃ -Tricyclic terpane	20S-13β(H),17α(H)-Cholestane (diasterane)
C ₂₄ -Tricyclic terpane	20R-13β(H),17α(H)-Cholestane (diasterane)
C ₂₅ -Tricyclic terpane	20S-5α(H),14α(H),17α(H)-Cholestane
C ₂₄ -Tricyclic terpane	20R-5α(H),14β(H),17β(H)-Cholestane (est.)
<i>Diagenetic (Rearranged) Hopanes</i>	24-ethyl-20S-13β(H),17α(H)-Cholestane (diasterane) (est.)
18α(H)-22,29,30-Trisnorneohopane	20S-5α(H),14β(H),17β(H)-Cholestane
17α(H)-22,29,30-Trisnorhopane	20R-5α(H),14α(H),17α(H)-Cholestane
17α(H),21β(H)-30-Norhopane	24-ethyl-20R-13β(H),17α(H)-Cholestane (diasterane)
17β(H),21α(H)-30-Normoretane	24-methyl-20R-5α(H),14α(H),17α(H)-Cholestane
17α(H),21β(H)-Hopane	24-ethyl-20S-5α(H),14α(H),17α(H)-Cholestane
22S and 22R-17α(H),21β(H)-Homohopane	24-ethyl-20R-5α(H),14β(H),17β(H)-Cholestane
22S and 22R-17α(H),21β(H)-Bishomohopane	24-ethyl-20S-5α(H),14β(H),17β(H)-Cholestane
22S and 22R-17α(H),21β(H)-Trishomohopane	24-ethyl-20R-5α(H),14α(H),17α(H)-Cholestane
<i>Biogenic Hopanes</i>	
22,29,30-Trisnorhop-17(21)-ene	
17β(H)-22,29,30-Trisnorhopane	
Neohop-13(18)-ene	
17β(H),21β(H)-30-Norhopane	
17β(H),21β(H)-Hopane	
Diploptene (hop-22(29)-ene)	

¹ These steranes are only a subset of the compounds present, but they are the only major compounds that can be reliably quantified without GC-MS-MS. The abbreviation “est.” indicates that the concentration is an estimate due to co-elution.

Table 6. Alkane concentrations for samples selected for hopane and sterane analysis ¹.

Phase	Date	Location	<i>n</i> -C ₁₃ -C ₂₂ + Isoprenoids	<i>n</i> -C ₂₃ -C ₃₃	Total Alkanes	UCM	Tricyclic Terpanes	Diagenetic Hopanes	Biogenic Hopanes	Steranes
<i>Suspended Particulate</i>						µg/g OC				
Centrifuge	Feb. 1987	Pattullo Bridge	138	374	523	2530	28	20	4.9	49
Filtration	Feb. 1987	Pattullo Bridge	3746	1585	5353	3200	625	139	8.0	577
Filtration	Feb. 1987	Steveston I.	5491	4861	10380	32300	537	182	32	685
Centrifuge	Oct. 1996	McBride	141	3307	3462	0	1.3	6.3	5.2	6.6
Centrifuge	Oct. 1996	Woodpecker	93	221	356	22700	54	36	4.8	57
Centrifuge	Oct. 1996	Marguerite	52	79	218	13700	43	34	6.2	51
Centrifuge	Nov. 1996	South Thompson	92	827	946	0	1.7	6.3	6.0	5.0
Centrifuge	Nov. 1996	Thompson River	148	575	748	14400	32	20	25	27
Centrifuge	Nov. 1996	Agassiz	111	842	992	6780	16	31	10	29
Centrifuge	Nov. 1996	North Arm	167	964	1226	5520	24	45	11	59
Centrifuge	Nov. 1996	Pattullo Bridge	108	714	877	5250	16	20	2.4	29
Centrifuge	Nov. 1996	Annacis Island	154	1050	1309	6700	18	34	5.5	48
<i>Sediment</i>										
0-1 cm	1994	Moose Lake	44	186	231	0	0.4	1.7	25	1.5
0-1 cm	1992	Stuart Lake	62	100	163	0	0.1	3.1	28	2.5
50-55 cm	~1580	Stuart Lake	99	148	249	0	0	3.7	30	0
0-3 cm	1995	Nechako River	60	429	490	0	0.1	1.3	1.2	0.1
0-1 cm	1993	Chilko Lake	42	87	129	0	0	1.1	8.5	0
0-3 cm	1995	Chilcotin River	77	849	928	0	0	2.2	1.4	0.4
0-1 cm	1994	Kamloops Lake	175	230	412	12100	46	25	30	35
5-6 cm	~1985	Kamloops Lake	602	431	1045	12600	94	39	25	161
60-65 cm	~1859	Kamloops Lake	35	132	170	0	0.2	1.0	11	0
0-1 cm	1993	Nicola Lake	231	218	449	0	0.3	3.6	70	0.2
0-1 cm	1993	Harrison Lake	142	276	431	0	1.1	1.8	38	2.2
14-16 cm	~1954	Harrison Lake	39	163	209	0	1.3	4.2	35	7.3
65-70 cm	~1759	Harrison Lake	13	127	147	0	0	0.1	12	0
0-1 cm	-	Station A	49	240	304	1850	25	32	20	51
45-50 cm	-	Station A	73	233	325	512	33	79	96	134

¹ See Table 5 for the list of terpanes, hopanes and steranes.

Table 7. Concentrations (mean \pm SD) and ranges for suspended particulate samples.

Geographic Region (Location) (see Table 1 for n)	Σ 178-278 PAH $\mu\text{g/g OC}$	Perylene $\mu\text{g/g OC}$	Alkyl PAH $\mu\text{g/g OC}$	Retene $\mu\text{g/g OC}$	OHC + THC + THP $\mu\text{g/g OC}$
Upper Fraser R. (McBride)	7.4	3.2	5.4	4.2	11
Prince George (Shelley)	5.8 \pm 3.8 1.9-10	4.4 \pm 2.1 2.0-6.4	-	-	-
Prince George–Quesnel (Woodpecker)	5.7 \pm 4.2 2.3-12	3.3 \pm 2.4 0.5-5.9	20	12	9.8
Quesnel–Lytton (Marguerite)	7.8 \pm 4.5 3.4-15	2.5 \pm 1.5 1.1-4.9	16	12	14
North Thompson (McLure)	5.1 \pm 4.0 2.7-9.8	3.8 \pm 3.5 1.6-7.9	-	-	-
South Thompson	10	5.1	15	5.0	19
Thompson R. (Savona)	7.4 \pm 2.1 5.0-10	3.1 \pm 3.9 0.5-8.7	10	5.9	3.3
Lytton–Chilliwack (Yale and Agassiz)	7.3 \pm 3.1 3.2-12	2.7 \pm 1.9 0.6-5.5	14	7.3	11
Fraser and North Arm (Pattullo and North Arm)	39 \pm 21 17-62	7.5 \pm 4.2 2.2-13	37 \pm 24 13-74	15 \pm 5.7 7.1-22	19 \pm 10 6.5-35
Fraser Main Arm (Annacis and Steveston)	76 \pm 17 57-99	11 \pm 3.6 6.0-15	101 \pm 53 25-143	16 \pm 5.9 10-24	29 \pm 11 12-39
WWTP Effluent (Annacis, Iona, Lions Gate and Lulu Island)	12 \pm 6.4 5.0-26	0.12 \pm 0.07 0.04-0.25	26 \pm 21 3.5-89	0.78 \pm 1.0 0.22-2.3	0.14 \pm 0.12 0.01-0.24

Alkyl PAHs include the C1-C4 naphthalenes, C1-C2 dibenzothiophenes and C1-C3 phenanthrene/anthracenes. Σ 178-278 parent PAHs are defined in Table 3. OHC + THC + THP indicates the sum of the alkylated octahydrochrysenes, tetrahydrochrysenes and tetrahydropicenes listed in Table 3.

Table 8. Concentrations (mean \pm SD) and ranges for sediment samples.

Geographic Region (Lake Core Locations) (see Table 2 for n)	Σ 178-278 PAH $\mu\text{g/g OC}$	Perylene (Surface only) $\mu\text{g/g OC}$	Alkyl PAH $\mu\text{g/g OC}$	Retene $\mu\text{g/g OC}$	OHC + THC + THP $\mu\text{g/g OC}$
Upper Fraser R. (Moose L.)	3.0 \pm 2.4 0.5-9.8	2.2 \pm 1.3 0.7-4.3	1.5 \pm 1.7 0.1-8.4	19 \pm 39 0.6-88	0.9 \pm 0.7 0.04-5.4
Nechako/Stuart R. (Stuart L.)	3.4 \pm 1.8 0.9-6.2	2.6 \pm 1.5 0.6-4.6	5.5 \pm 2.9 1.1-11	3.9 \pm 3.7 0.5-11	7.2 \pm 5.7 0.3-16
Prince George	4.2 \pm 3.1 0.4-9.5	3.9 \pm 2.7 1.0-8.8	3.0 \pm 3.6 0.3-7.1	3.9 \pm 2.6 0.9-5.8	- -
Prince George–Quesnel	3.7 \pm 1.2 2.2-5.0	4.1 \pm 1.3 2.4-5.1	5.7 \pm 3.2 3.4-7.9	7.4 \pm 0.9 6.8-8.0	- -
Quesnel–Lytton	3.3 \pm 1.6 1.5-7.1	4.5 \pm 2.0 2.3-7.4	5.4 \pm 3.1 2.6-9.6	9.8 \pm 9.0 3.4-23	- -
Quesnel/Chilcotin R. (Chilko L.)	5.0 \pm 3.4 1.5-11	1.1 \pm 0.8 0.2-2.5	7.8 \pm 6.6 2.0-15	1.2 \pm 1.3 0.2-2.7	1.9 \pm 2.0 0.3-3.3
North Thompson	3.4 \pm 3.5 1.0-11	1.9 \pm 0.8 0.5-2.8	0.6 \pm 0.4 0.1-1.0	1.8 \pm 1.1 0.1-2.5	- -
South Thompson	6.1 \pm 7.4 1.0-21	2.0 \pm 1.4 0.2-4.5	4.9 \pm 5.6 1.3-11	8.3 \pm 12 0.7-22	- -
Kamloops	33 \pm 33 5.6-109	14 \pm 28 1.4-87	15 \pm 15 3.6-39	14 \pm 14 1.7-31	- -
Thompson R. (Kamloops L.)	7.7 \pm 3.9 2.3-20	1.6 \pm 1.3 0.1-3.3	15 \pm 1.3 0.9-40	2.1 \pm 1.5 0.5-6.0	3.4 \pm 0.6 1.1-5.6
Nicola (Nicola L.)	2.1 \pm 1.1 1.1-3.9	3.7 \pm 0.5 3.1-4.1	1.6 \pm 0.5 0.9-2.1	0.4 \pm 0.1 0.3-0.4	14 \pm 11 4.4-32
Harrison (Harrison L.)	10 \pm 0.8 3.9-26	2.2 \pm 1.2 1.2-3.5	3.0 \pm 1.7 1.5-4.3	1.3 \pm 0.1 0.3-3.5	4.2 \pm 3.1 1.4-9.5
Lytton–Chilliwack	4.8 \pm 2.8 1.7-10	3.0 \pm 2.0 0.9-7.5	4.6 \pm 2.8 2.6-11	6.0 \pm 5.1 2.4-17	- -
Fraser Main Stem and North Arm (McDonald Slough)	39 \pm 23 18-90	5.2 \pm 2.8 2.7-13	26 \pm 20 9.4-89	13 \pm 7.4 3.4-28	15 \pm 3.8 12-18
Fraser Main Arm (Gunn Is.)	12 \pm 5.0 5.8-24	5.0 \pm 1.1 3.6-6.5	9.3 \pm 4.1 5.0-24	3.6 \pm 1.3 1.7-6.3	15 \pm 1.1 14-15
Pre-1988 Iona Outfall (Iona)	112 \pm 111 24-237	7.6 \pm 3.0 4.7-10.8	86 \pm 63 21-148	4.2 \pm 2.0 2.4-6.4	19 \pm 5.8 14-26
Vancouver Harbour (Centre, Port Moody)	131 \pm 27 42-323	3.3 \pm 0.3 2.6-4.3	67 \pm 17 17-184	1.5 \pm 0.6 0.8-3.6	14 \pm 2.1 7.1-20
Sturgeon and Roberts Banks	11.0 \pm 3.1 7.8-19	4.9 \pm 4.6 1.5-13	18 \pm 25 4.6-84	3.0 \pm 1.4 1.5-6.7	6.8 \pm 6.1 1.9-21
Station A (core)	38 \pm 6.7 29-50	6.9 \pm 0.6 5.6-7.9	49 \pm 11 37-76	5.8 \pm 2.0 4.2-10	10 \pm 1.6 8.0-13
Station CM2 (core)	19 \pm 4.2	6.3 \pm 0.3	44 \pm 2.9	2.7 \pm 0.4	9.5 \pm 2.3

Table 9. Baseline PAH concentrations for sediment cores from the Fraser basin lakes and the Strait of Georgia.

Location	Σ 178-278 PAH ng/g	Alkyl PAH ng/g	Retene ng/g	Σ 178-278 PAH ¹ $\mu\text{g/g OC}$	Alkyl PAH ¹ $\mu\text{g/g OC}$	Retene $\mu\text{g/g OC}$
<i>Fraser River Basin</i>						
Moose Lake (~1918 and older)	9.8	4.3	24	1.1	0.49	2.8
Stuart Lake (~1962 and older)	132	297	15	4.1	9.3	0.46
Chilko Lake (~1930 and older)	24	18	4.0	2.5	1.8	0.41
Kamloops Lake (~1893 and older)	29	7.6	6.1	1.5	0.40	0.32
Nicola Lake (~1871 and older)	34	44	12	0.78	1.0	0.27
Harrison Lake (~1835 and older)	7.2	2.9	5.7	0.61	0.25	0.48
Mean (excluding Stuart Lake for the Σ 178-278 and Alkyl PAH, and Moose Lake for retene)	21	15	8.6	1.3	0.79	0.39
<i>Strait of Georgia</i>						
Station A	630	720	85	38	44	5.1
Station CM2	240	610	40	18	45	2.9

¹ Surface carbon concentrations have been used for the calculation of $\mu\text{g/g OC}$ concentrations.

Table 10. Numbers of sediment samples in each geographic region and their concentration ranges for samples that exceed either B.C. provincial or interim federal sediment quality guidelines for the protection of aquatic life.

Geographic Region	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene
B.C. Freshwater (ng/g)	10		150	200	40	600	2000
B.C. Marine (ng/g)	10		150	200			
Canada Freshwater (ng/g)	34.6	5.87	6.71	21.2	41.9	46.9	111
Canada Marine (ng/g)	34.6	5.87	6.71	21.2	86.7	46.9	113
Number of samples over the guideline (concentration range in ng/g)							
Upper Fraser R.	2 (4.0-13)						
Nechako/Stuart R.	2 (3.0-6.8)				2 (47-48)		
Prince George							
Prince George–Quesnel							
Quesnel–Lytton	1 (22)						
Quesnel/Chilcotin R.	3 (5.4-9.0)						
North Thompson	3(1.8-3.6)						
South Thompson							
Kamloops	3 (2.0-6.0)				2 (5.4-38)		
Thompson R.	10 (6.1-74)	6 (7.7-33)			5 (48-76)		
Nicola	3 (40-52)	7 (6.0-14)					
Harrison							
Lytton–Chilliwack	5 (2.7-18)						
Fraser Main Stem and North Arm	8 (7.8-23)	1 (6.6)	5 (8.0-17)	3 (22-30)	8 (33-93)		3 (130-170)
Fraser Main Arm	2 (4.0-12)						
Pre-1988 Iona Outfall	3 (8.0-22)	2 (7.0-15)					2 (120-140)
Vancouver Harbour	7 (26-290)	7 (7.2-100)	8 (8.0-62)	6 (22-110)	7 (110-550)	5 (110-180)	8 (140-730)
Sturgeon and Roberts Banks	5 (1.5-12)						
Station A	13 (35-60)	6 (7.0-10)	3 (7.0-13)	1 (24)	2 (92-100)		2 (120-120)
Station CM2	4 (14-18)						

Sediment PAH guidelines are from Canadian Council of the Ministers of the Environment (1998) and British Columbia Ministry of Environment, Lands and Parks (2000). See notes following table.

Table 10 continued.

Geographic Region	Pyrene	Benz[<i>a</i>]anthracene	Chrysene	Benzo[<i>a</i>]pyrene	Dibenz[<i>a,c/a,h</i>]-anthracene	C ₁ Naphthalenes
B.C. Freshwater (ng/g)		200		60		
B.C. Marine (ng/g)			200	60		
Canada Freshwater (ng/g)	53	31.7	57.1	31.9	6.22	20.2
Canada Marine (ng/g)	153	74.8	108	88.8	6.22	20.2
Number of samples over the guideline (concentration range in ng/g)						
Upper Fraser R.						
Nechako/Stuart R.						
Prince George						
Prince George–Quesnel						
Quesnel–Lytton						
Quesnel/Chilcotin R.						
North Thompson						
South Thompson						
Kamloops	2 (68-71)	1 (34)	1 (59)	2 (32-35)		
Thompson R.	2 (54-77)					1 (53)
Nicola						
Harrison						
Lytton–Chilliwack						
Fraser Main Stem and North Arm	9 (55-140)	6 (35-54)	4 (68-87)	6 (34-51)	3 (6.5-7.6)	
Fraser Main Arm						
Pre-1988 Iona Outfall		1 (87)	1 (96)	1 (89)	1 (9.2)	
Vancouver Harbour	8 (160-1000)	8 (84-330)	7 (110-410)	7 (110-300)	8 (14-54)	5 (110-220)
Sturgeon and Roberts Banks						3 (46-51)
Station A					11 (7.0-10)	13 (54-82)
Station CM2						9 (48-70)

See notes following table.

Notes for Table 10:

1. B.C. freshwater and marine sediment criteria (British Columbia Ministry of Environment Lands and Parks, 2000) are for a sediment organic carbon content of 1%. Before comparisons are made the B.C. criteria are adjusted for the actual sediment carbon content, with the result that PAH concentrations can be below the nominal criteria concentration and still exceed the guideline.

2. Canadian guidelines (Canadian Council of the Ministers of the Environment, 1998) shown for the C₁ naphthalenes are for 2-methylnaphthlene alone. In determining whether the C₁ naphthalenes exceed the guideline it has been assumed that 2-methylnaphthlene and 1-methylnaphthlene each constitute 50% of the C₁ naphthalenes total. Since 2-methylnaphthalene is often the major isomer (e.g., Yunker and Macdonald, 1995), this will likely underestimate the number of samples where concentrations are over the guideline.

Table 11. Comparison of the PAH flux on suspended particulate in the lower Fraser River to effluent suspended particulate in the discharge from the four Greater Vancouver Regional District WWTPs.

Location	Date	Flow m ³ /s	SPM mg/L	TOC %	Parent PAH ng/g dry wt.	Alkyl PAH ng/g dry wt.	Parent PAH kg/day	Alkyl PAH kg/day
Agassiz	21-Nov-96	1700	16.8	0.69	58	93	0.14	0.23
Pattullo Bridge	13-Nov-96	3387	16.3	0.72	220	160	1.03	0.74
Annacis Is.	12-Nov-96	2196	8.8	0.87	520	220	0.87	0.36
North Arm	14-Nov-96	627	20.1	0.85	540	280	0.59	0.31
Iona Primary Effluent	07-Oct-97	5.42	78	32.8	2800	15000	0.10	0.54
	23-Oct-97	5.15	75	26.3	4100	24000	0.14	0.78
	04-Nov-97	7.55	91	30.8	3500	12000	0.21	0.69
	27-Nov-97	8.63	97	32.3	6100	11000	0.44	0.81
Lion's Gate Primary Effluent	09-Oct-97	1.47	51	29.3	3100	6800	0.020	0.044
	21-Oct-97	1.11	54	35.4	3600	7300	0.019	0.038
	06-Nov-97	1.98	66	30.1	3500	7600	0.040	0.086
	25-Nov-97	1.27	52	36.0	2800	7500	0.016	0.043
Annacis Secondary Effluent	14-Oct-97	2.33	8	25.6	5100	7100	0.008	0.011
	30-Oct-97	2.56	7	30.5	7700	1100	0.012	0.002
	18-Nov-97	2.85	17	28.8	1900	1000	0.008	0.004
	04-Dec-97	2.71	12	32.4	2800	1500	0.008	0.004
Lulu Primary Effluent	16-Oct-97	0.80	63	31.1	4500	6700	0.019	0.029
	28-Oct-97	0.80	69	33.5	3200	4500	0.015	0.022
	20-Nov-97	0.80	58	35.4	9600	11000	0.038	0.044
	02-Dec-97	0.78	34	31.6	6900	6200	0.016	0.014

Notes: 1. Effluent parameters are from Bertold and Stock (1999). All suspended particulate concentrations have been calculated directly from the Axys data reports, taking ND (non-detect) values as zero and NDR (non-detect ratio) values as the stated concentration.

2. Parent PAHs include the Σ 178-278 PAH (Table 3) plus naphthalene, acenaphthylene, acenaphthene, and fluorene. Alkyl-substituted PAHs include the C₁-C₄ naphthalenes, C₁-C₃ phenanthrene/anthracenes and C₁-C₂ dibenzothiophenes.

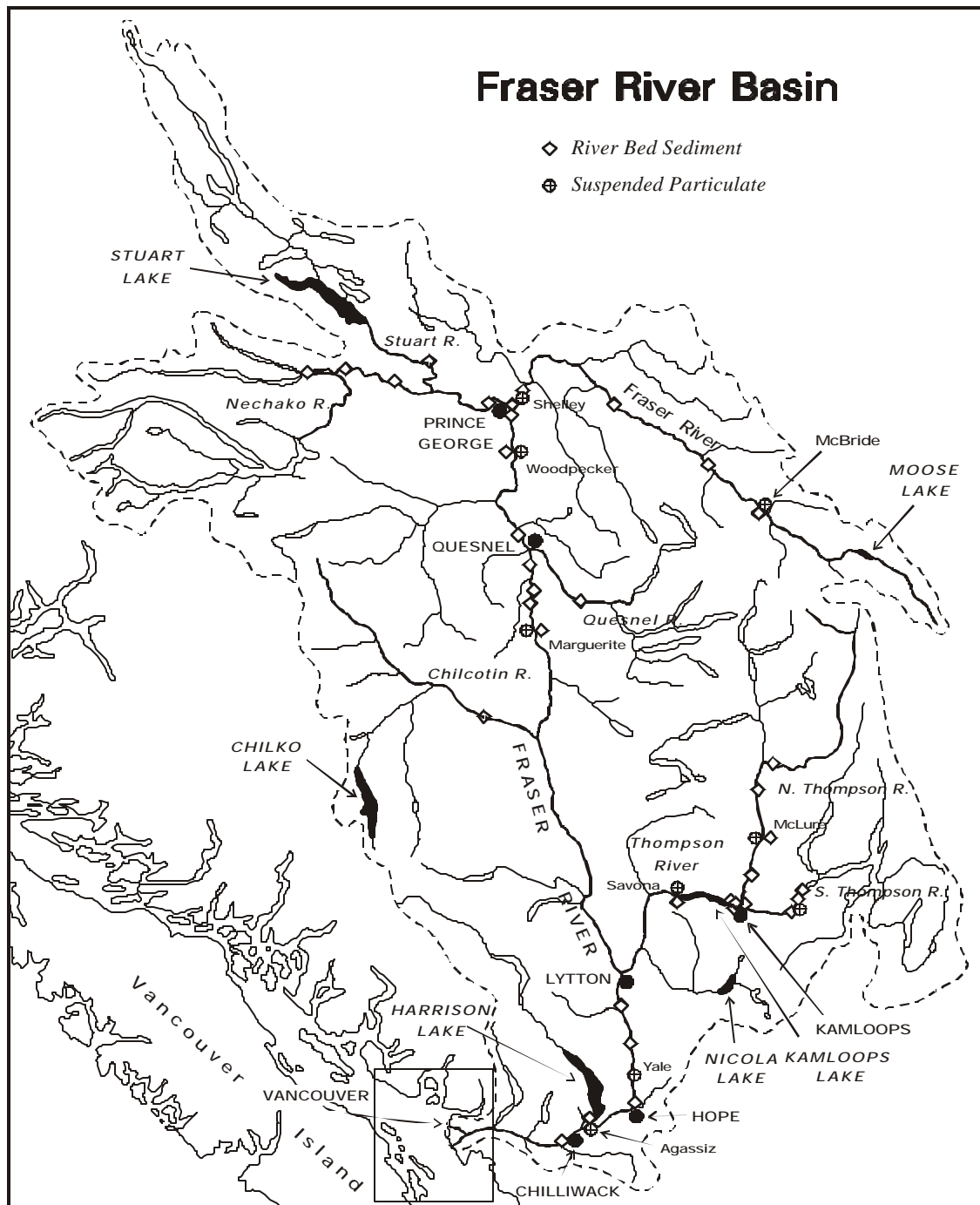


Figure 1. Map of the Fraser River basin showing sample locations on the major tributaries and the locations of the six lakes where sediment cores were obtained.

