Tab 3. Petroleum Hydrocarbons in the Fish and Sediments of NPRA Teshekpuk Lake and the Colville and Ikpikpuk Rivers. April 2007

Petroleum Hydrocarbons in Fish and Sediments of NPR-A: Teshekpuk Lake and Colville and Ikpikpuk Rivers

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Introduction:

Research has recently focused on the environmental levels and potential effects of toxic substances on Native communities within subsistence cultures of the Arctic. For example, this has been a major component of the Arctic Monitoring and Assessment Program (AMAP 1998). Responses to contaminants range from direct hazards to health and survival to more subtle changes in lifestyle patterns (AMAP 1997; Jensen 1998).

Among the least well-examined classes of contaminants along the North Slope of Alaska is the petroleum hydrocarbons (HCs). More specifically, the polycyclic aromatic hydrocarbons (PAHs) represent the most toxic fraction of oil, and sixteen PAHs are included on lists of priority chemical contaminants by the World Health Organization and the U.S. Environmental Protection Agency (EPA). These toxicants may enter local environments in a variety of ways, including natural seeps, discharges from tanks and vessels, loss associated with escalating oil and gas development, and catastrophic spills.

Although, as noted, PAHs have not been well studied in the environment or living organisms of Alaska's North Slope, recent, current, and proposed future oil and gas activities make it vitally important that research and monitoring programs be initiated immediately to create baselines and provide empirical information needed for possible mitigation. Of particular concern are areas within the National Petroleum Reserve-Alaska (NPR-A).

The NPR-A represents the largest single block of publicly owned land in the United States: 23.5 million acres. The area has recognized value for a number of disparate reasons, including as a site of oil and gas exploration and development, a location with diverse and abundant wildlife, and a resource for Alaska Natives (Inupiat people) who have hunted, fished, and lived there for millennia (http://www.audubonalaska.org/m3item5.html). The NPR-A was established originally as the Naval Petroleum Reserve Number 4 by President Harding in 1923, but it was not until 1980 that Congress authorized leasing and development activities for oil. Such activities now fall under the jurisdiction of the Department of the Interior and must be done in ways that ensure protection of "surface values" including wildlife populations. The Minerals Management Service has estimated that the northeastern corner of the NPR-A *alone* contains more than 3 billion barrels of technically recoverable oil and almost 10 trillion cubic feet of gas (http://www.agiweb.org/gap/legis106/npra.html), a huge resource that will provide a challenge in terms of an effective balance between exploration/development and environmental conservation.

Thus, most oil and gas-related activities in the NPR-A are of recent origin. Until recently oil and gas leases had been let for a little more than 5% of the NPR-A (1.3 million acres), but in 2004, 8.8 million acres in the northwestern NPR-A Planning Area were made available for oil and gas leasing (http://www.blm.gov/ak/nepa_arctic/ea06-003.pdf). Of particular concern is the fact that the current no-lease zone to the north and east of Teshekpuk Lake is being reconsidered for future activities (http://www.audubonalaska.org/m3item5.html).

In the face of expanding oil and gas activities, concern continues to exist for several reasons including effects on the internationally important wildlife populations for which the area is well known and the safety and well-being of the Alaska Native communities who continue to use the

NPR-A to hunt and fish for food important to their subsistence lifestyle (Huntington et al. 1998). Some areas of the NPR-A have been the sites of oil and gas development for some time (70 wells to date), and expansion of exploration and development to the west across the Colville River (e.g., Umiat site) has heightened the perceived risk to and concern of local residents regarding chronic and acute PAH pollution.

As summarized recently by Reynolds et al. (2006), multiple benefits derive from a subsistence lifestyle for Alaska Natives, including include facilitating self-definition and self-determination, maintaining communities as close-knit entities, providing economic gain, and promoting good nutrition and health (Egeland et al., 1998; Hild, 2002; Arnold and Middaugh, 2004; Verbrugge and Middaugh, 2004). In some cases, perceptions regarding the possible presence and levels of anthropogenic contaminants in subsistence harvested food have caused a reduction in consumption of traditional foods, followed by documented health effects (Egeland et al., 1998; Arnold and Middaugh, 2004; Verbrugge and Middaugh, 2004). Whereas traditional diets high in marine mammals and fish have historically been suggested to reduce the likelihood of cardiovascular disease (heart attacks and strokes), diabetes, and other adverse health conditions in Alaska Natives, recent changes in dietary preferences have been associated with increased prevalence of these diseases in some Native communities (e.g., Nobmann et al., 1992; Egeland et al., 1998; Hild, 2002; McLaughlin et al., 2004). Verbrugge and Middaugh (2004; page 2) concluded that "the potential risks associated with POP [persistent organic pollutant] exposure through subsistence food consumption are smaller than the risks associated with a decreased us of traditional foods..." The same may be true for other classes of chemical contaminants as well.