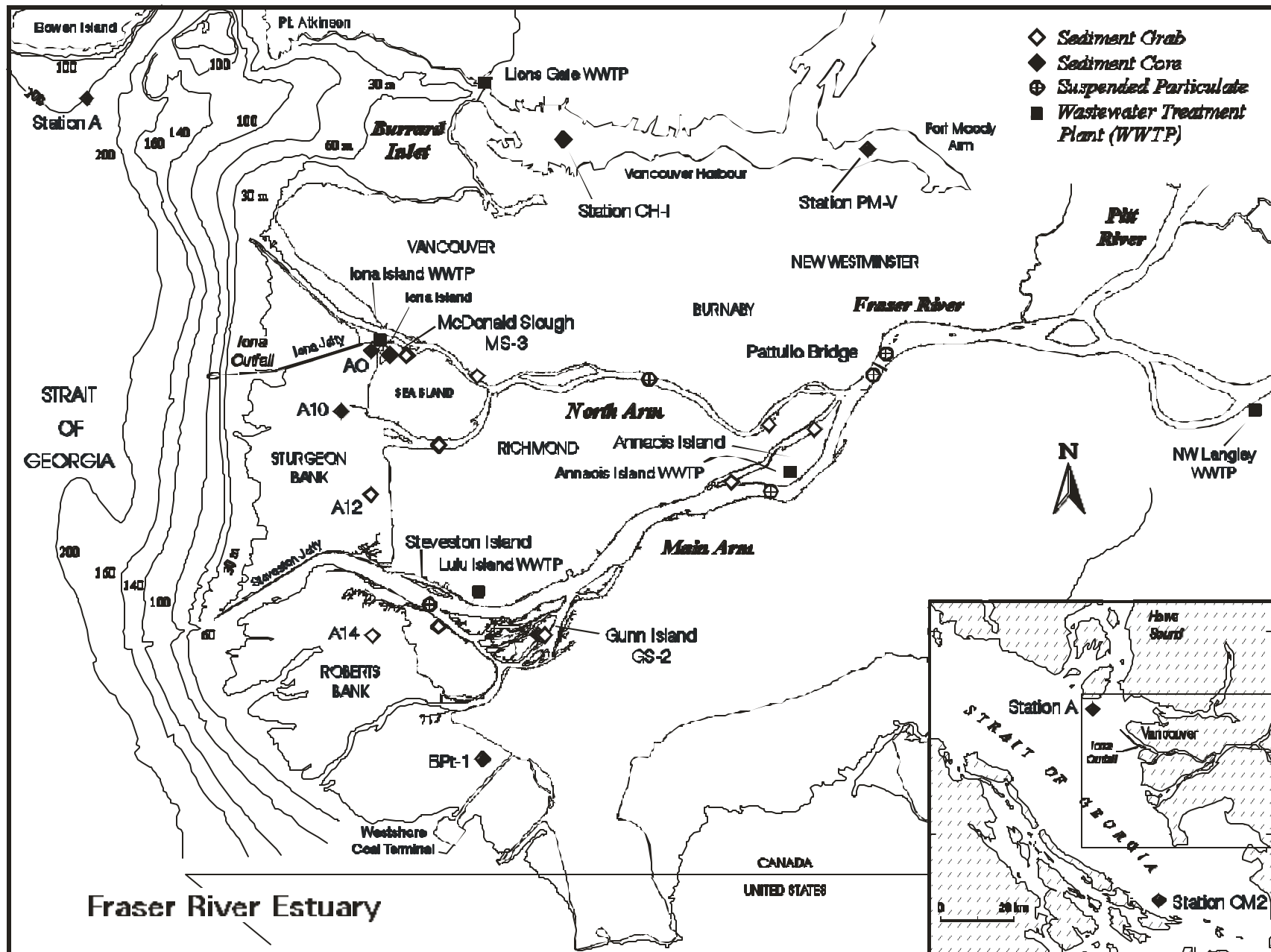


Figure 2. Map of the Fraser River estuary and Strait of Georgia showing sample and WWTP locations.

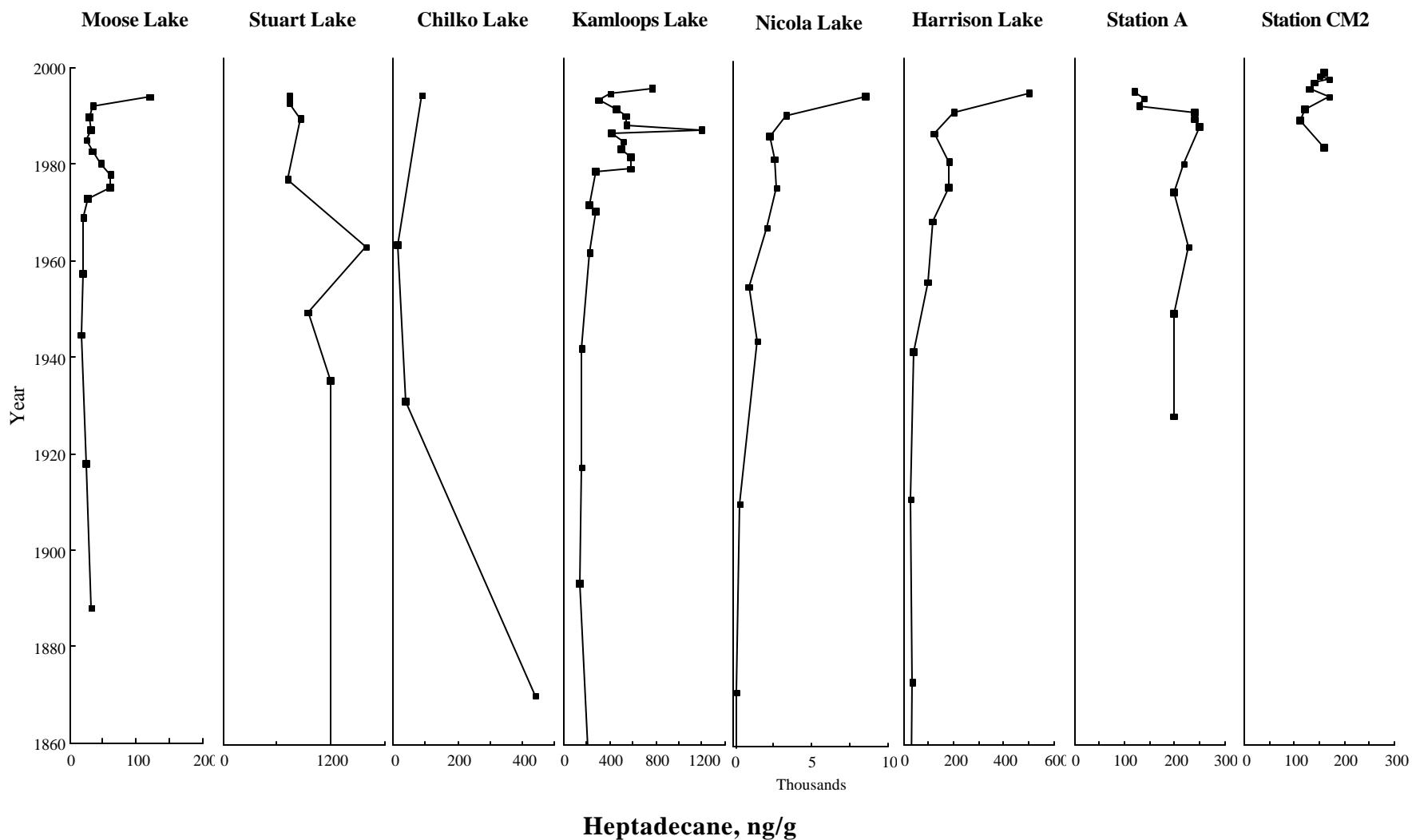


Figure 3. Alkane downcore profiles by ^{210}Pb date for core samples from the six lakes and the Strait of Georgia. Station A and CM2 (Saturna Basin) dates are approximations based on the sedimentation velocity only and do not consider surface mixing. (a). Heptadecane.

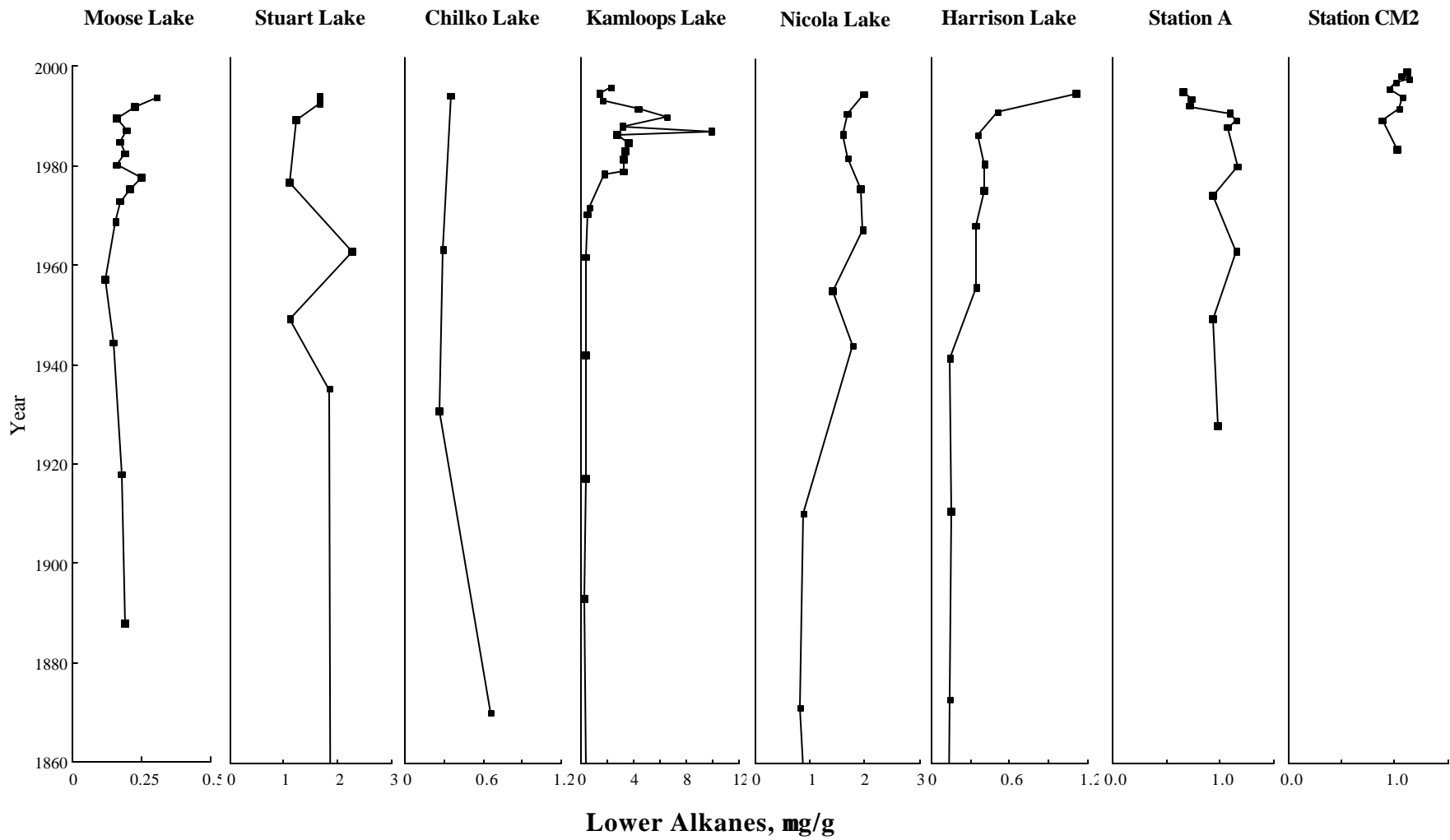


Figure 3 (b). Lower alkanes ($n\text{-C}_{13}\text{-C}_{22}$ plus isoprenoids) minus heptadecane ($n\text{-C}_{17}$).

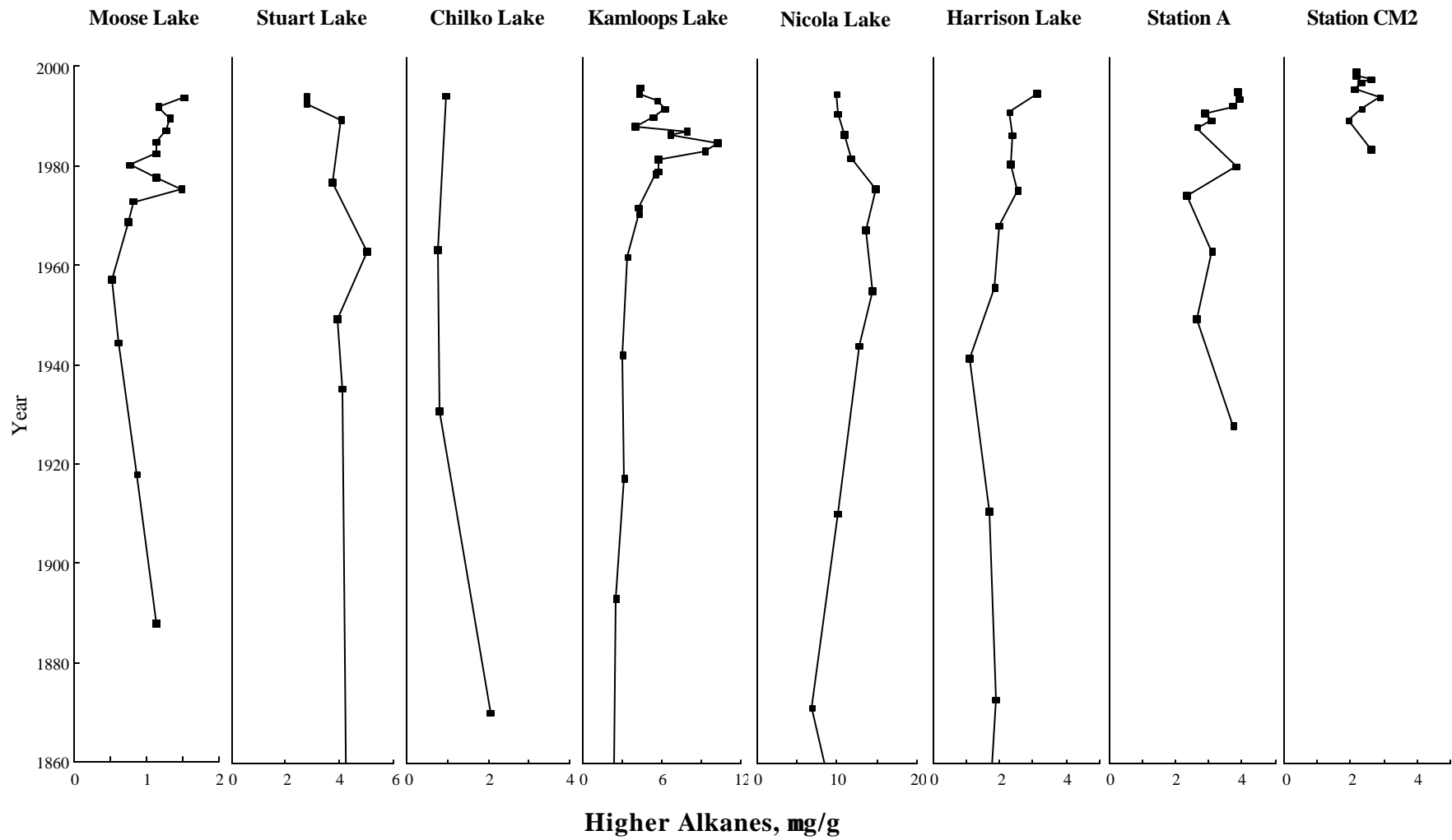


Figure 3 (c). Higher alkanes ($n\text{-C}_{23}\text{-C}_{33}$).

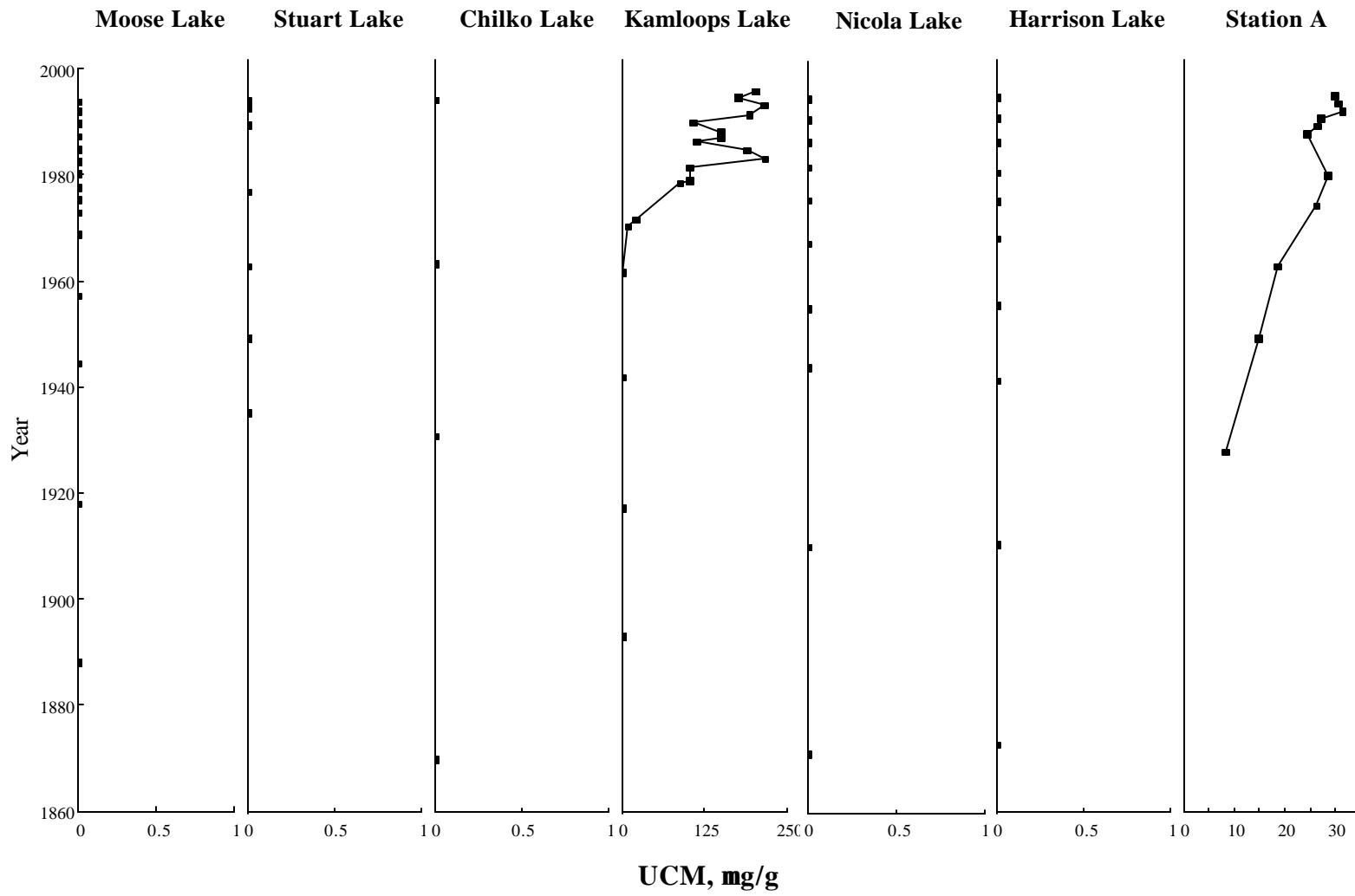


Figure 3 (d). Alkane unresolved complex mixture (UCM).

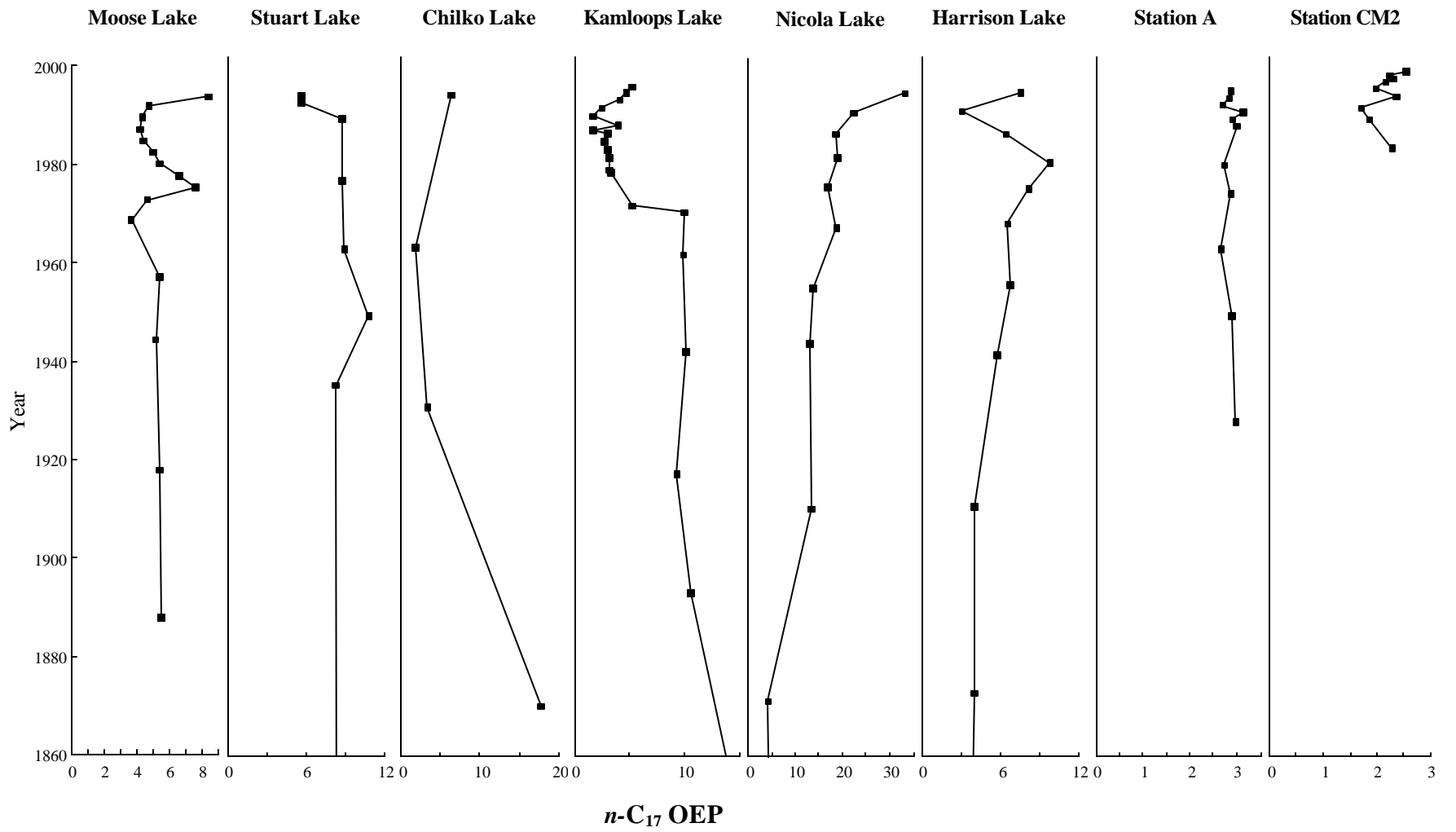


Figure 3 (e). n -C₁₇ odd-even predominance $(n\text{-C}_{15} + 6 \times n\text{-C}_{17} + n\text{-C}_{19}) / 4 \times (n\text{-C}_{16} + n\text{-C}_{18})$.

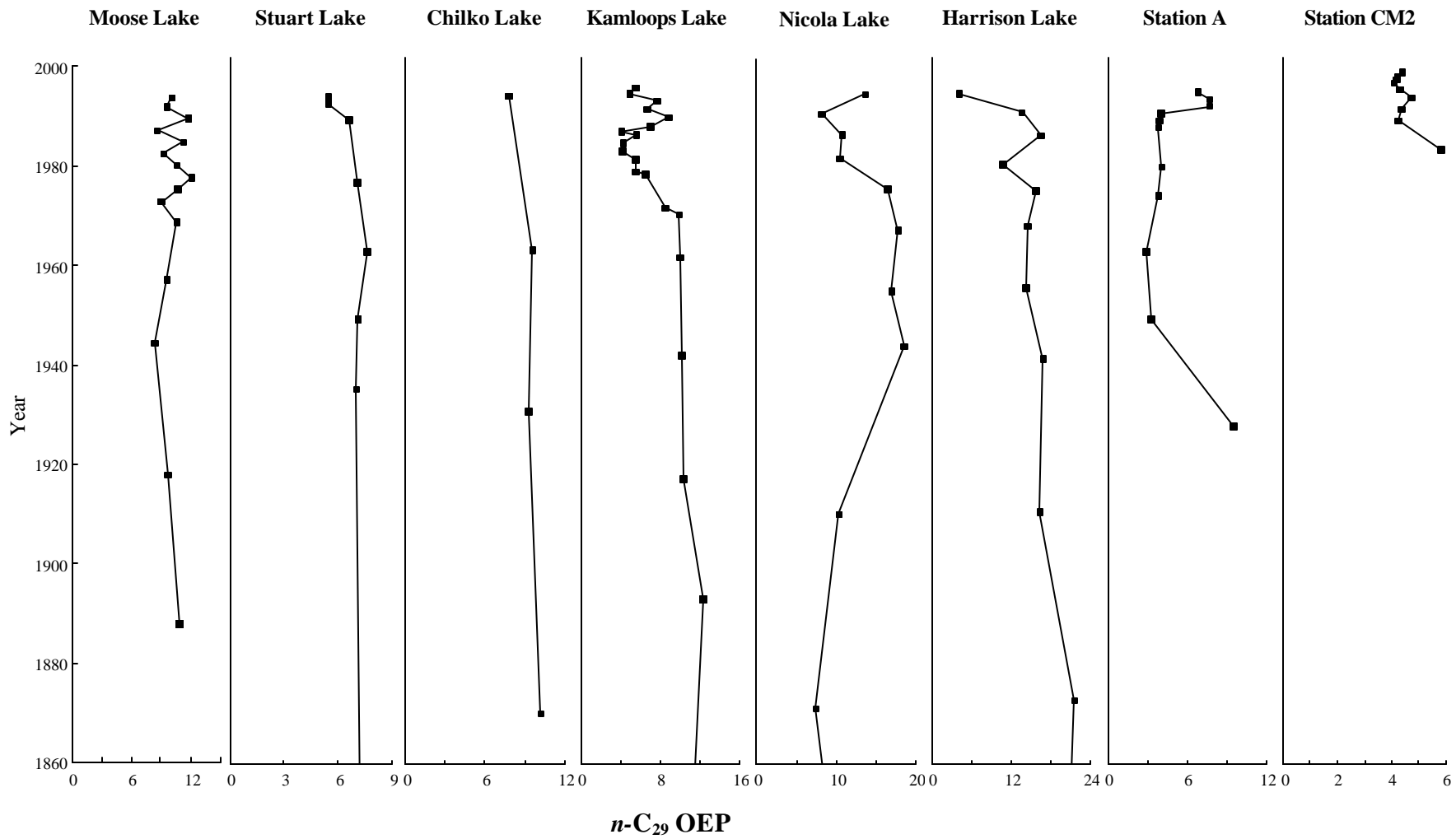


Figure 3 (f). n -C₂₉ odd-even predominance $(n-C_{27} + 6 \times n-C_{29} + n-C_{31}) / 4 \times (n-C_{28} + n-C_{30})$.

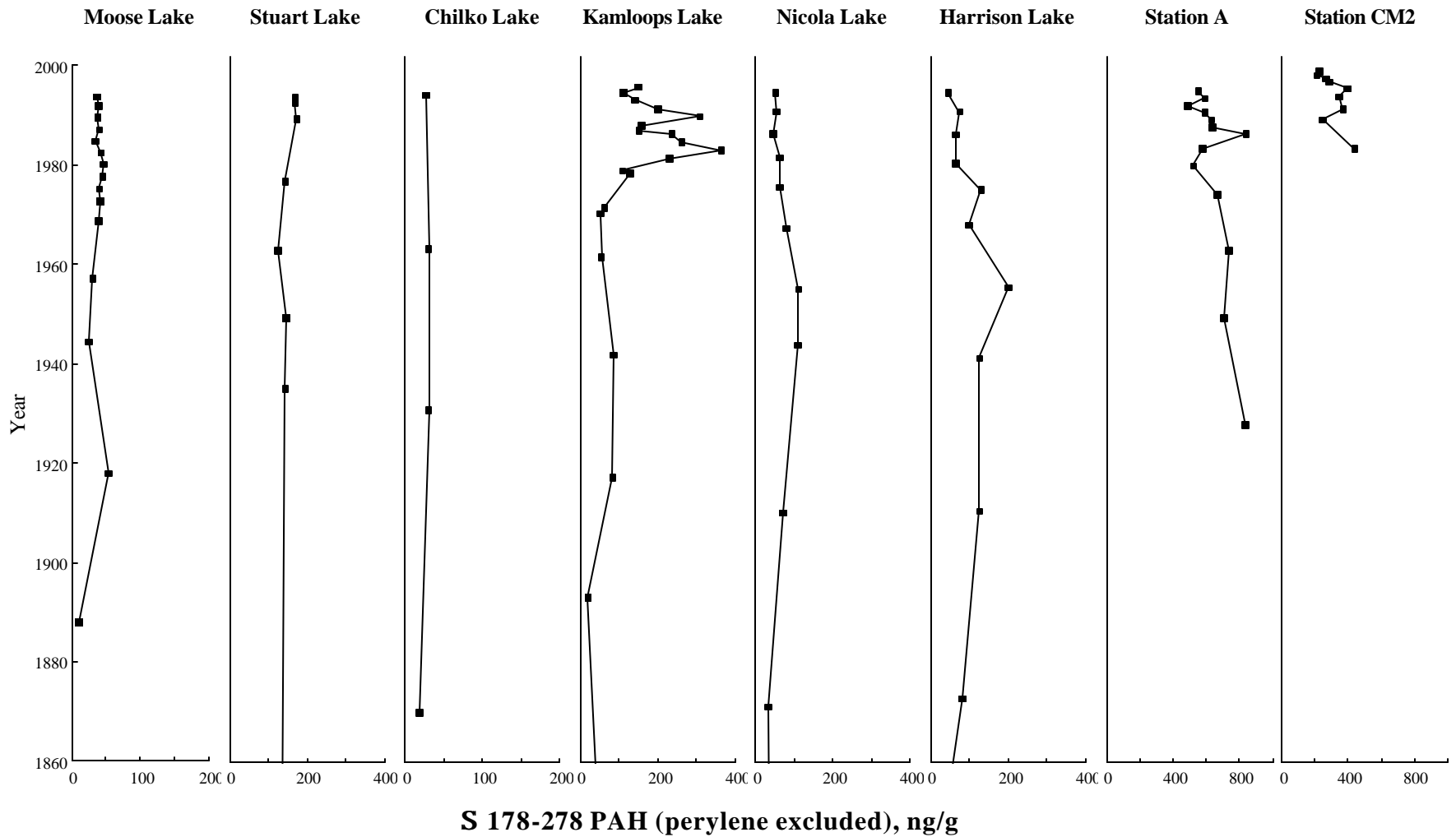


Figure 4. PAH downcore profiles by ^{210}Pb date for core samples from the six lakes and the Strait of Georgia. Station A and CM2 (Saturna Basin) dates are approximations based on the sedimentation velocity only and do not consider surface mixing. (a). Σ 178-278 parent PAHs.

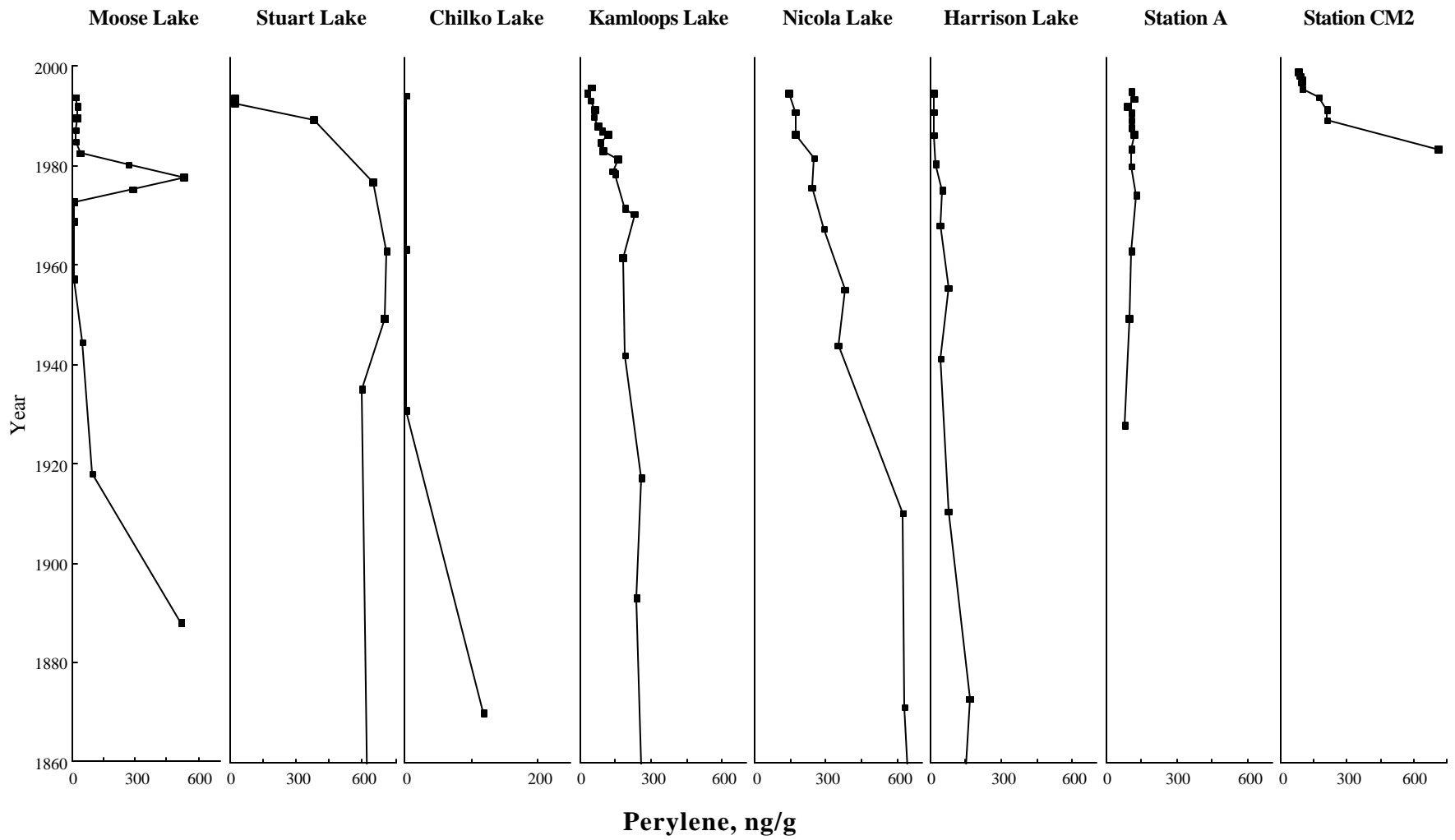


Figure 4. (b). Perylene.

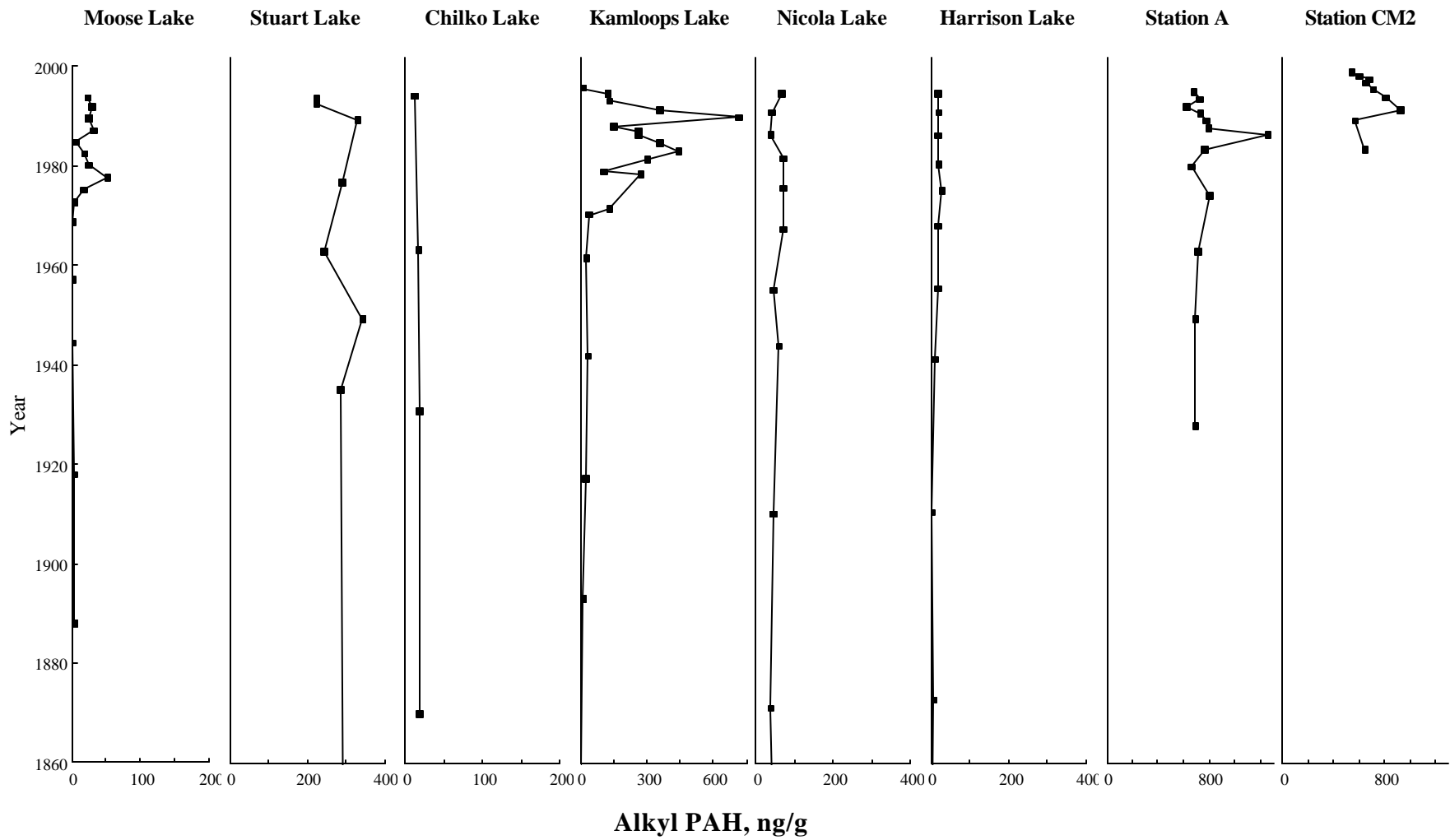


Figure 4. (c). Alkyl PAHs (C_1 - C_4 naphthalenes, C_1 - C_3 phenanthrene/anthracenes and C_1 - C_2 dibenzothiophenes).

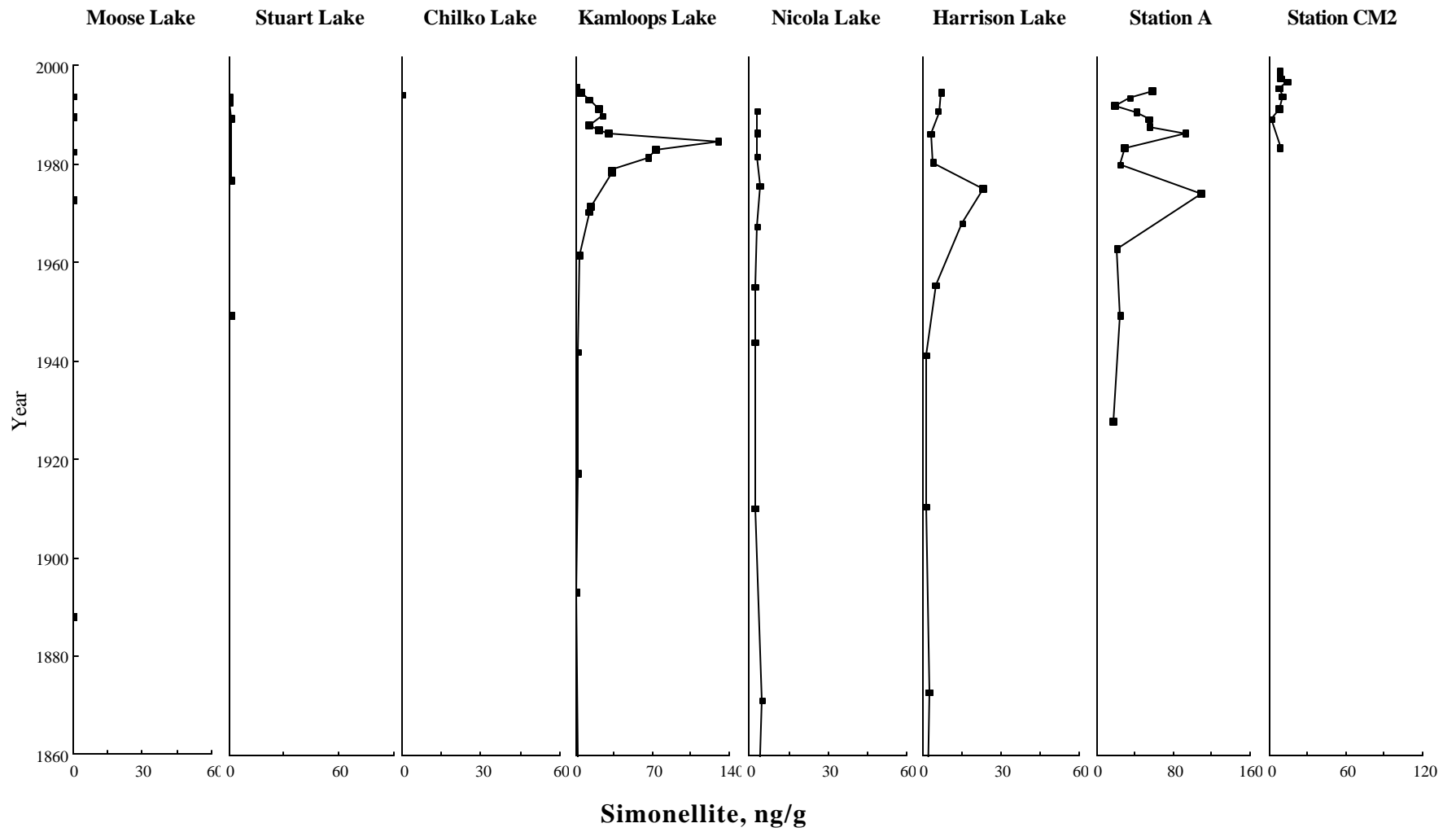


Figure 4. (d). Simonellite.

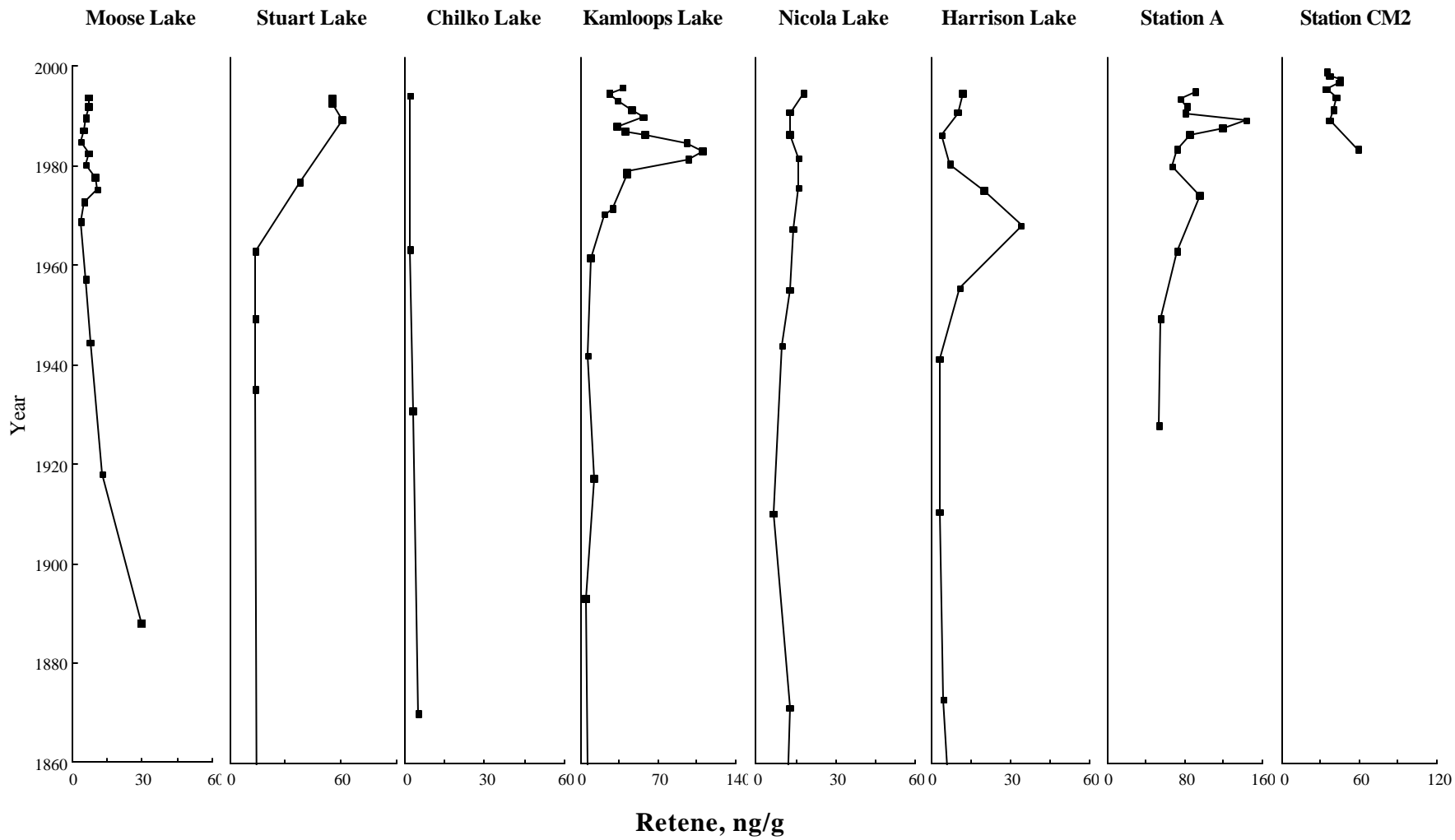


Figure 4. (e). Retene.

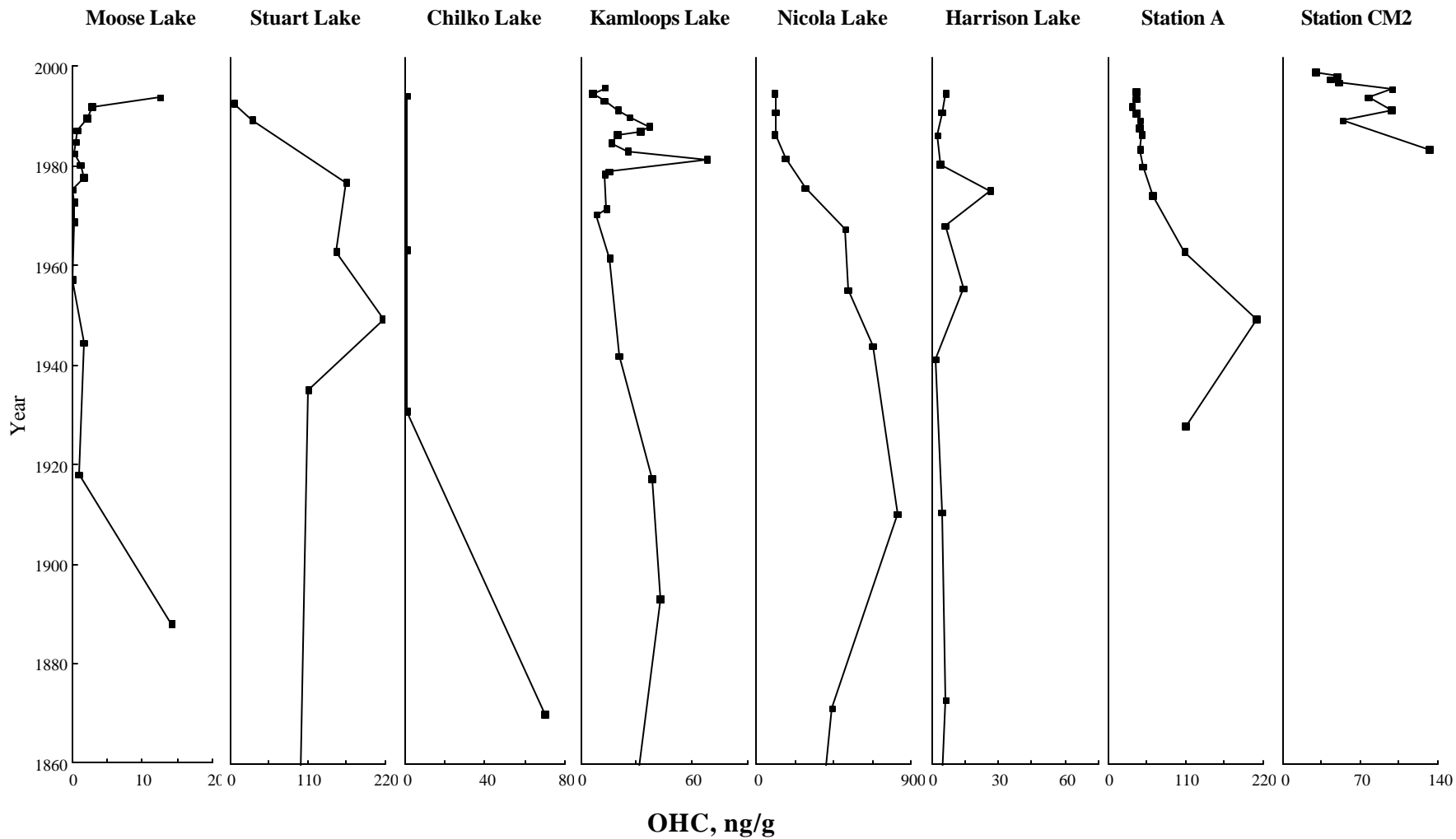


Figure 4. (f). Tetramethyl octahydrochrysenes (OHC; three tetramethyl isomers of 1,2,3,4,4a,11,12,12a-octahydrochrysene; with most likely the 3,3,7,12a- and 3,4,7,12a-isomers, plus one other isomer).