To date, most concern has centered around catastrophic or acute events such as oil spills. The direct effects of acute oil pollution could affect socio-economic and cultural activities, as well as include a variety of health effects (http://oils.gpa.unep.org/facts/economy-health.htm). However, in wildlife (e.g., marine mammals) the health effects of chronic oil contamination may also be significant, and could include a range of conditions, such as carcinogenesis and mutagenesis; disruption of immune and endocrine system function; dermal irritation; and other ailments. In light of such possibilities, subsistence communities of the North Slope are concerned that PAHs could enter humans through consumption of a variety of species that constitute important parts of the Inupiat diet. In response to these concerns, coupled with the importance for subsistence and the vulnerability to contamination of the fish stocks of the NPR-A, this project had several objectives, as follows:

- establish baseline values of PAHs in sediments collected from locations in Teshekpuk and Tusikvaak lakes and the Colville and Ikpikpuk rivers (see **Figure 1**);
- examine PAH levels in the muscle (meat) and liver of four fish species (broad whitefish, *Coregonus nasus*; round whitefish, *Prosopium cylindraceum*; burbot, *Lota lota;* lake trout, *Salvelinus namaycush*) commonly consumed by local communities around Teshekpuk and Tusikvaak lakes and the Colville and Ikpikpuk Rivers;
- assess the origin or oil pollution through "fingerprinting" to clarify whether PAHs are primarily from fresh or combusted oil sources; and
- provide our results (presentations, maps, reports) to the scientific community and to local residents.

Although we felt that it is unlikely that current concentrations of petroleum hydrocarbons would be high in the locations we sampled because anthropogenic inputs (spills and runoff) have been minimal to date, it is vital to ascertain contaminant levels and to establish baselines against which to assess effects of future oil inputs. Only with empirical data in hand can informed decisions regarding human health and nutritional risks be made.

Methods:

PAH analyses-Sediments and tissue samples from the four fish species were collected during 2004 and 2005. Tissue samples from net-caught fish included meat and liver that were sub-sampled in the field using fresh solvent-cleaned, stainless steel scalpels for each sample. Each tissue was stored in a separate pre-cleaned glass jar with a Teflon lined lid and placed on ice for transport back to the laboratory. Sediments were collected using a sediment grab and stored as above. Samples were shipped to Mote Marine Laboratory and stored frozen until extraction occurred.

An aliquot from each sample was removed for moisture content analysis. Approximately 30 g each of sediments, 5 g of liver and 10 g of meat tissue were weighed out to the nearest 0.1 g and appropriate polycyclic aromatic hydrocarbon (PAH) internal standards were then added. All samples were extracted using a Dionex ASE 300, extraction system following modified EPA methods (EPA 1998).

The extracts were then evaporated to near dryness, and re-dissolved in 1 ml hexane. Total lipid content was determined gravimetrically for each sample. The extracts were further purified by silica gel-alumina column chromatography. Field blanks, laboratory blanks, matrix spikes and duplicates were included for each set of samples collected.

All extracts were analyzed by a Thermo Finnigan DSQ quadrapole gas chromatograph–mass spectrometer (GCMS) equipped with a 30 m DB-5 fused silica column for qualitative and quantitative identification of 37 individual PAH's, including parent compounds and homologs (**Table 1**). Oven temperature program was held at 50°C for two minutes and then programmed from 50°C to 280°C at 6°C min^{-1} and held at 280°C for 15 minutes with helium as the carrier gas. The mass spectrometer scanned from mass 40-500 in 0.5 sec at an ionization potential of 70 eV. All mass spectral data were compared to spectra produced by authentic standards and to previously published library spectra and by quantifying the base peak ion of each PAH against the base peak of the internal standard. The laboratory minimum detectable amounts have been calculated at 10 ng/g. Laboratory analytical precision has been previously determined in our laboratory by making replicate injections of PAH standards to ascertain reproducibility. Standard deviations for the standards used indicated a maximum laboratory error of ± 11%, and an average standard deviation of ± 3%.