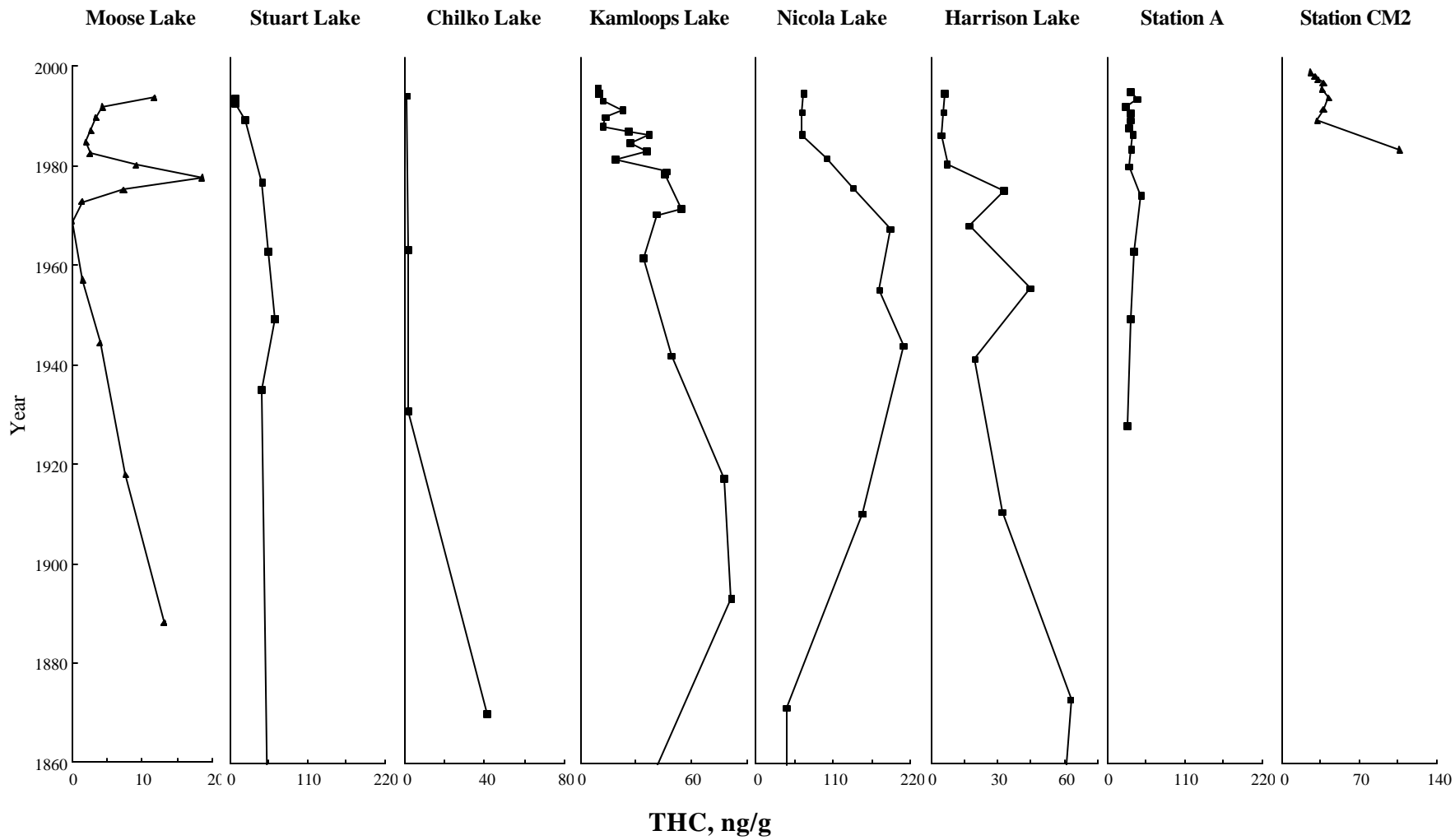


Figure 4. (g). Trimethyl tetrahydrochrysenes (THC; the 3,4,7- and 3,3,7-isomers of 1,2,3,4-tetrahydrochrysenes).

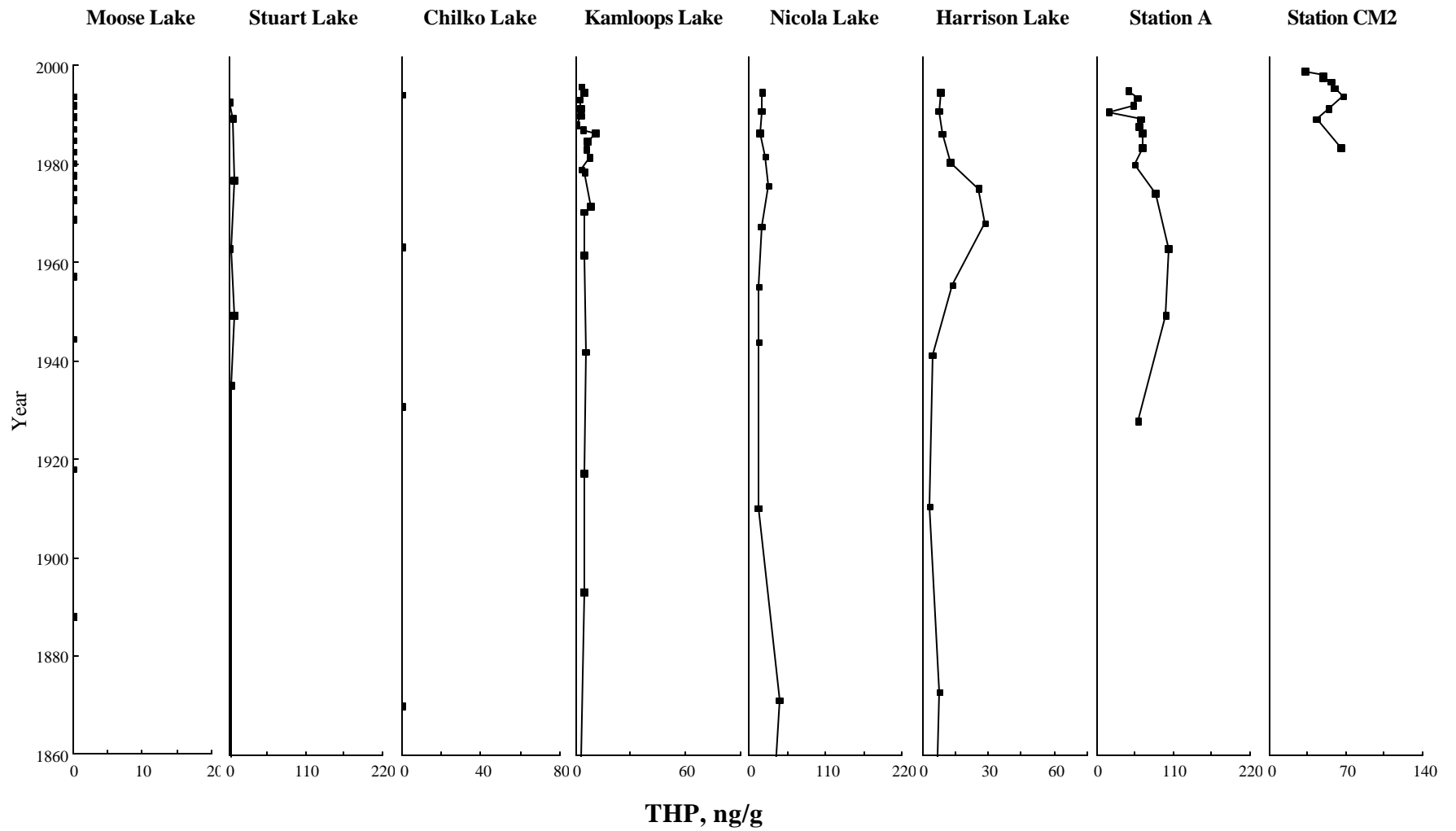


Figure 4. (h). Trimethyl tetrahydropicenes (THP; the 1,2,9- and 2,2,9-isomers of 1,2,3,4-tetrahydropicene).

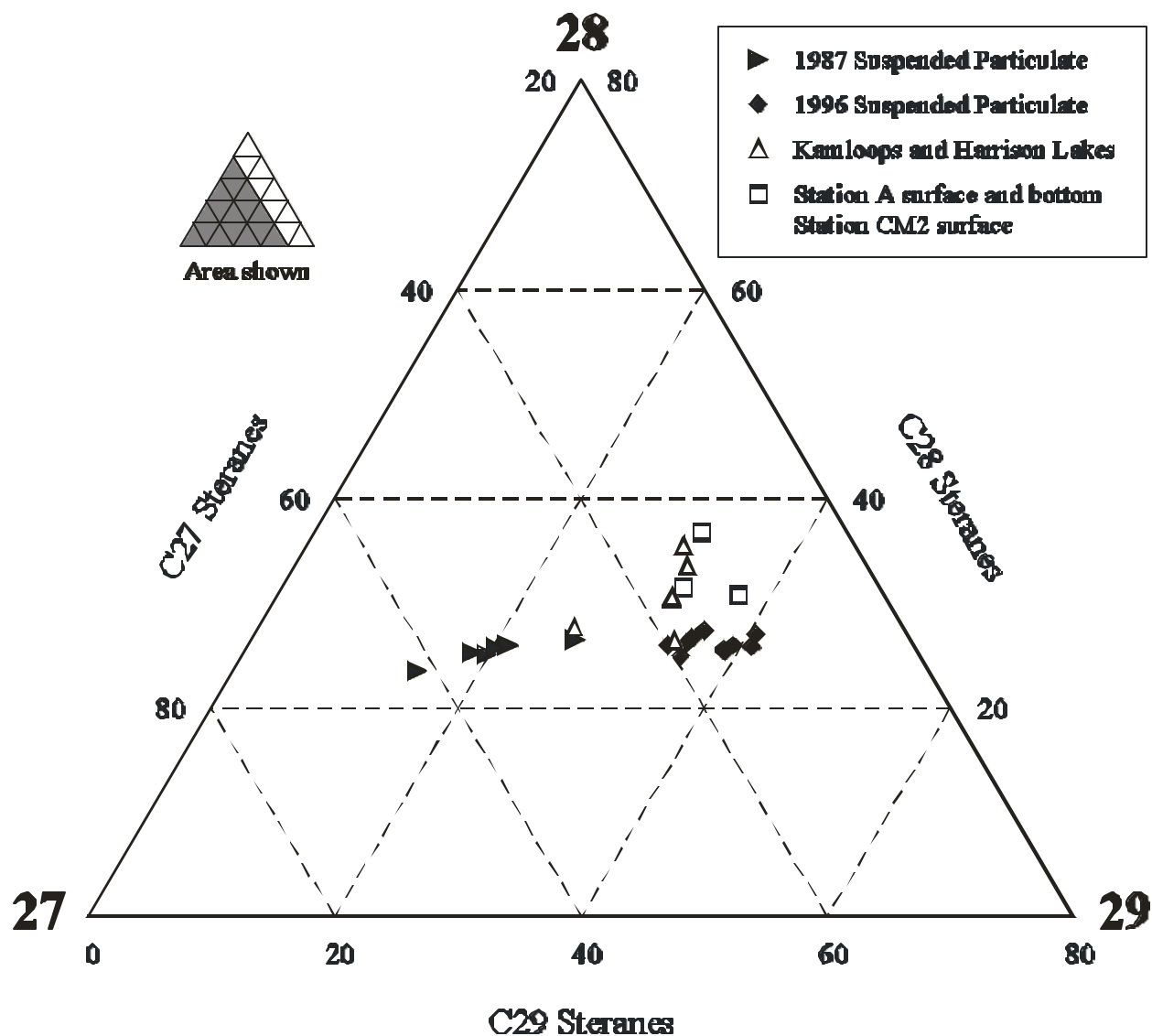


Figure 5. Ternary diagram showing the relative abundances of the diagenetic (rearranged) 27, 28 and 29 carbon $\beta\beta$ steranes (R + S $5\alpha(H),14\beta(H),17\beta(H)$ -cholestane, and its 24-methyl and 24-ethyl derivatives) as percentages based on peak heights from m/z 218 mass chromatograms.

Following pages:

Figure 6. Mean (bar), mean + 1 SE (open symbols) and maximum (filled symbols) concentrations for samples of suspended particulate and sediment, respectively, from the Fraser River basin and the Strait of Georgia. Shown are (a) Σ 178-278 parent PAH total (perylene excluded), (b) the alkyl PAH total (C_1 - C_4 naphthalenes, C_1 - C_3 phenanthrene/anthracenes and C_1 - C_2 dibenzothiophenes), (c) perylene (surface sediment only) and (d) retene.

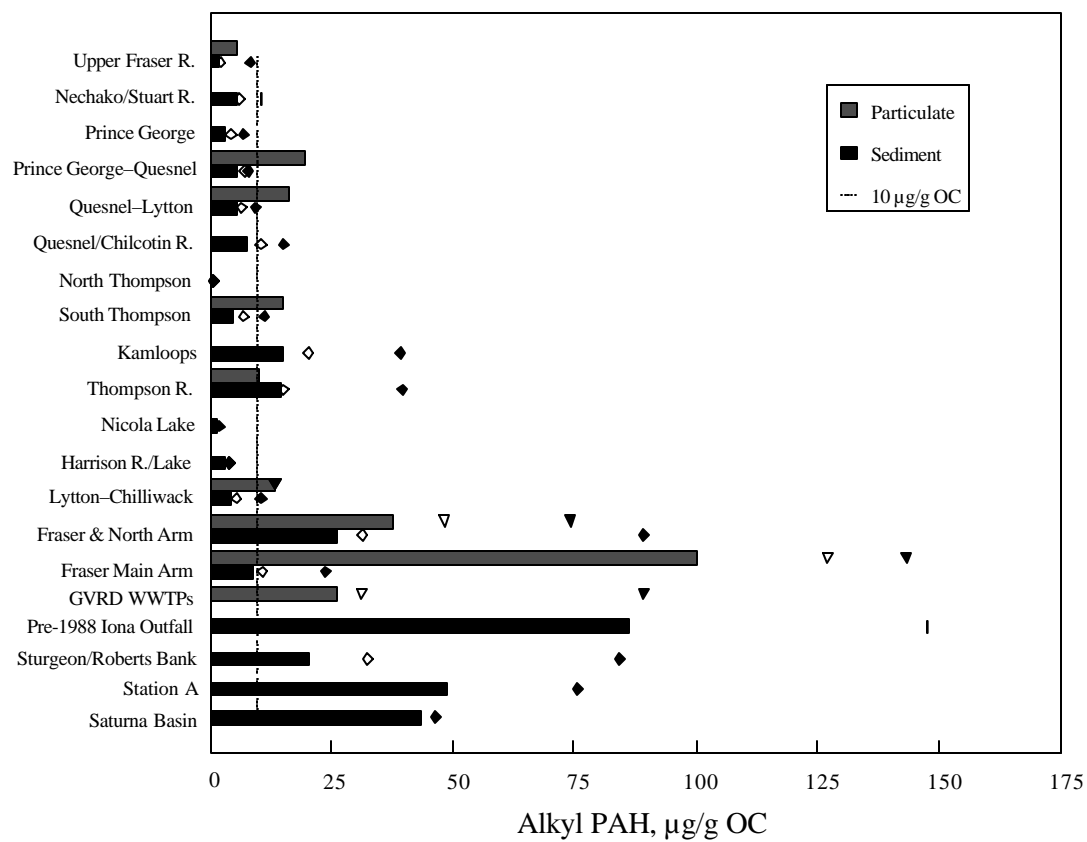
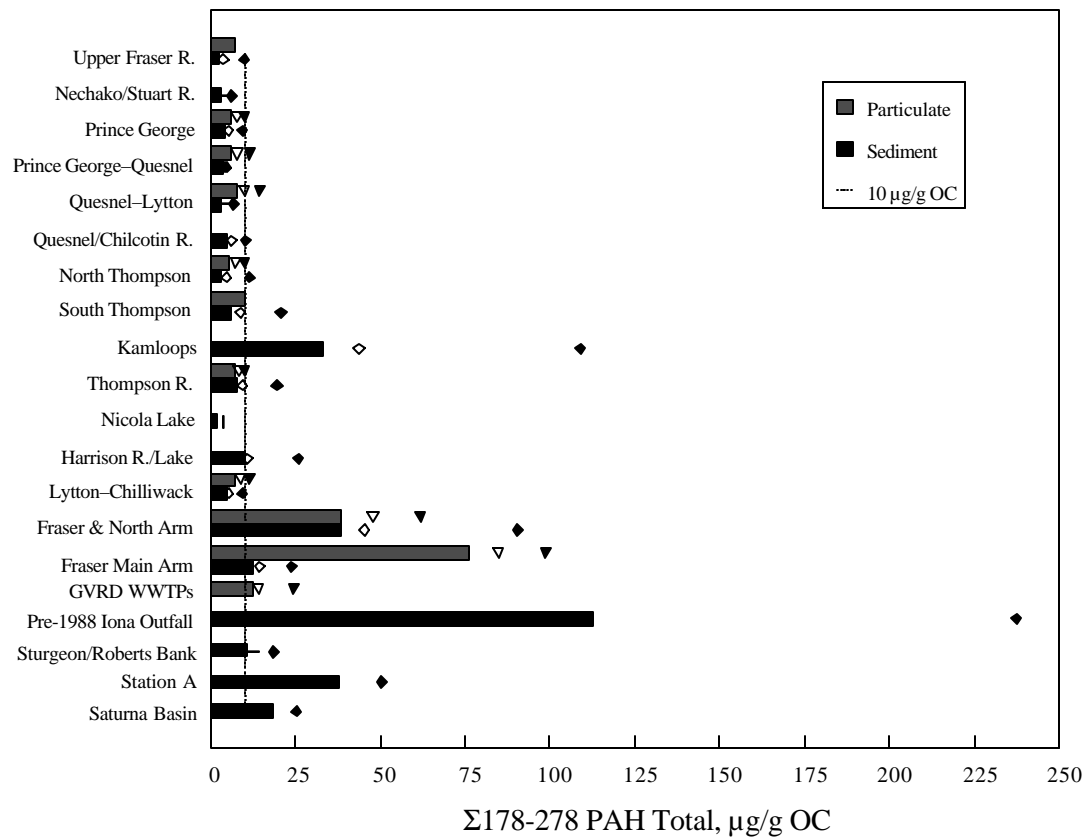


Figure 6a-b

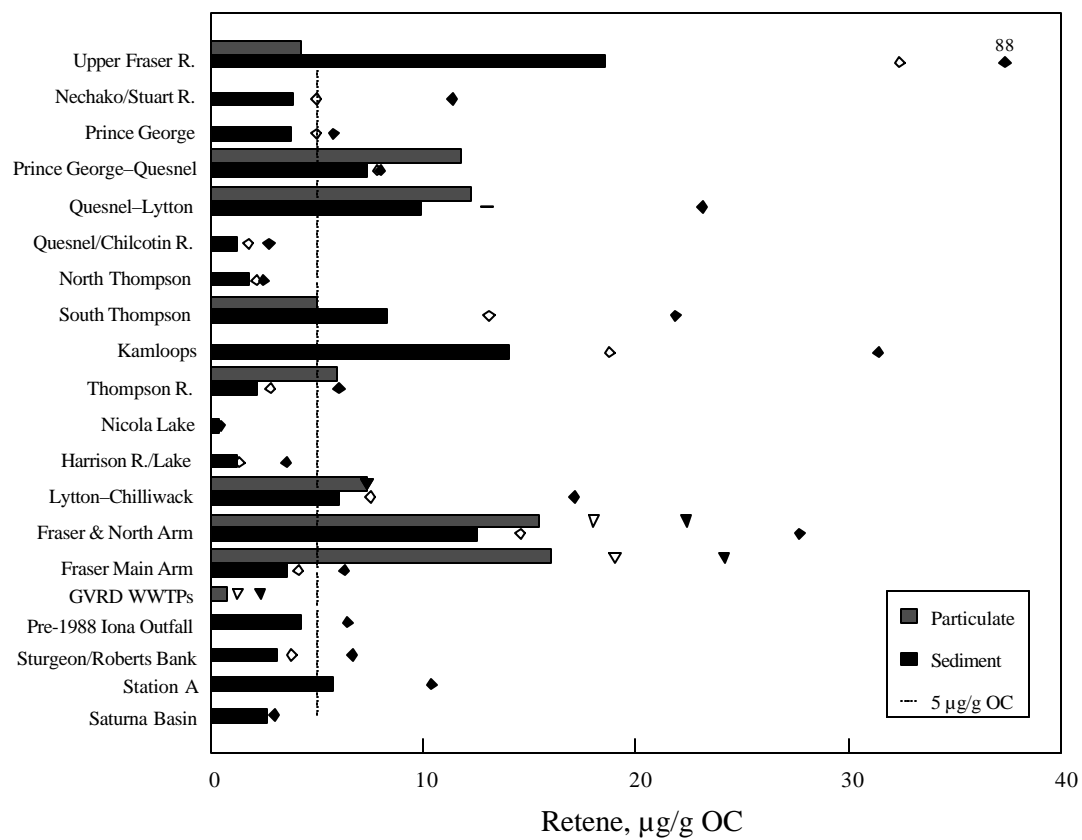
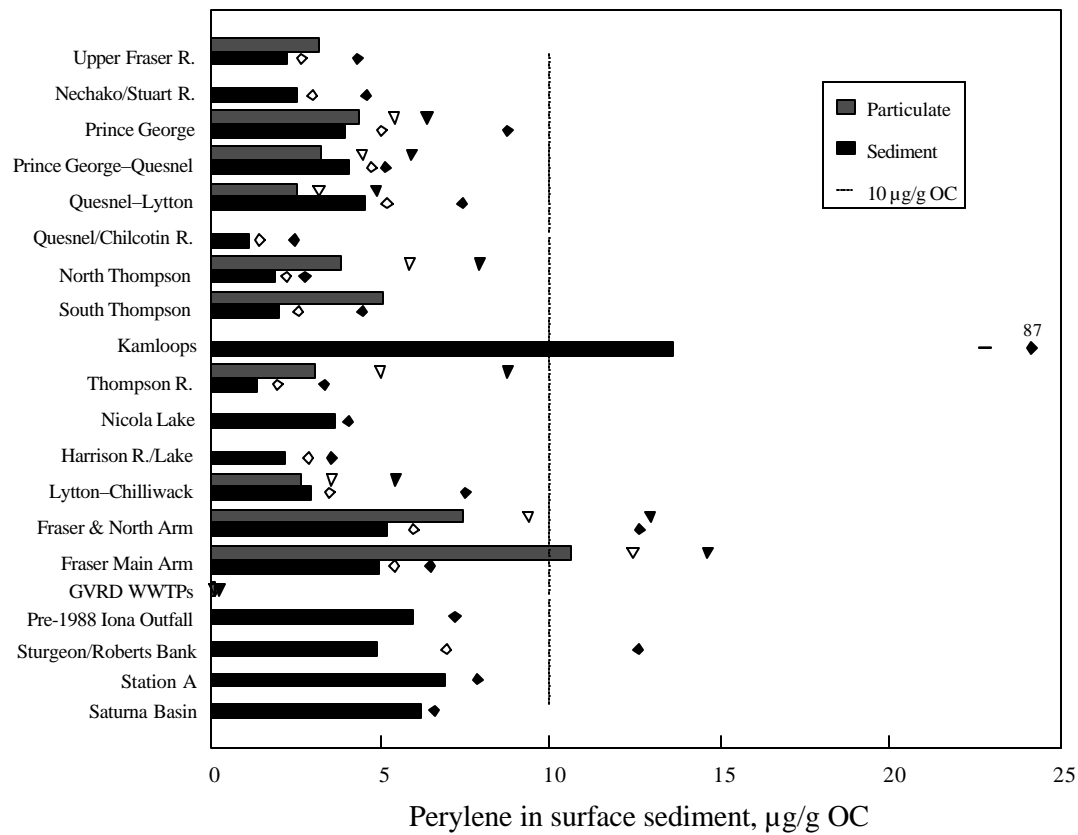


Figure 6c-d

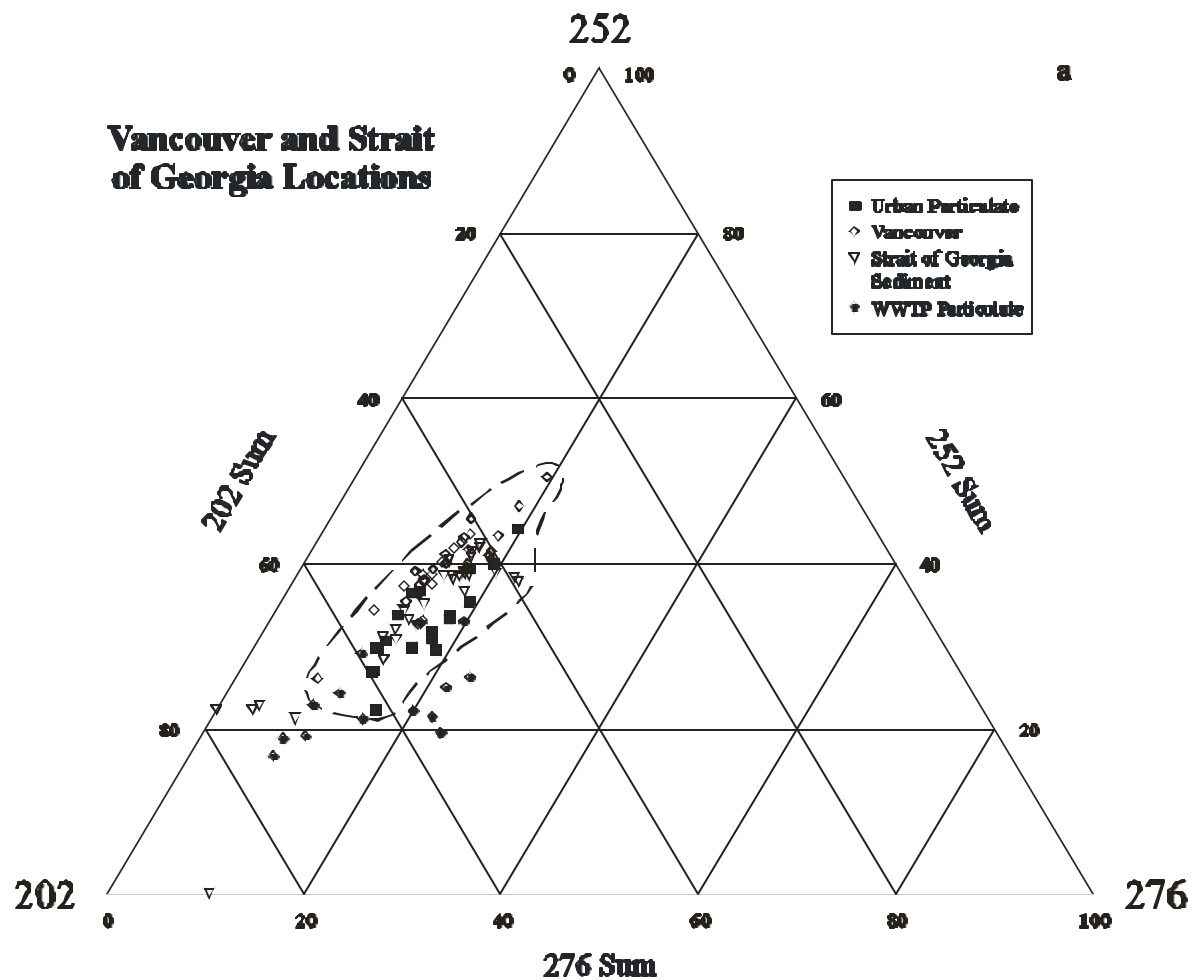


Figure 7. Ternary diagrams showing the relative abundances of the principal parent PAHs of molecular mass 202 (fluoranthene and pyrene), 252 (benzo[*b/j/k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene) and 276 (indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene) in the Fraser basin. (a) Urban-influenced locations.

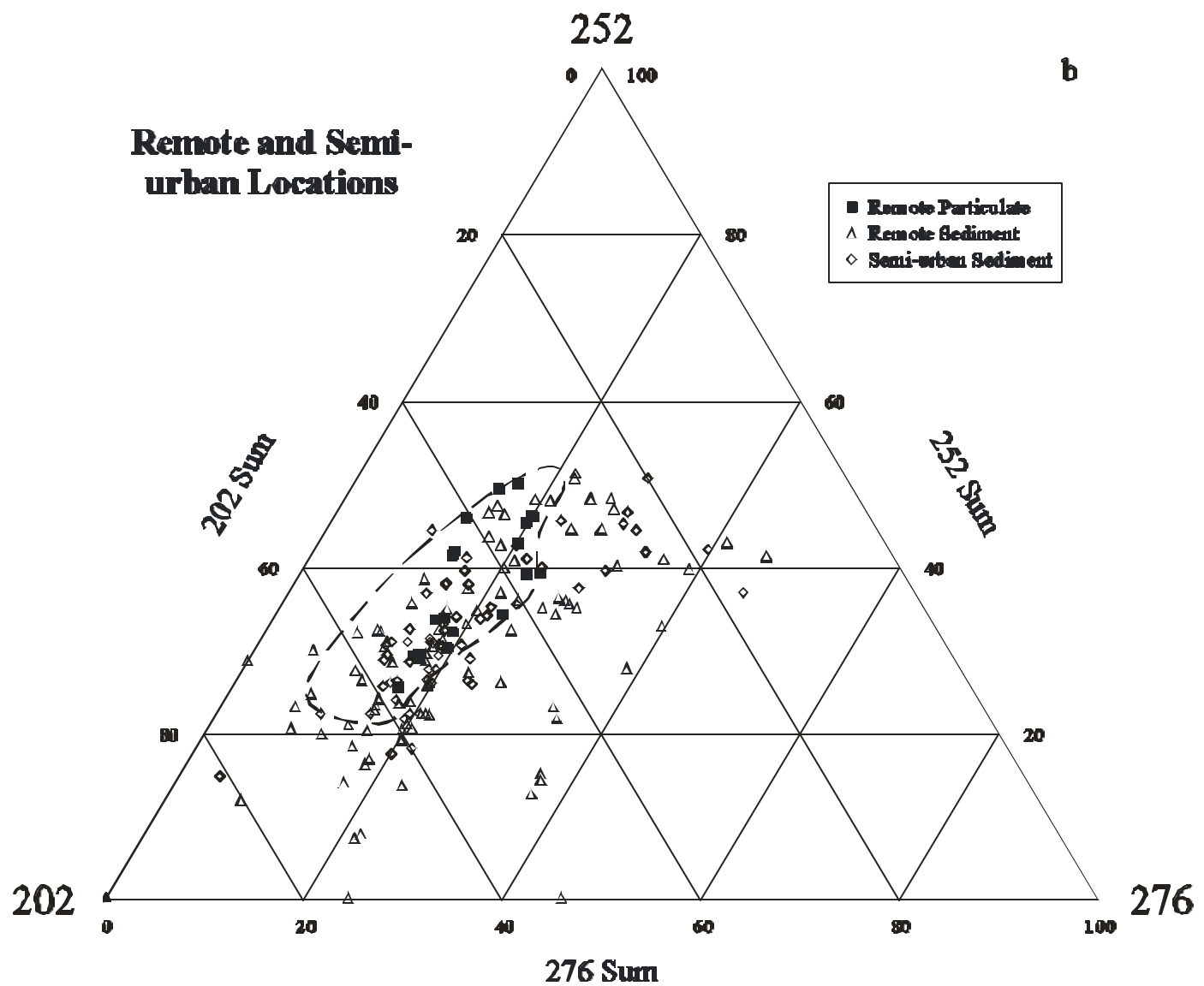


Figure 7. (b) Remote locations.

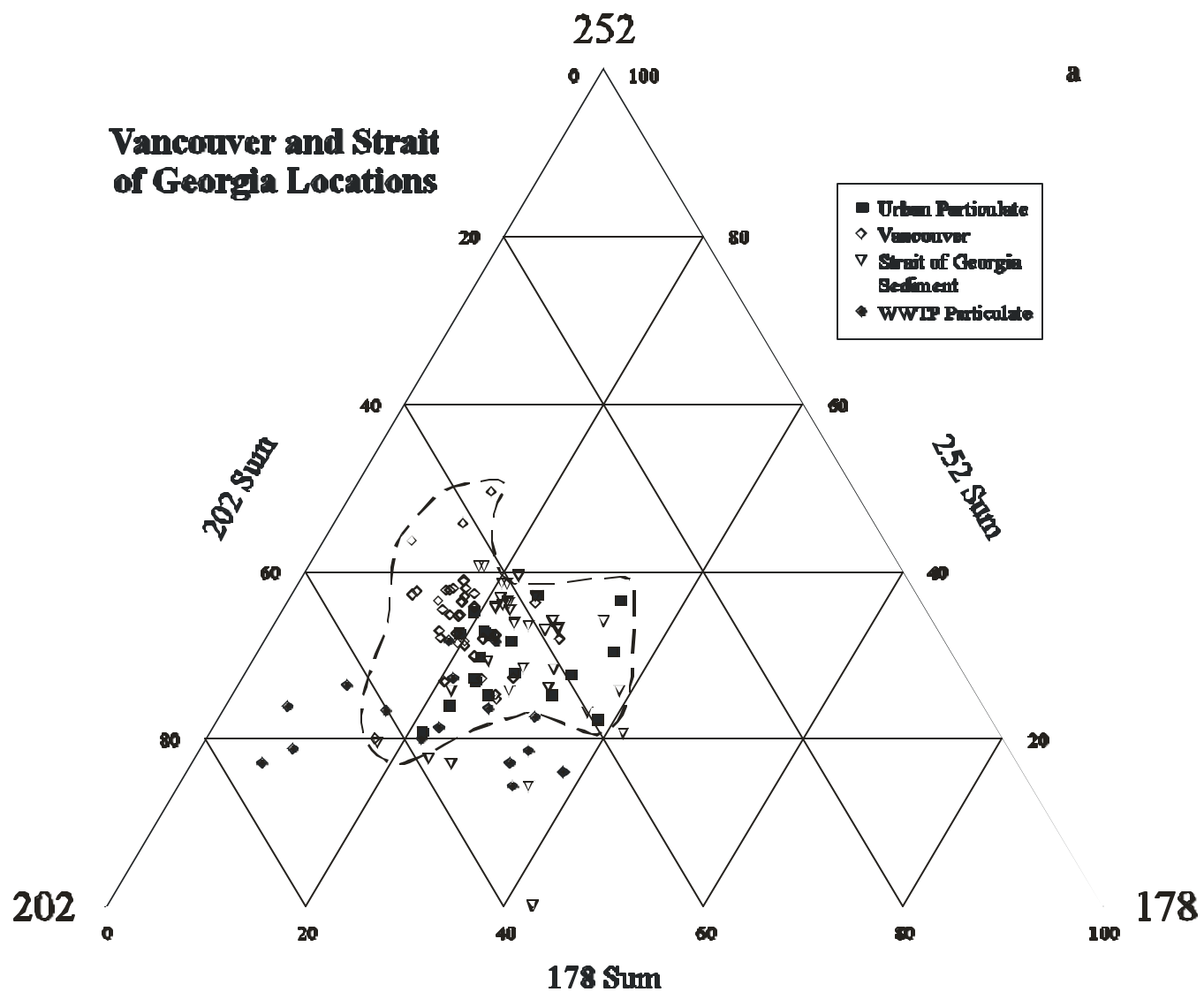


Figure 8. Ternary diagrams showing the relative abundances of the principal parent PAHs of molecular mass 178 (phenanthrene and anthracene), 202 (fluoranthene and pyrene) and 252 (benzo[*b/j/k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene) in the Fraser basin. (a) Urban-influenced locations.

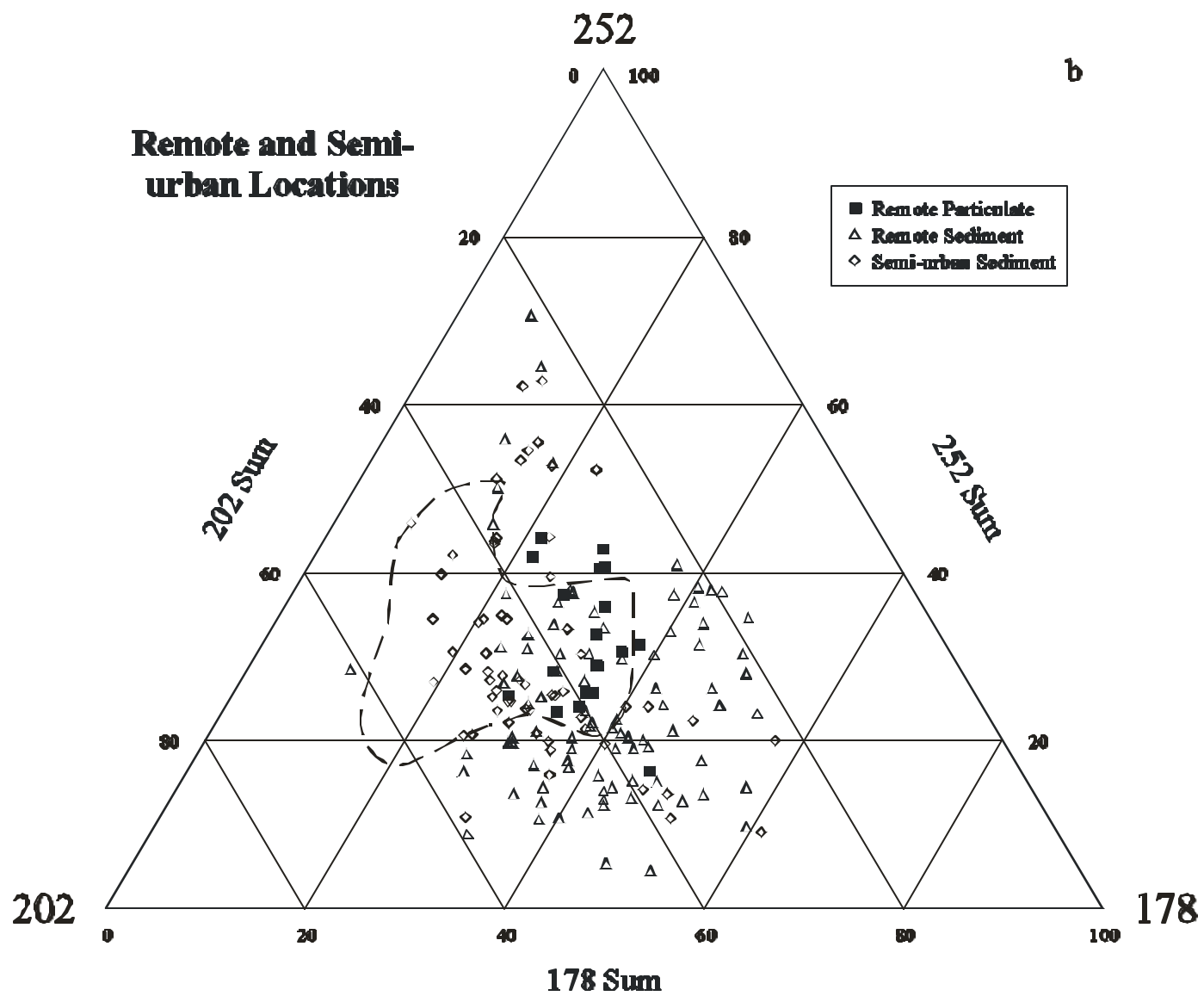


Figure 8. (b) Remote locations.

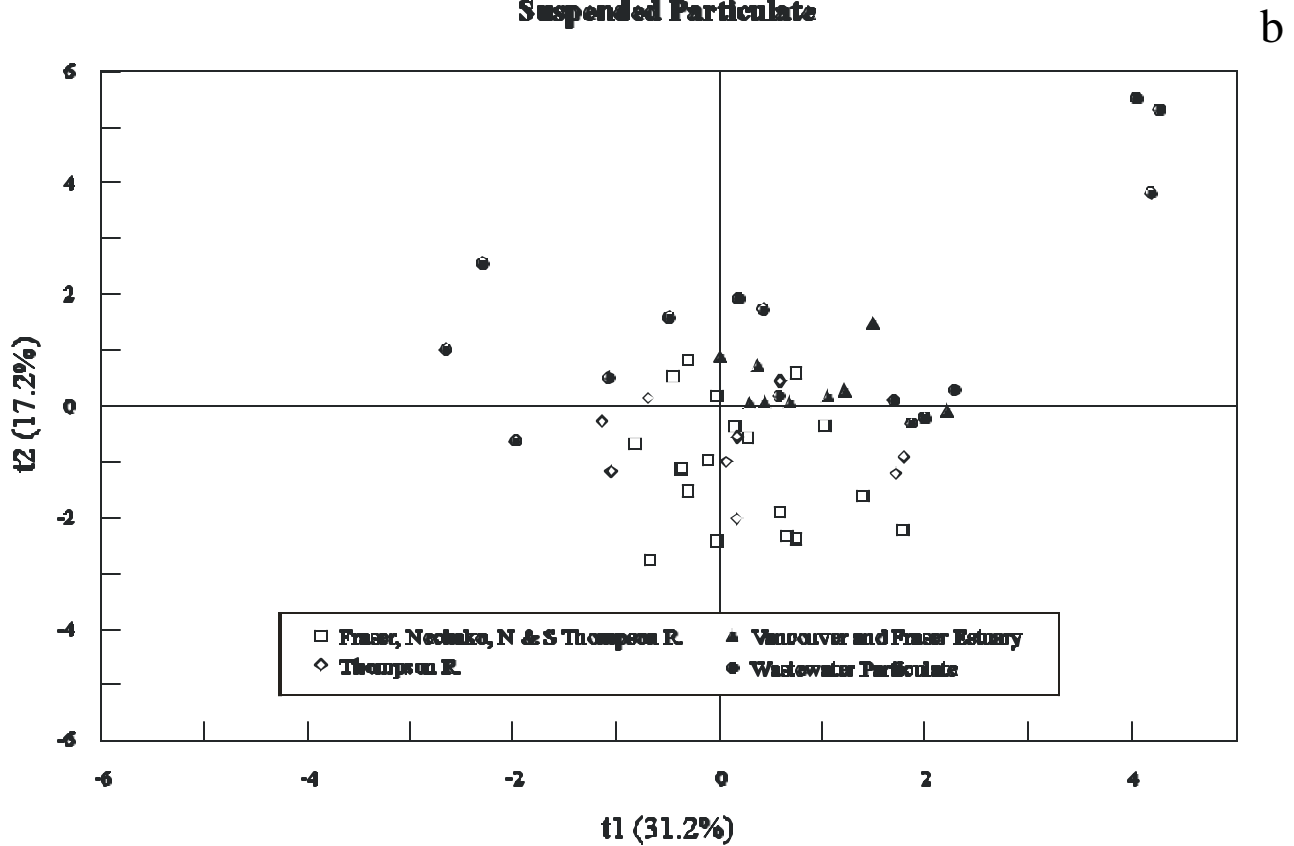
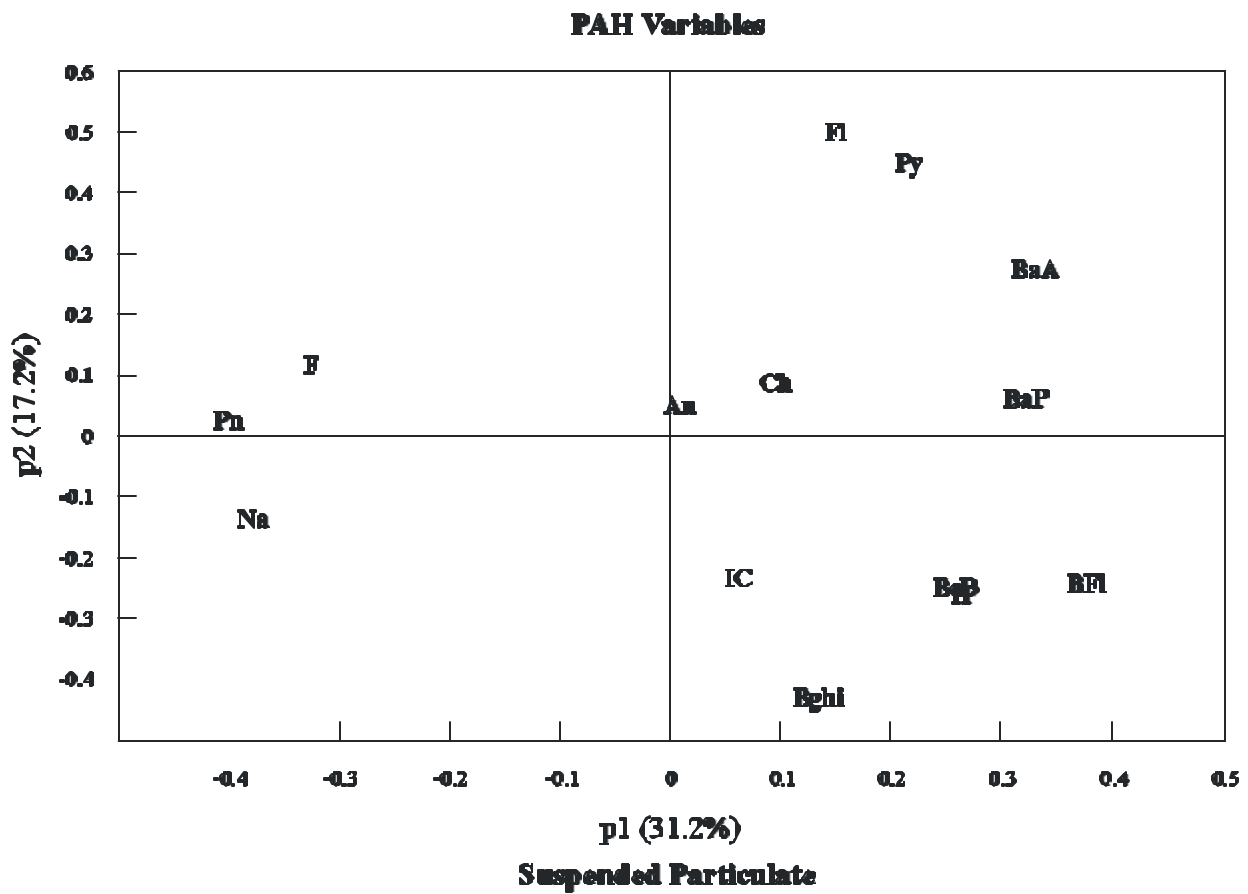


Figure 9. PCA projections of (a) PAH variables (see Table 3) and samples and (b) suspended particulate. The variance accounted for by each PC is shown in brackets after the axis label.

Sediment

C

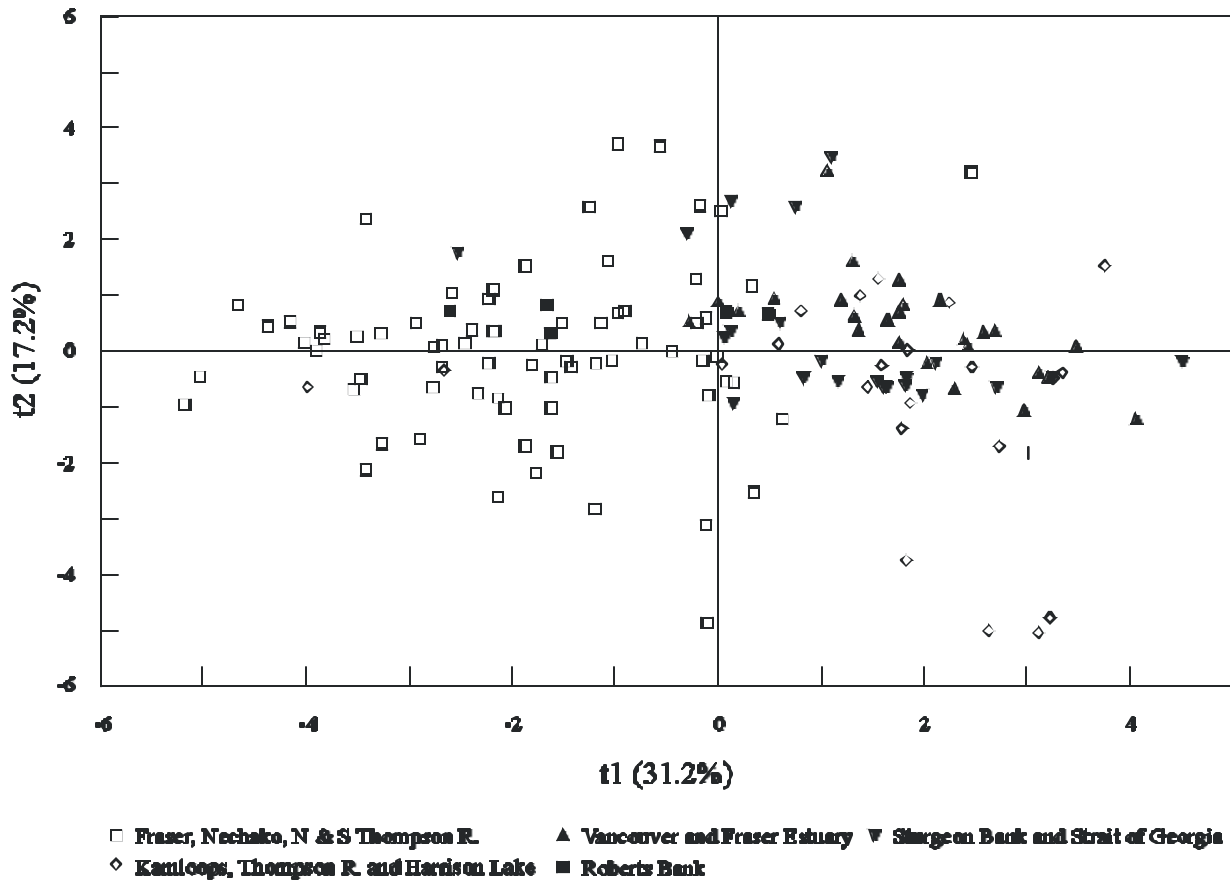


Figure 9. PCA projections of (c) sediment

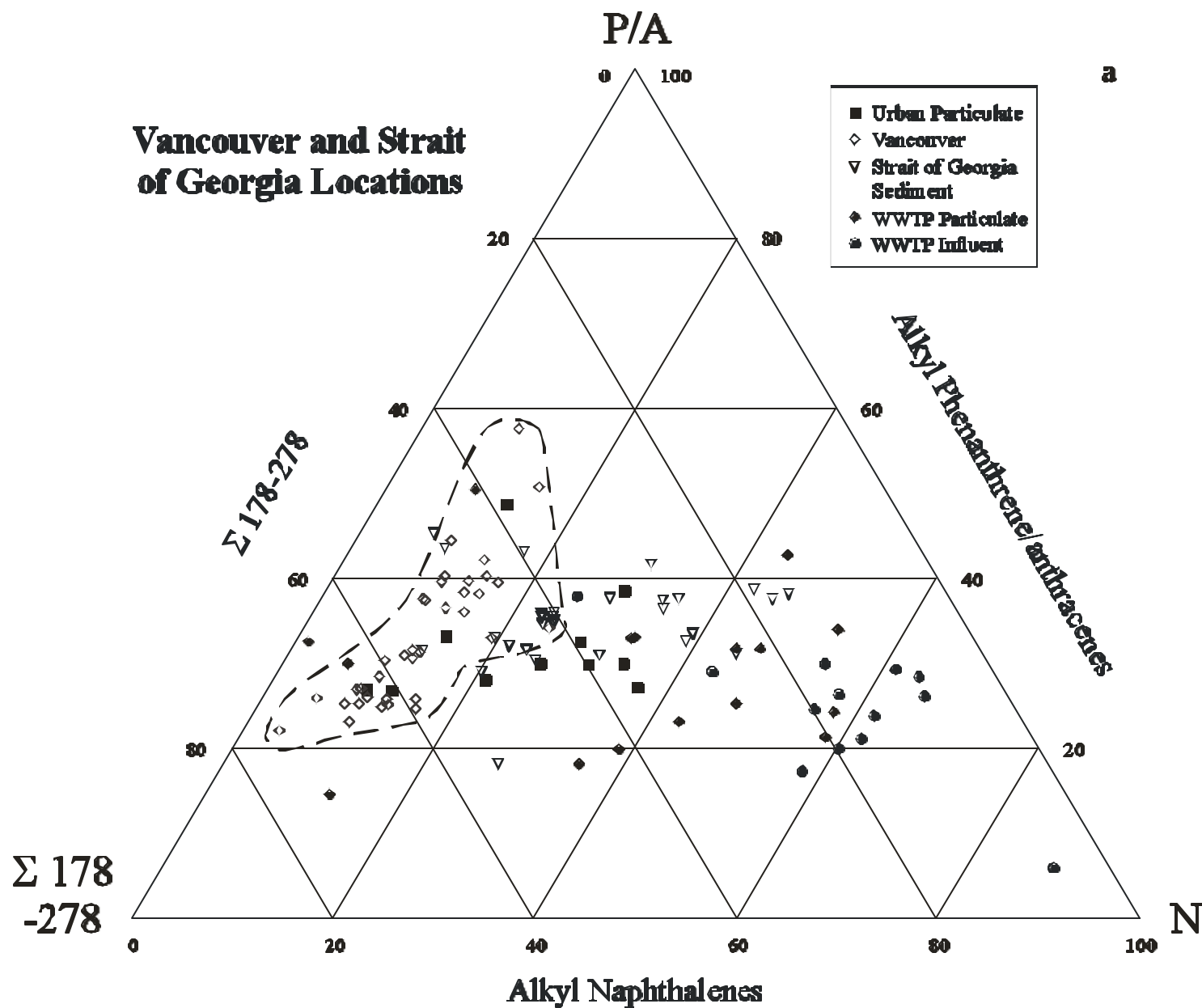


Figure 10. Ternary diagrams showing the relative abundances of the Σ 178-278 parent PAHs, C_0 - C_4 alkyl naphthalenes (N) and C_0 - C_3 alkyl phenanthrene/anthracenes (P/A). (a) Urban-influenced locations.

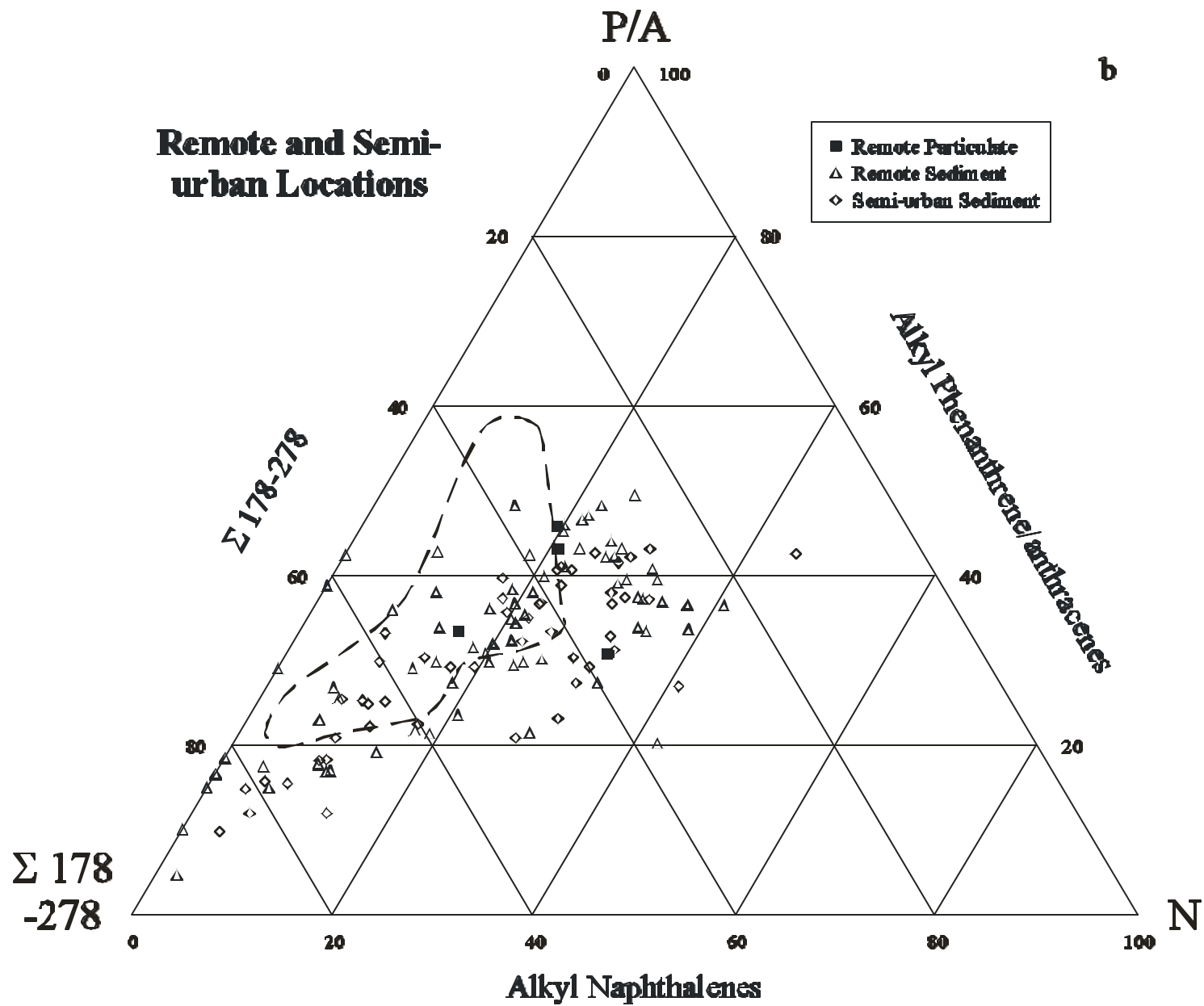


Figure 10. (b) Remote locations.

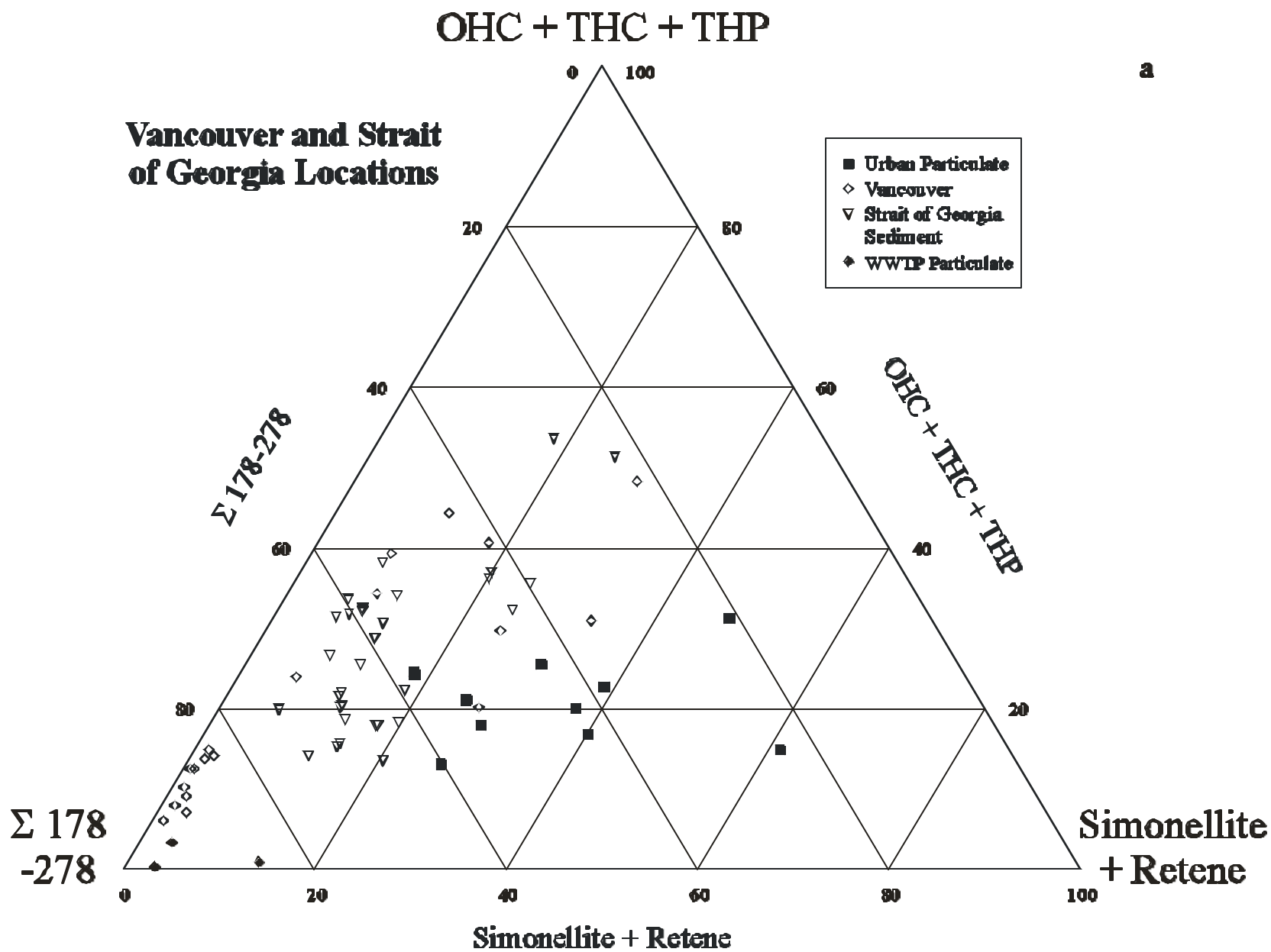


Figure 11. Ternary diagrams showing the relative abundances of the Σ 178-278 parent PAHs, simonellite plus retene and the sum of the methylated octa- and tetrahydrochrysenes (OHC and THC, respectively) and tetrahydropicenes (THP). (a) Urban-influenced locations.

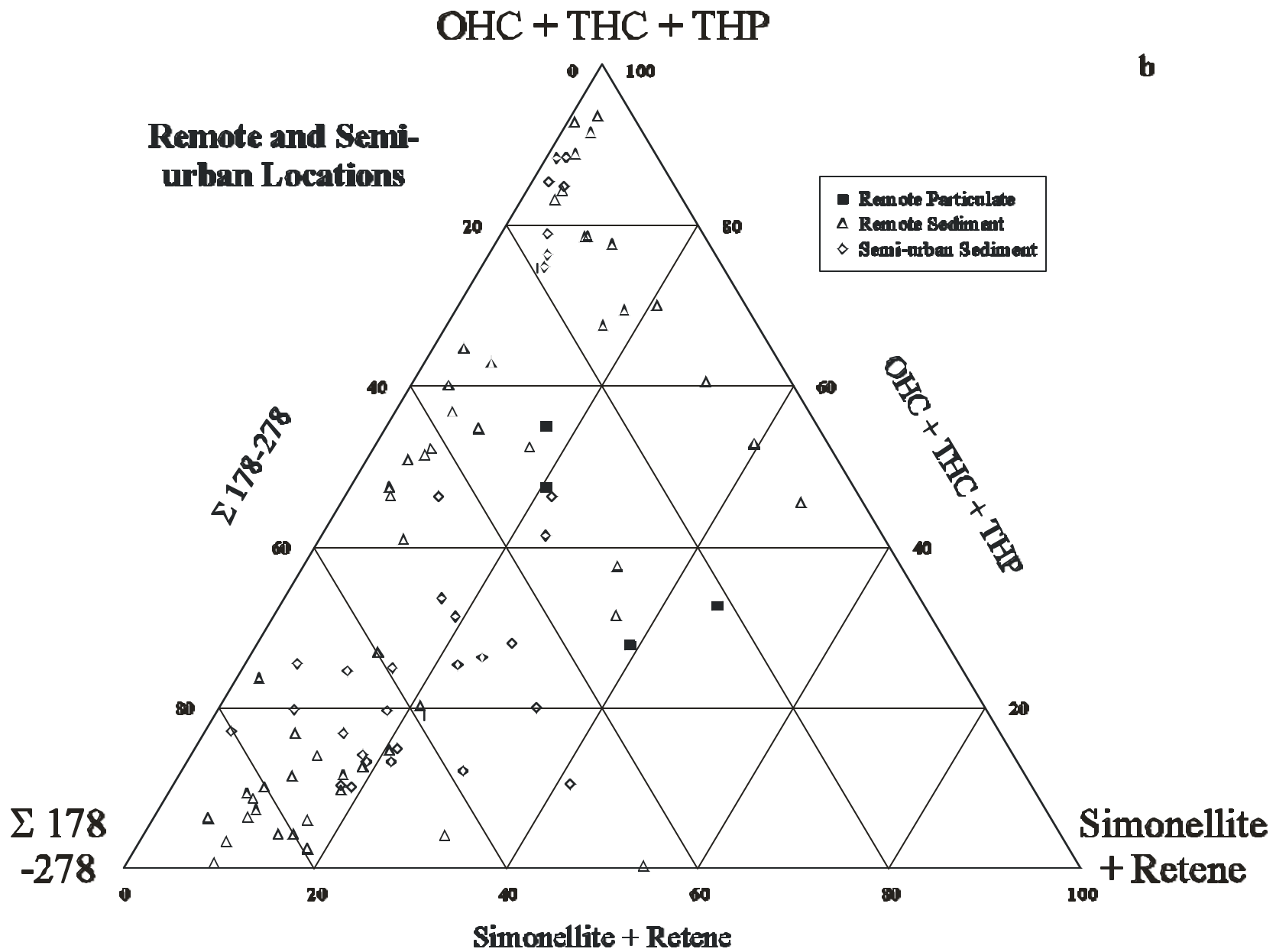


Figure 11. (b) Remote locations.

Remote and Semi-urban Locations

a

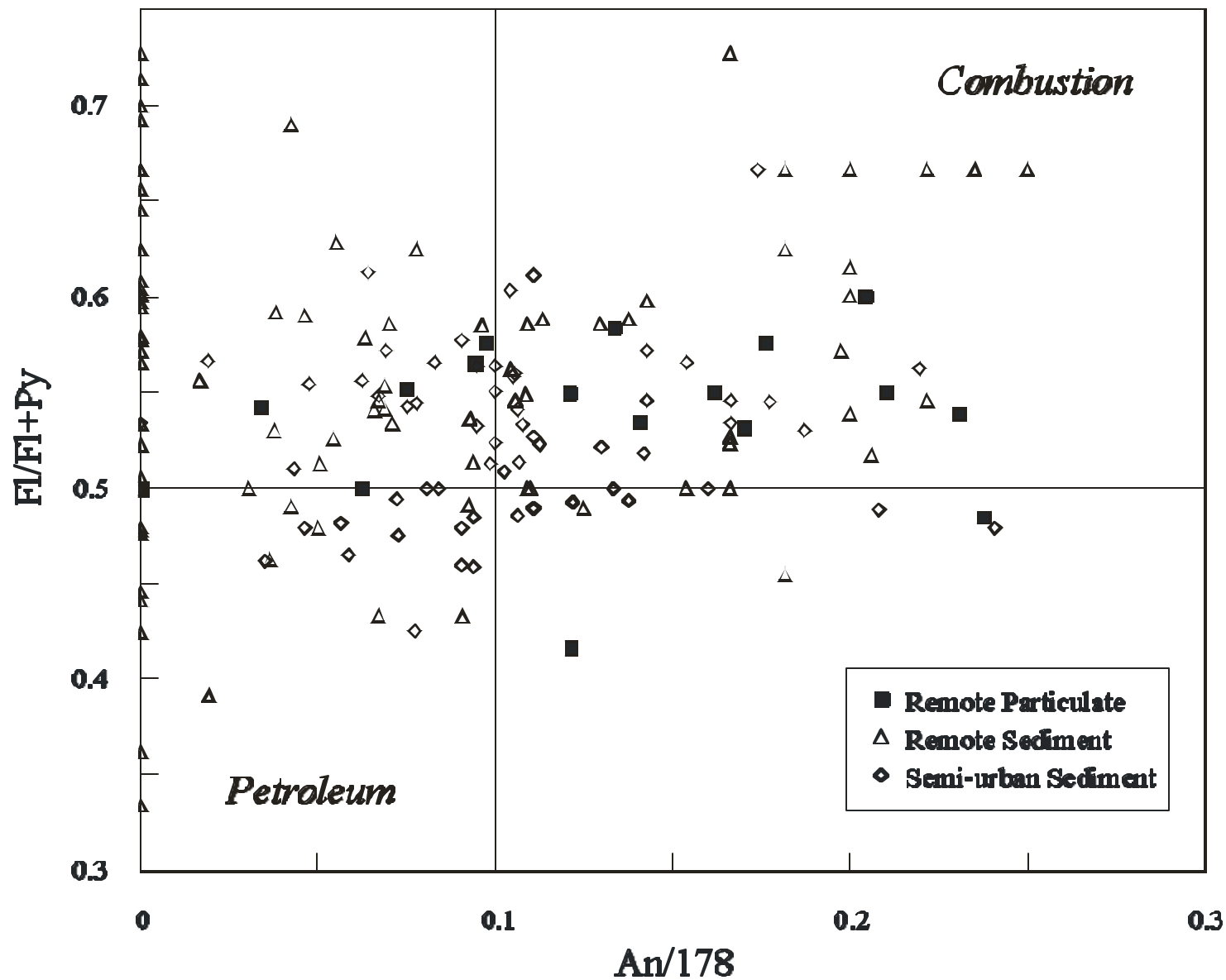


Figure 12. Plot of the ratio of fluoranthene (FI) to fluoranthene plus pyrene (Py) vs. the ratio of anthracene (An) to anthracene plus phenanthrene (178). (a) Less-industrialized locations.

Vancouver and Strait of Georgia Locations

b

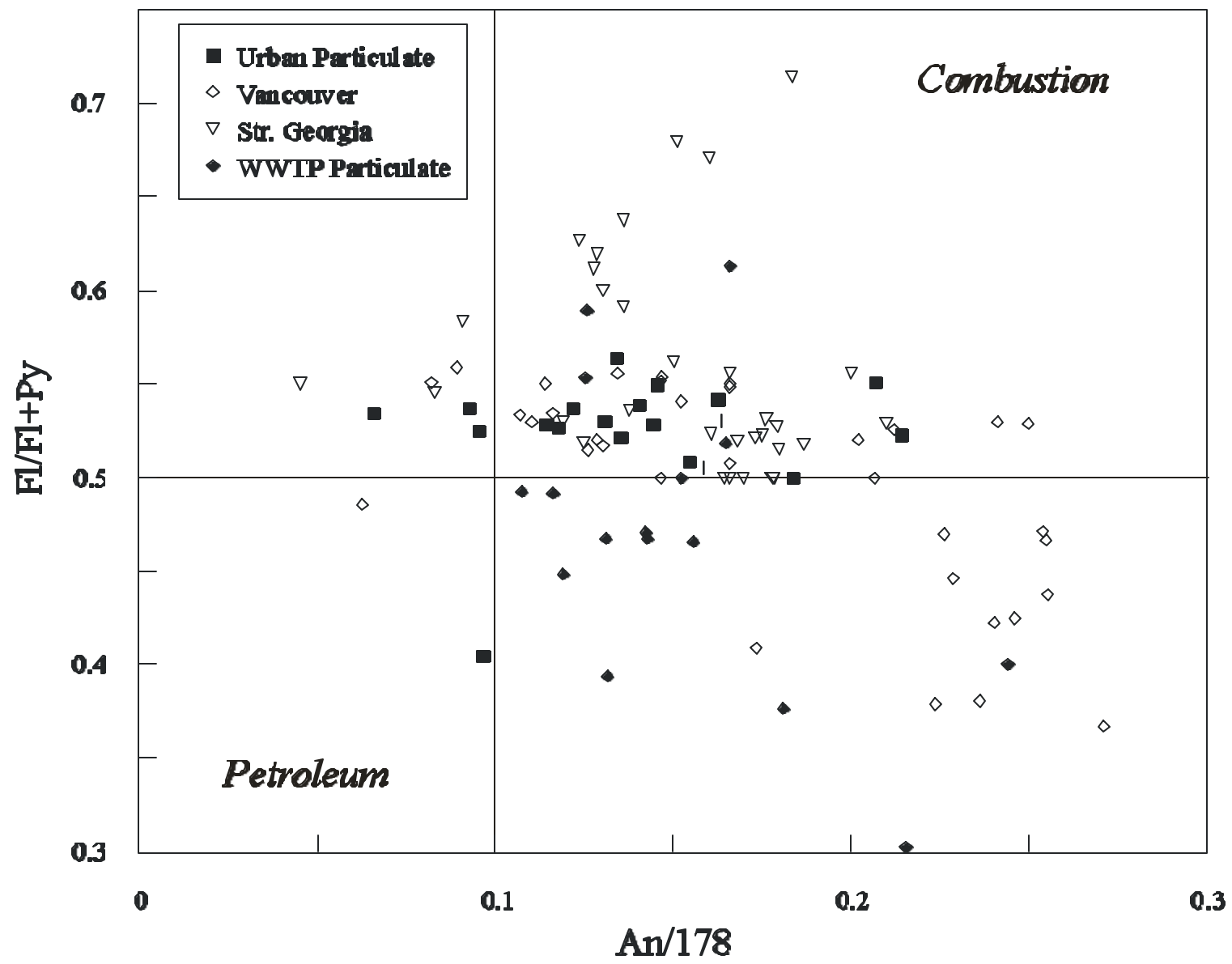


Figure 12. (b) Urbanised regions of the Fraser River estuary and Strait of Georgia.

Remote and Semi-urban Locations

a

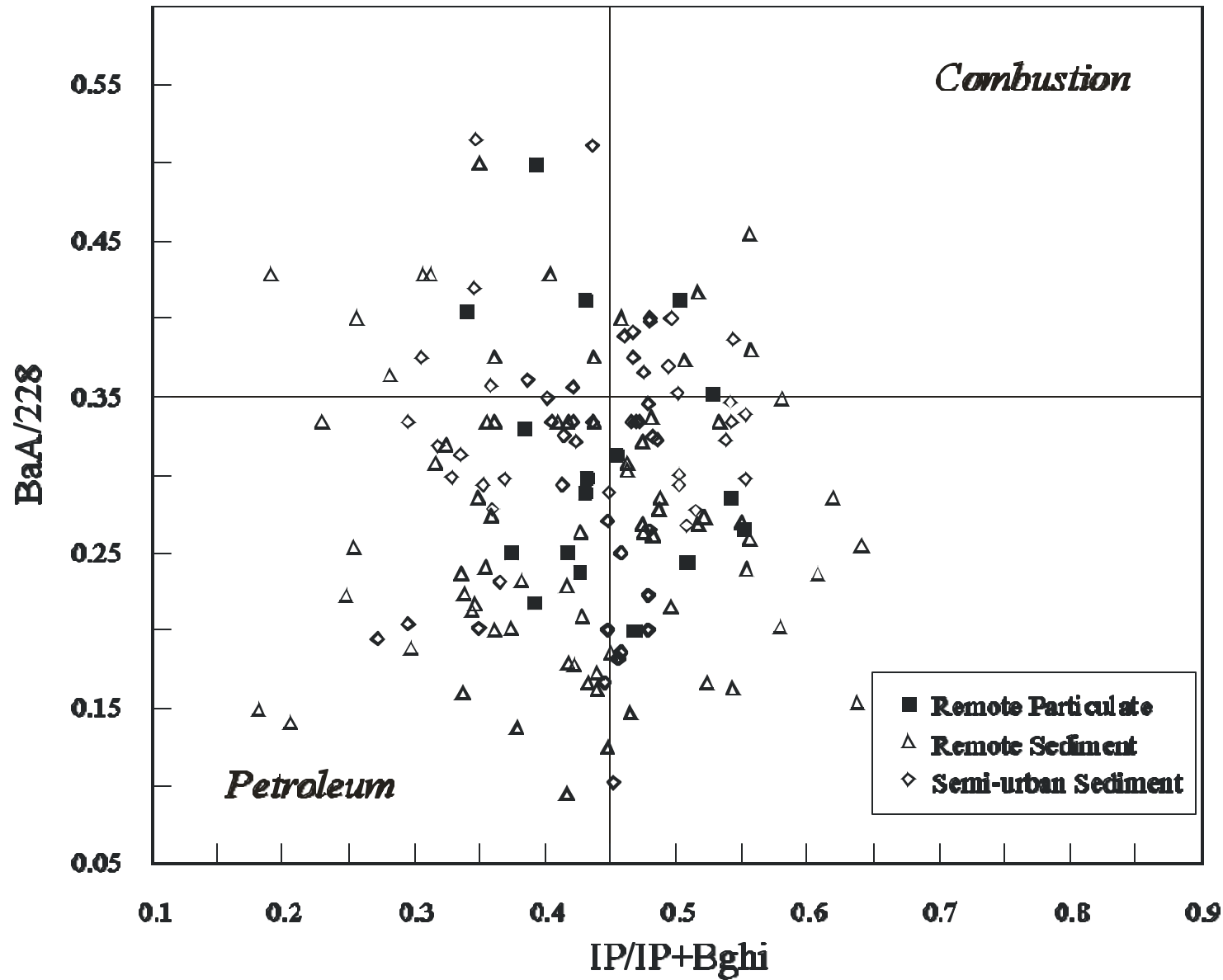


Figure 13. Plot of the ratio of benz[*a*]anthracene (BaA) to BaA plus chrysene (228) vs. the ratio of indeno[1,2,3-*cd*]pyrene (IP) to IP plus benzo[*ghi*]perylene (IP + Bghi). (a) Less-industrialized locations.

Vancouver and Strait of Georgia Locations

b

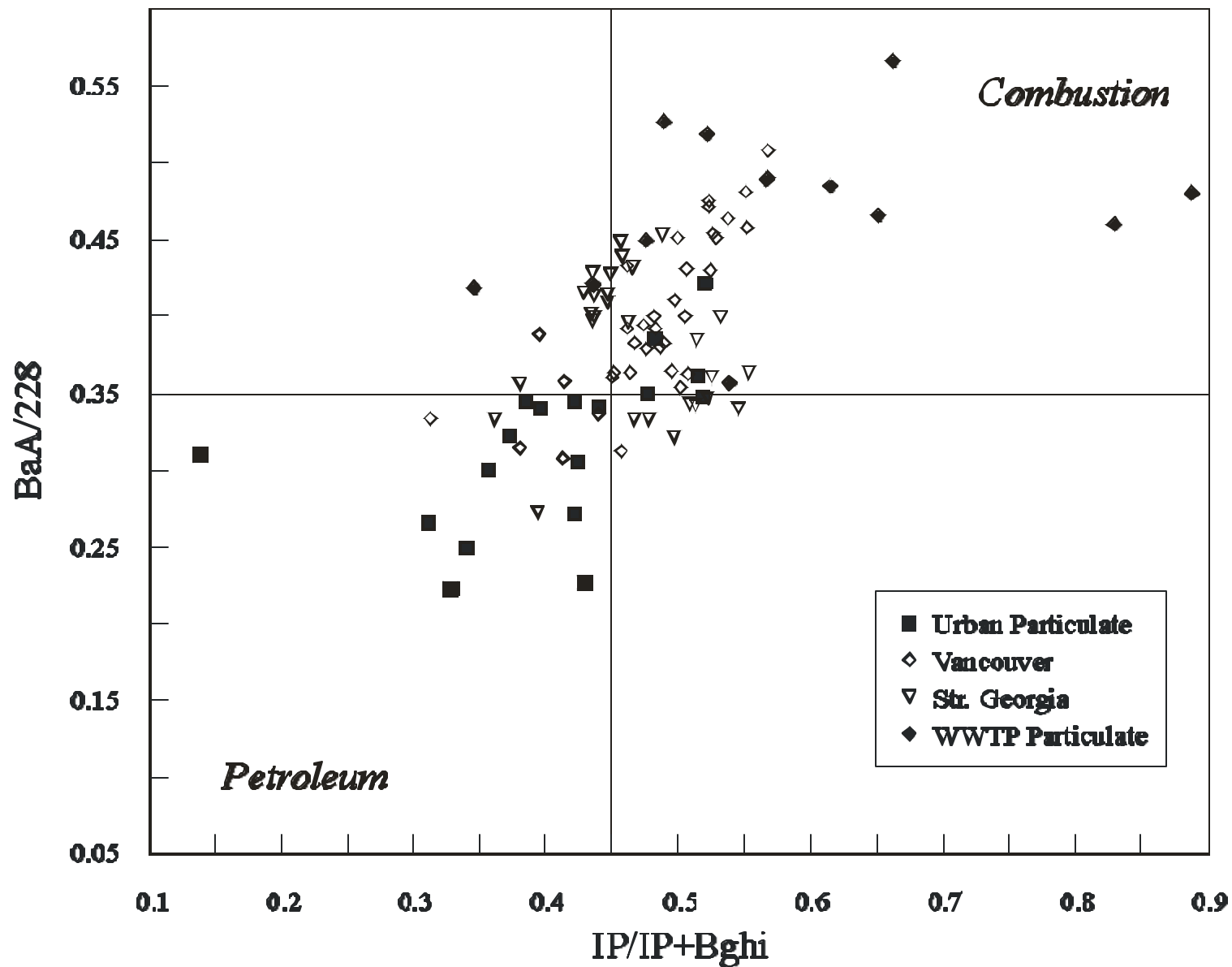


Figure 13. (b) Urbanised regions of the Fraser River estuary and Strait of Georgia.

Remote and Semi-urban Locations

a

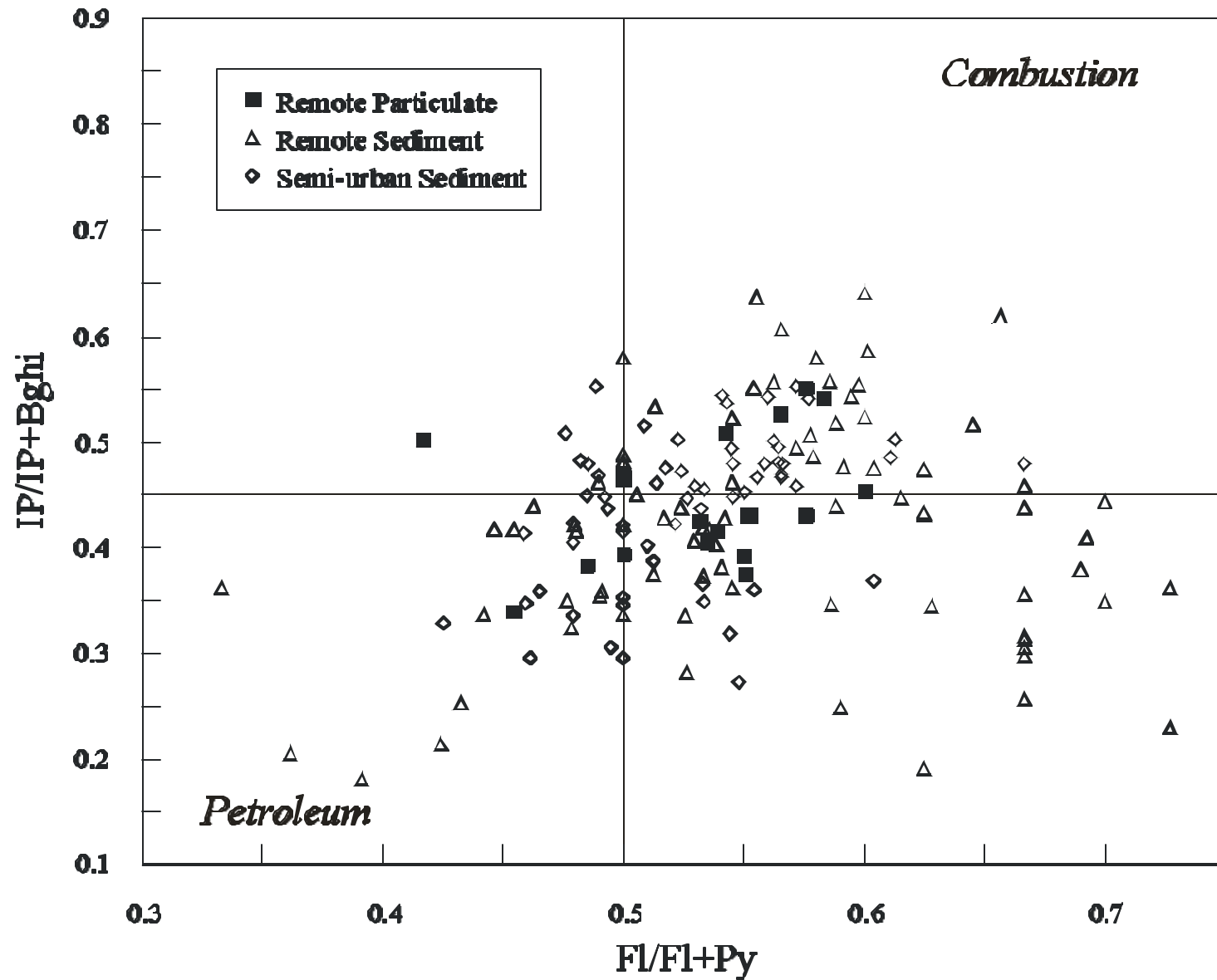


Figure 14. Plot of the ratio of indeno[1,2,3-*cd*]pyrene to indeno[1,2,3-*cd*]pyrene plus benzo[*ghi*]perylene vs. the ratio of fluoranthene to fluoranthene plus pyrene. (a) Less-industrialized locations.

Vancouver and Strait of Georgia Locations

b

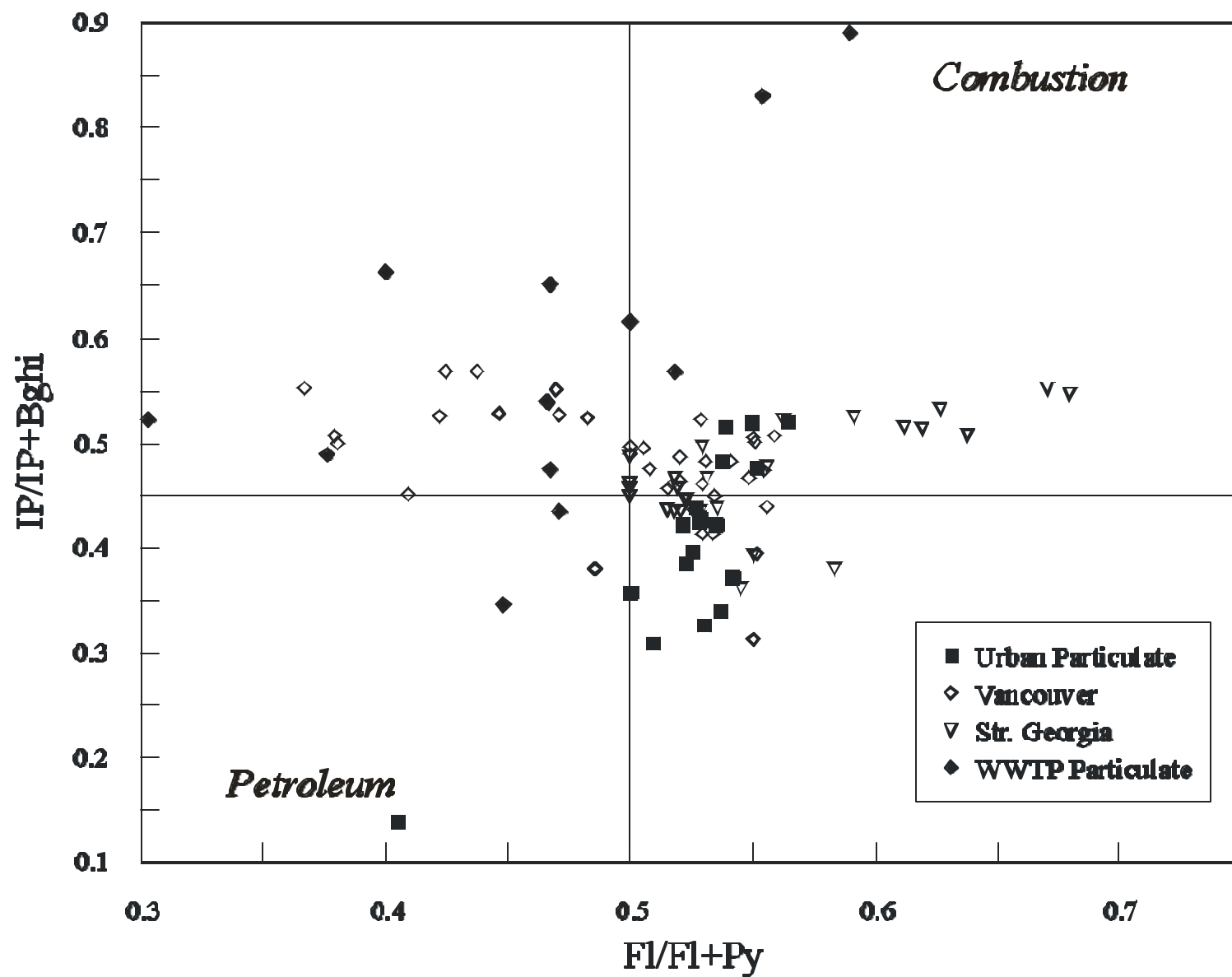


Figure 14. (b) Urbanised regions of the Fraser River estuary and Strait of Georgia.

a

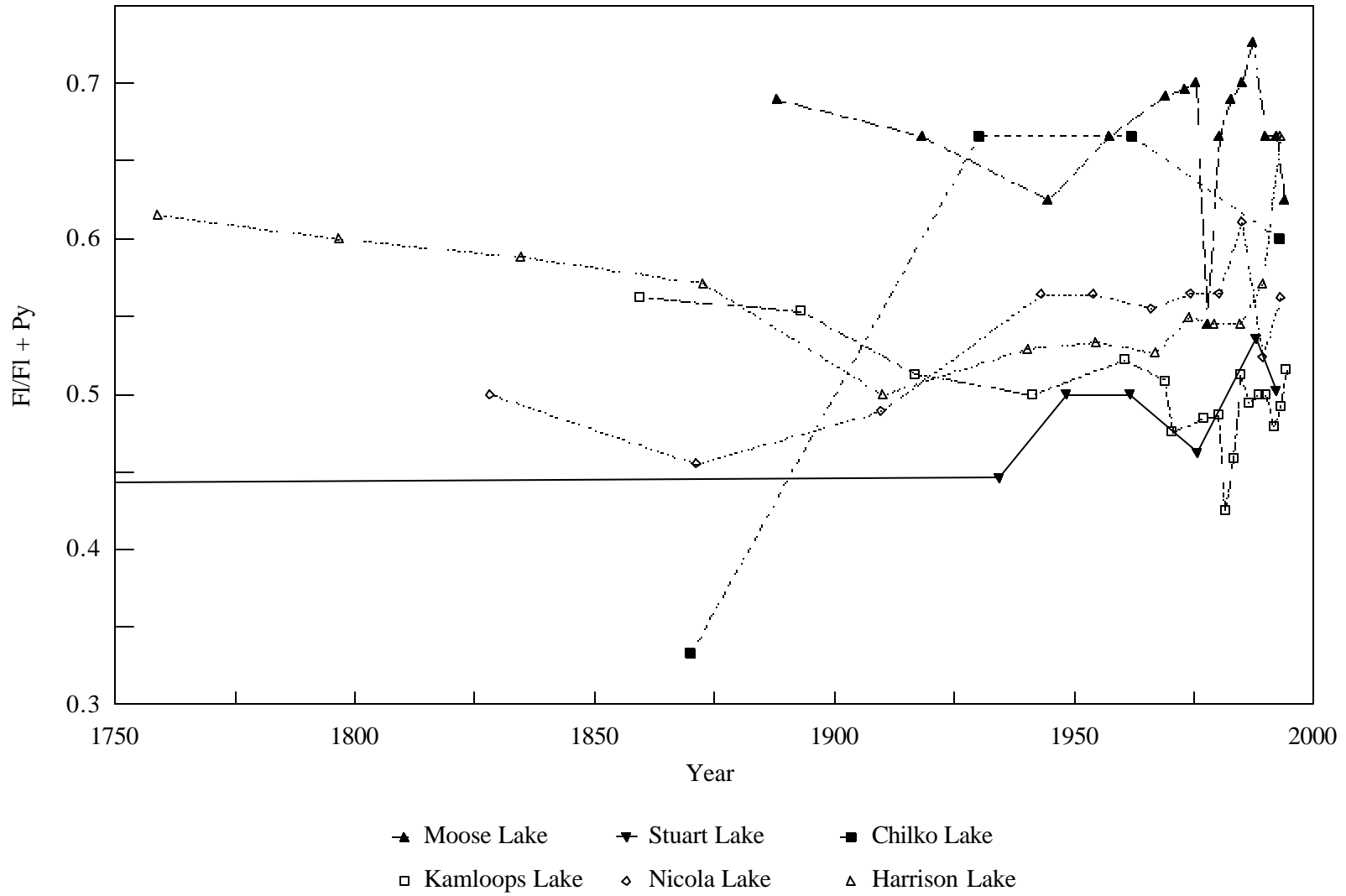


Figure 15. Downcore profiles by ^{210}Pb date for PAH ratios for core samples from Moose Lake, Stuart Lake, Chilko Lake, Kamloops Lake, Nicola Lake and Harrison Lake. (a). Fluoranthene/ fluoranthene + pyrene (Fl/Fl + Py).

b

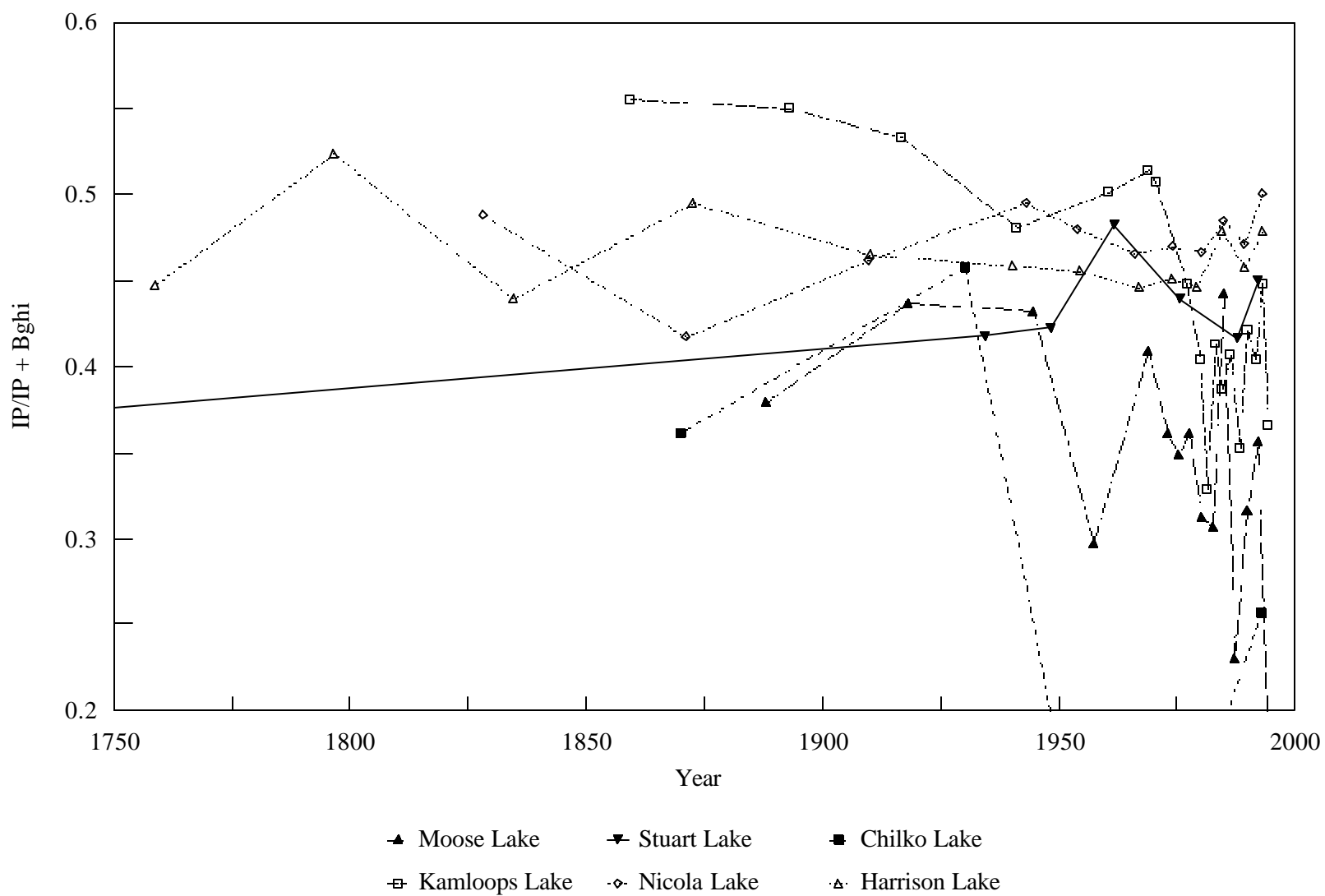


Figure 15. (b). Indeno[1,2,3-*cd*]pyrene/ indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene (IP/IP + Bghi).

Vancouver Harbour station CH-I, 0-1 cm

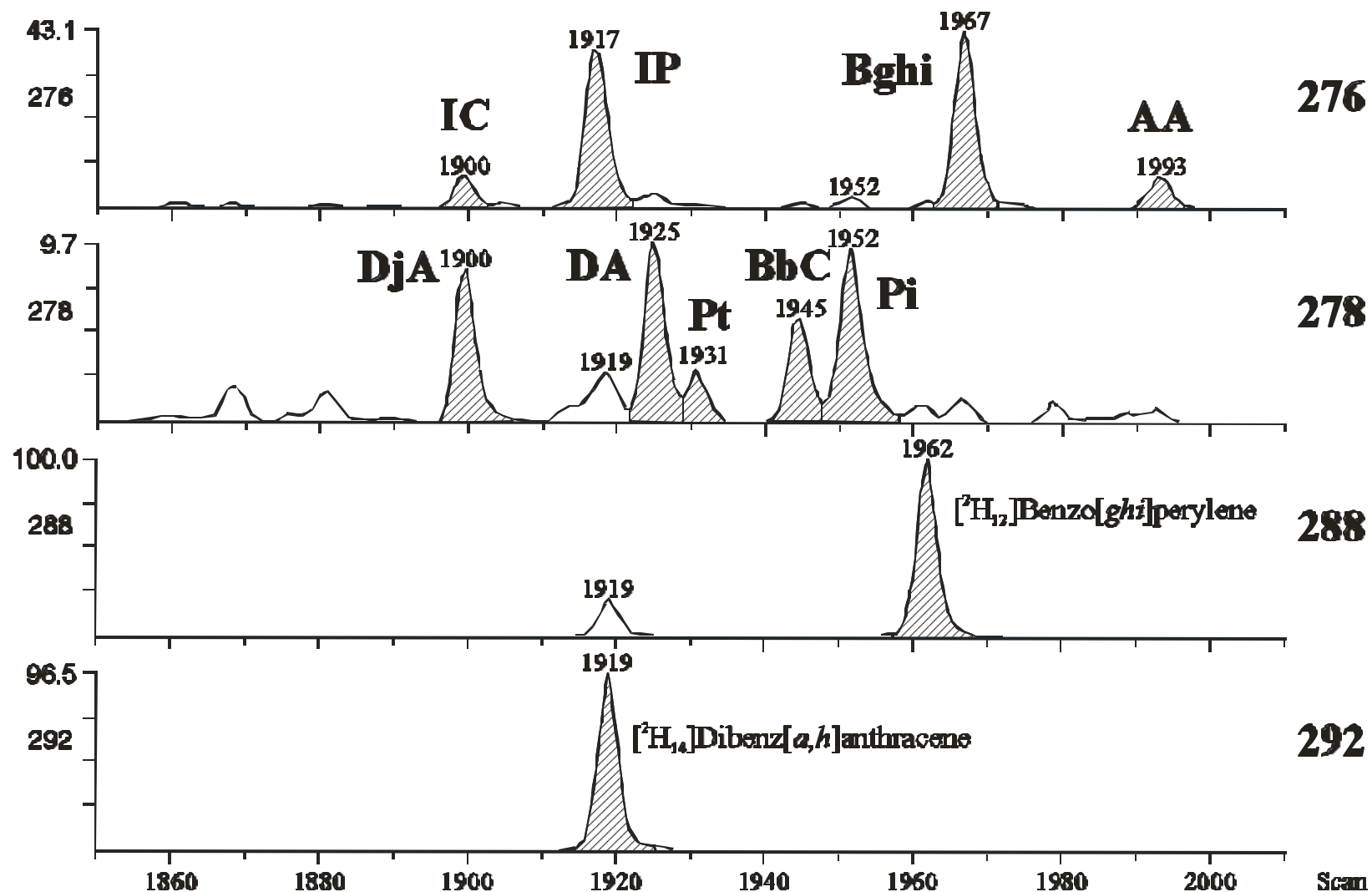


Figure 16. GC/MS selected ion chromatograph showing compound identifications and elution orders for the molecular mass 276 and 278 PAHs that were quantified in this study. Positions of the respective perdeuterated standards are also shown. Abbreviations for PAHs follow Table 3. This figure has been adapted from Yunker *et al.* (1999b).

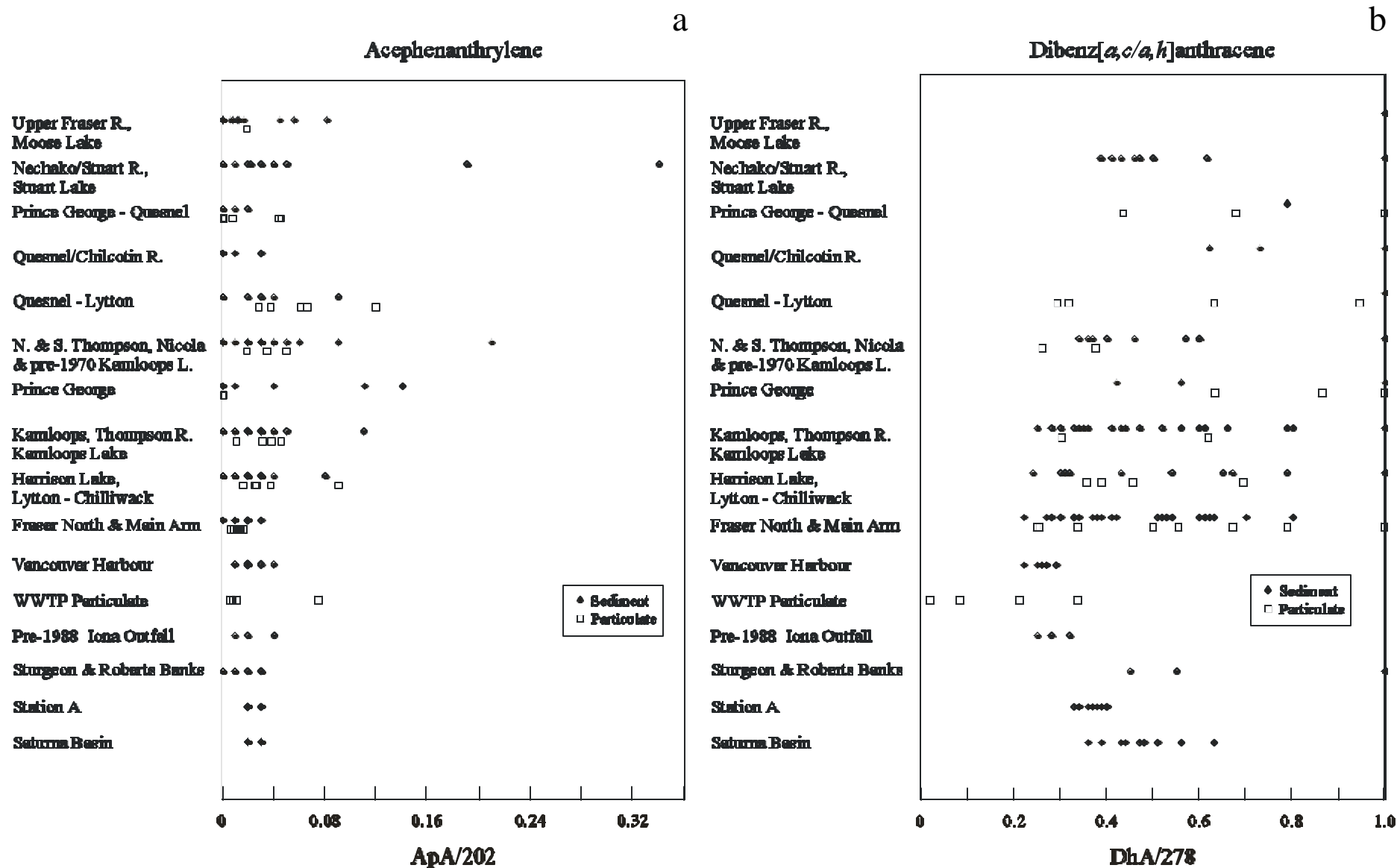


Figure 17. PAH ratios for suspended particulate and sediment samples from different regions of the Fraser River basin and Strait of Georgia. Ratios shown are for (a) acephenanthrylene (ApA) to ApA plus fluoranthene and pyrene, and (b) dibenz[*a,c/a,h*]anthracene (DhA) to DhA plus dibenz[*a,j*]anthracene, pentaphene, benzo[*b*]chrysene and picene (278).

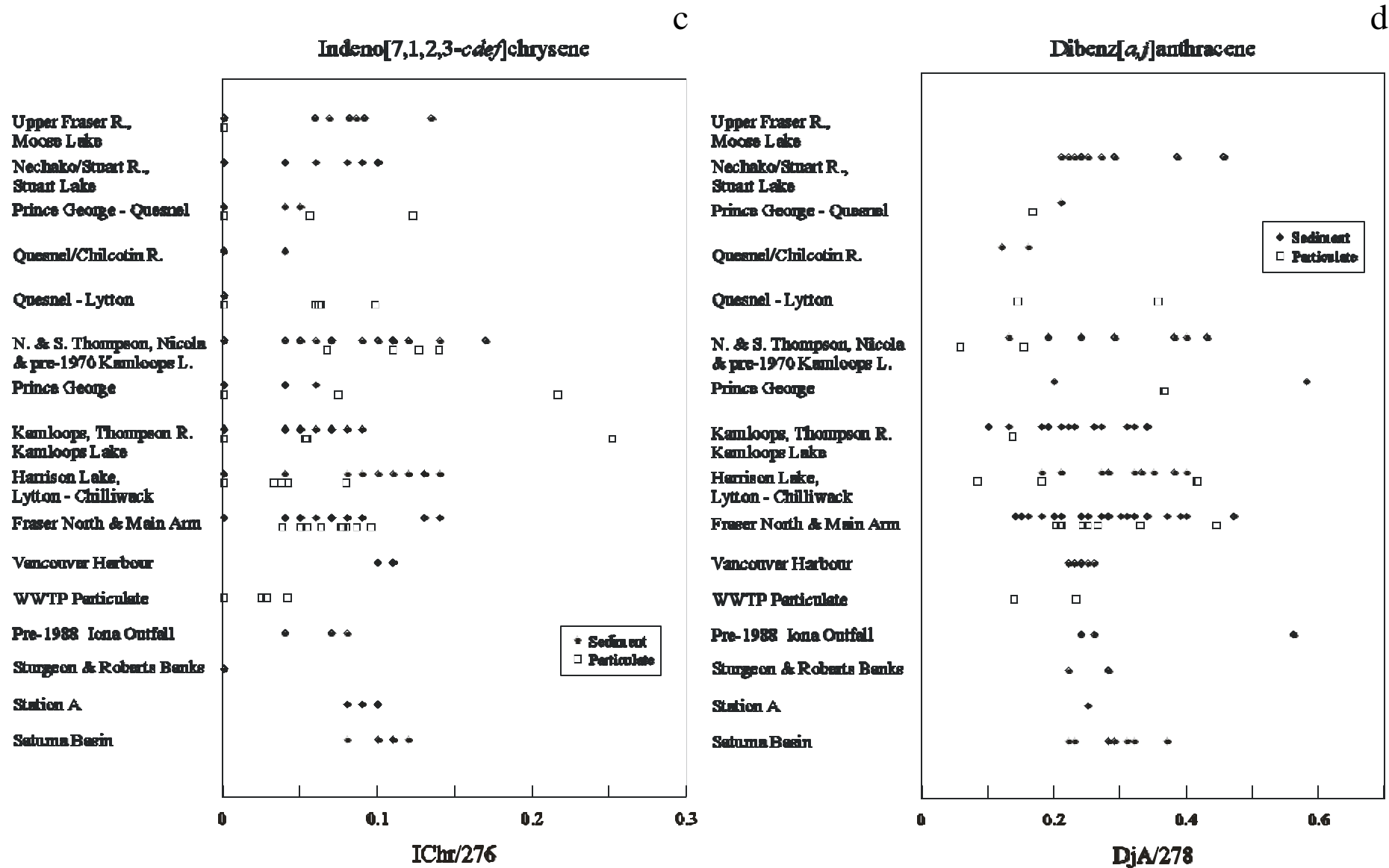


Figure 17. Ratios shown are for (c) indeno[7,1,2,3-*cd*]chrysene (IChr) to IChr plus anthanthrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene (276), and (d) dibenz[*a,j*]anthracene (DjA) to 278.

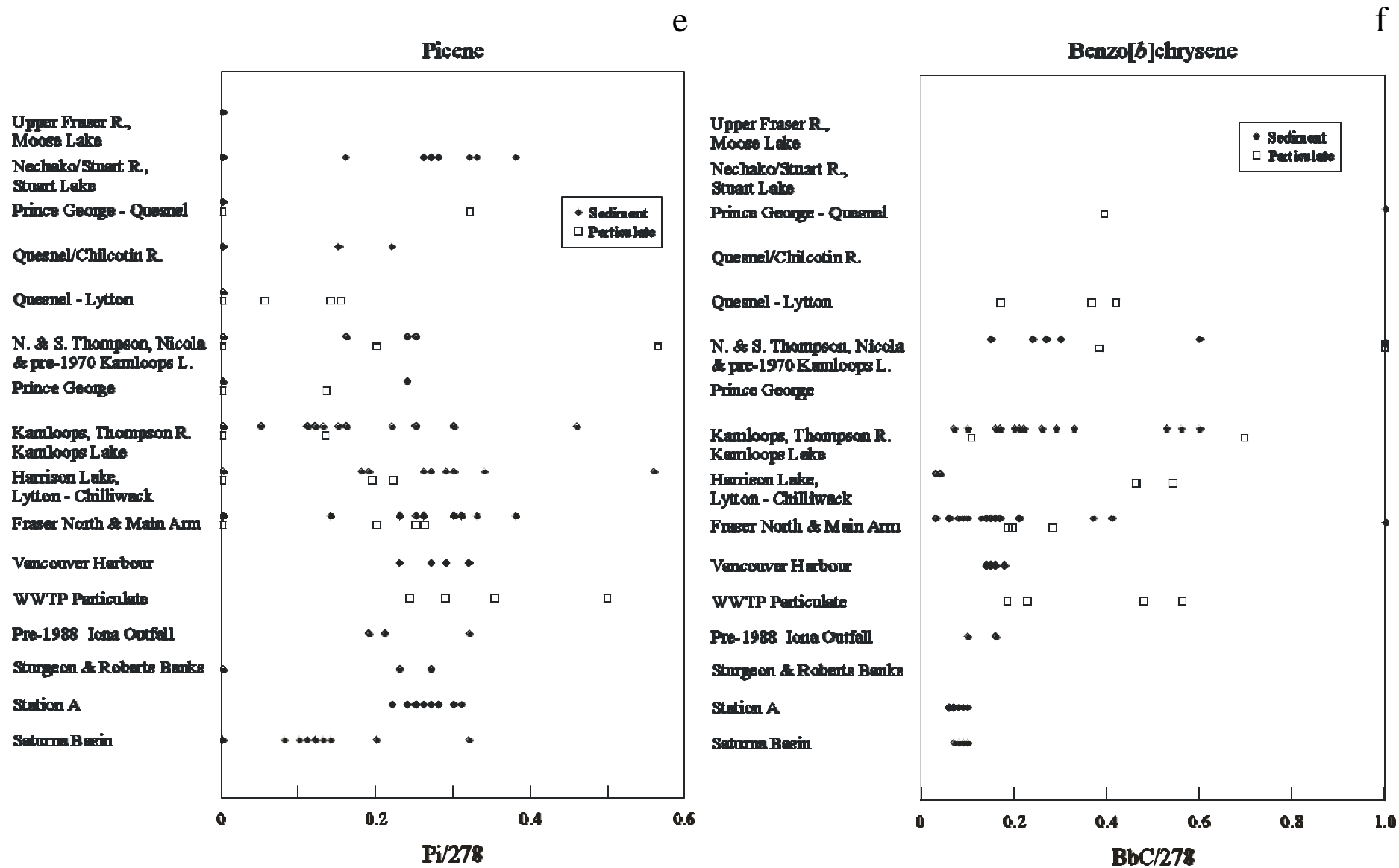


Figure 17. Ratios shown are for (e) picene (Pi) to 278, and (f) benzo[*b*]chrysene (BbC) to 278.

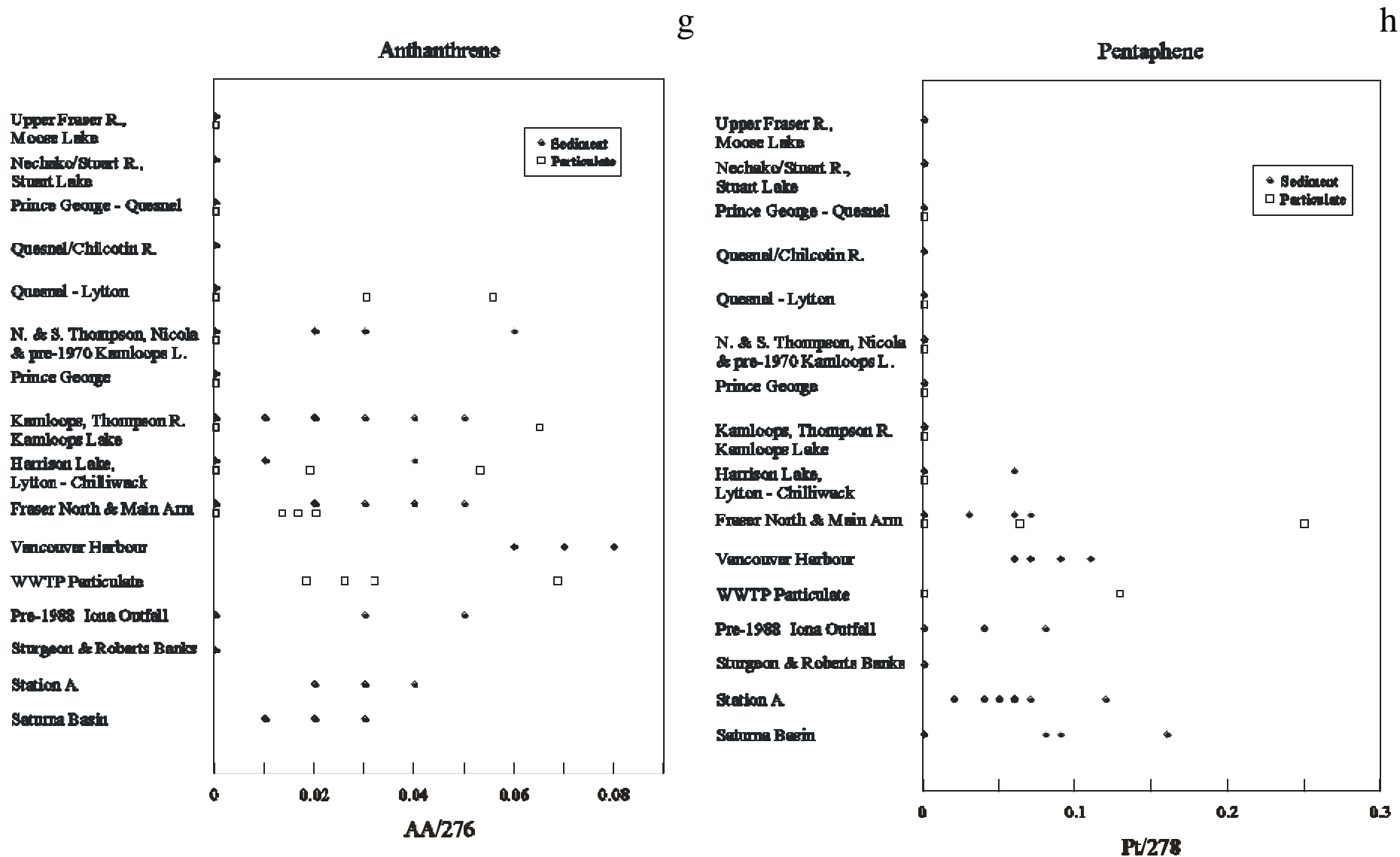


Figure 17. Ratios shown are for (g) anthanthrene (AA) to 276, and (h) pentaphene (Pt) to 278.

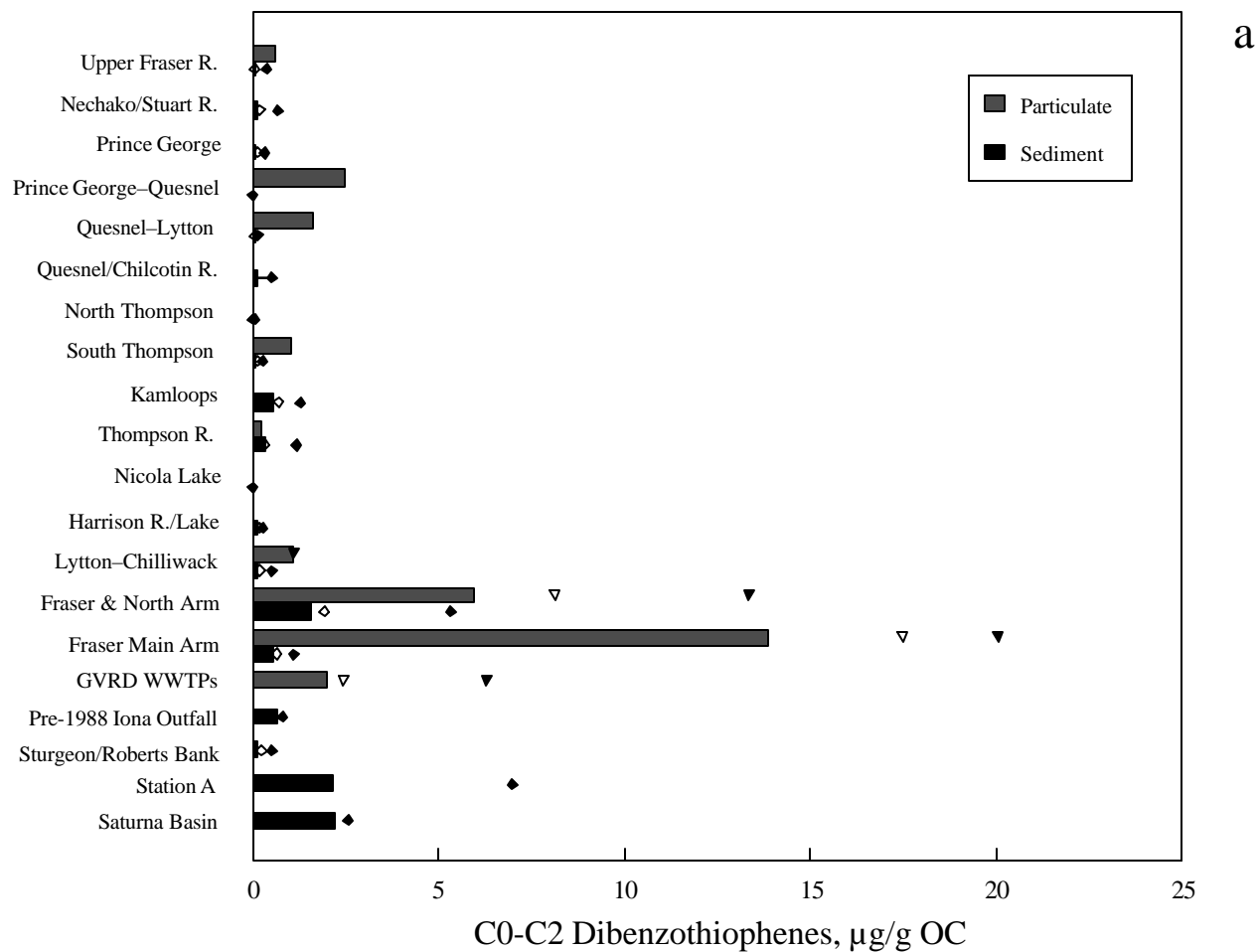


Figure 18. Mean (bar), mean + 1 SE (open symbols) and maximum (filled symbols) concentrations for samples of suspended particulate and sediment from the Fraser River basin and the Strait of Georgia. Shown are (a) concentrations of the C₀-C₂ dibenzothiophenes, and ratios of (b) the C₀-C₂ dibenzothiophenes to the C₀-C₂ phenanthrene/anthracenes plus the C₀-C₂ dibenzothiophenes (D0-D2/P0-P2 + D0-D2) and (c) the C₂ dibenzothiophenes to the C₂ phenanthrene/anthracenes plus the C₂ dibenzothiophenes (D2/P2 + D2).

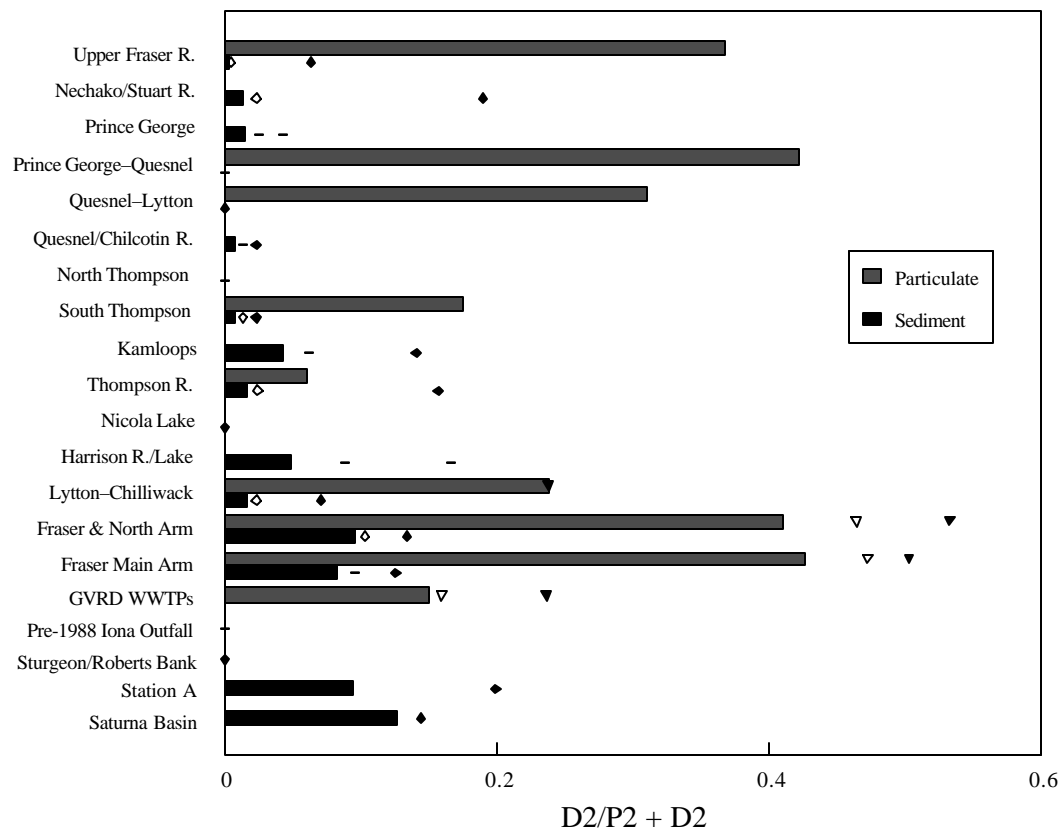
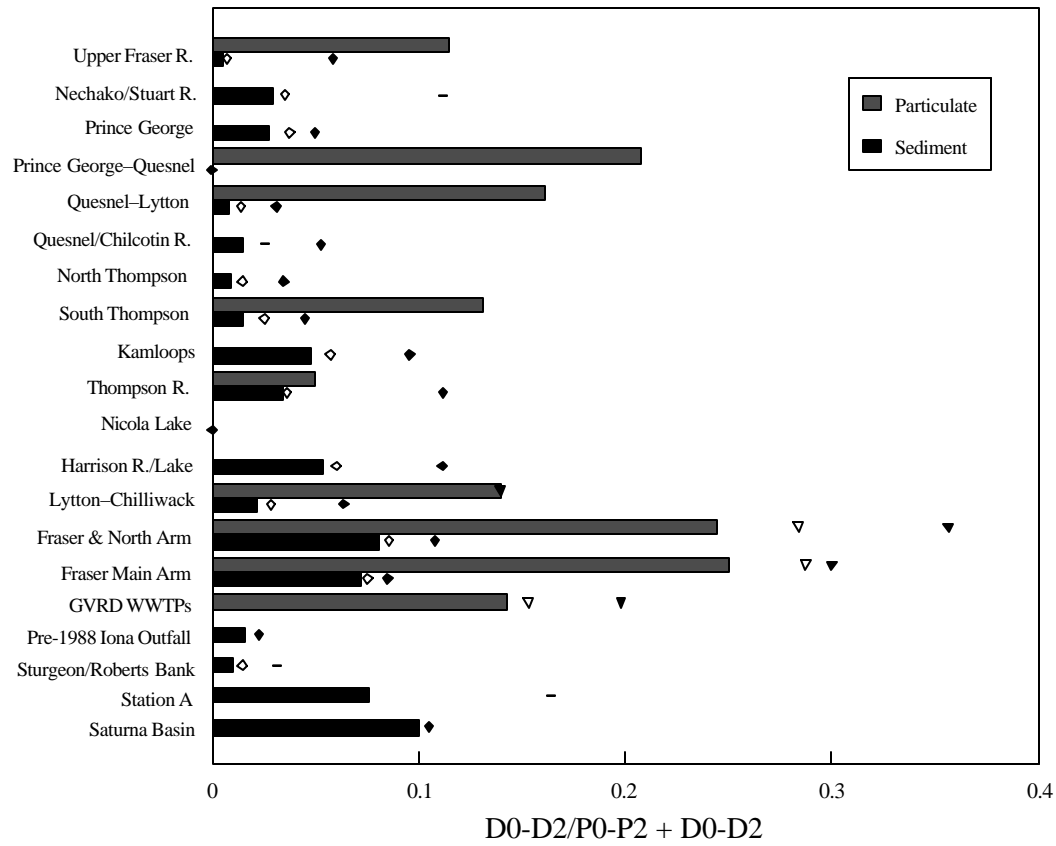


Figure 18 continued.

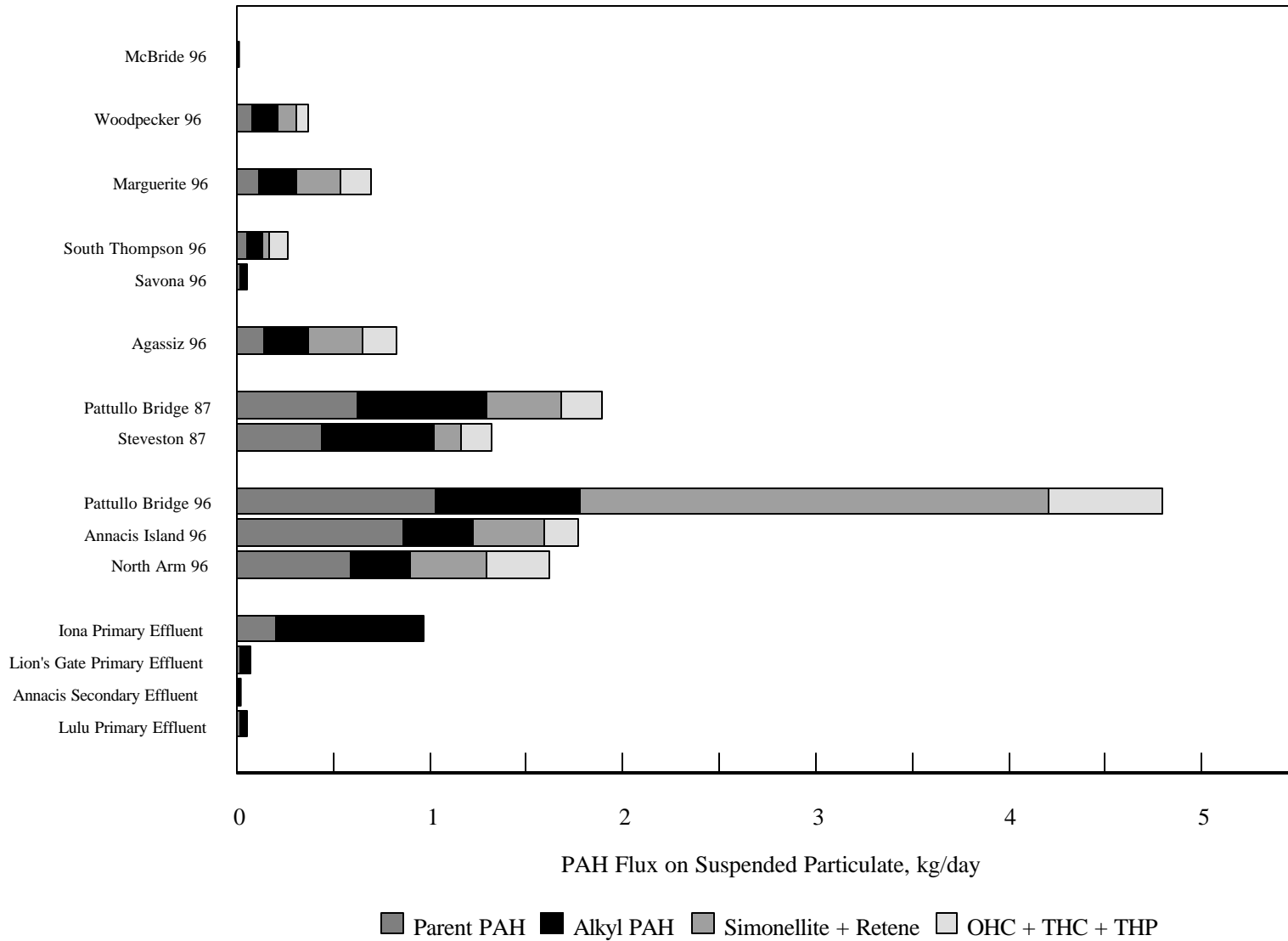


Figure 19. Fluxes of the parent PAHs (Σ 178-278 plus naphthalene, acenaphthylene, acenaphthene and fluorene), the alkyl PAH total (C_1 - C_4 naphthalenes, C_1 - C_3 phenanthrene/anthracenes and C_1 - C_2 dibenzothiophenes), and the higher plant PAHs simonellite, retene and the sum of the methylated tetra- and octahydrochrysenes (THC and OHC, respectively) and tetrahydropicenes (THP) in suspended particulate samples from the Fraser River and the four main GVRD WWTPs.