Bile Metabolites -Fish bile samples were collected in cryovials during dissection and snap frozen. Samples were shipped in a liquid nitrogen shipping dewar and stored in a -80^{0}C Freezer until analysis. The samples were then thawed and placed in autosampler vials with glass inserts (150 µL). Sub-samples were taken for bile weights with 5 µL samples averaged.

Standards were obtained from several sources. The parent compounds (naphthalene, phenanthrene, and benzo-*a*-pyrene) were purchased from Absolute Standards. The BAP metabolite standards (1-OH BAP and 3-OH BAP) were purchased from Midwest Research Institute. The naphthalene and phenanthrene metabolite standards (1-naphthol, 2-naphthol, 9-phenanthrol, and 2-phenylphenol) were purchased from Acros Organics (Fisher Scientific).

An aliquot of 2.1 µL of bile was injected directly onto a Waters PAH C18 5µm – 3 x 250 mm column with a Waters Sentry Guard Column – Symmetry C18 5µm 3.9 x 20 mm and an Upchurch Scientific stainless steel Frit Filter 0.5 µm pre-filter. The samples with eluted with a linear gradient from 100% water (with 5 µL/L Acetic Acid) to 100% methanol at a flow of 0.510 mL/min. The total run time for each sample was 60 minutes. The column temperature was 50^{0}C.

Every sample was run in duplicate, once for naphthalene-like and BAP-like metabolites and then a second time for phenanthrene-like metabolites. Two methanol blanks were run between each sample. Standards were run in triplicate before and after a sample set (10 samples). During each run, the FLD Wavelengths were set to analyze for each set of compounds based upon published excitation/emission wavelengths including: naphthalene-like metabolites (Ex/Em 293/335), phenanthrene-like metabolites (Ex/Em 260/380) and BAP-like metabolites (Ex/Em 380/430) as published previously (Krahn et al., 1986; da Silva et al., 2006).

Results:

Year 1

Sediment-Triplicate sediment samples were collected and analyzed from the following locations (**Figure 2**):

1) Ikpikpuk South
2) Ikpikpuk North
3) Joe Creek
4) Teshekpuk Lake (two sites)
5) Trib 3
6) Itta Camp (only one sample collected at this location).

The average total PAH concentrations (in dry wt.) ranged from 3.55 to 6.62 ug/g (**Table 2**, **Figure 2**). The highest average values were found in the North and South Ikpikpuk River samples, although they were not significantly higher than the other sediment samples analyzed from the 2004 collections. **Appendix I** shows the PAH distribution patterns for samples taken from these sediment collection locations. In general, the distribution profiles of the PAHs found in the Trib 3 and Itta Camp and two of the Joe Creek and one of the Teshekpuk Lake samples show a dominance of the phenanthrene/anthracenes, naphthalenes and fluoranthene/pyrenes

followed by the other monitored series' of PAHs, with contributions from most of each of the homologs within each series. The profiles from the North and South Ikpikpuk and five of the Teshekpuk Lake sediments were similar to each other but different from the samples above. Although there was a predominance of the same PAH series' (phenananthrene/anthracenes, naphthalenes and fluoranthene/pyrenes) there are few of the other monitored PAHs present. Additionally, the homolog distributions are weighted towards the less substituted PAHs rather than representing all alkyl substituted homologs as was generally found in the other sediment samples. Sample collection GPS station locations for all samples in years 1 and 2 can be found in **Table 3**.

Fish tissue- Fish liver and meat tissue were collected from multiple fish and analyzed individually for PAHs from the following locations (**Figures 3** and **4**):

1) Ikpikpuk South
2) Joe Station
3) Joe Creek
4) Teshekpuk Lake
5) Trib 3

The results of these analyses indicate that fish meat samples had very low levels of detectable PAHs present and were found only in the broad whitefish collected in year 1 (**Table 2**, **Figure 3**). The total PAH concentrations ranged from undetected to 0.07 ug/g (dry wt.) with the highest values found in Joe Creek fish samples. Liver, sub-sampled from the fish above, had average levels of PAHs ranging from undetected to 0.27 ug/g (dry wt.) in the Trib 3 samples (**Table 2, Figure 4**). Generally, few homologs of the naphthalene series were found in either the liver or the meat of the broad whitefish; however, some of the liver samples collected from Joe Creek and Trib 3 also had low, but measurable levels of some of the higher molecular weight PAHs (**Appendix I**).

Year 2

Sediment-Triplicate sediment samples were collected and analyzed from the following locations (**Figure 5**):

1) Puvisuk
2) Uyagagvik Nigliq
3) CD2 location 1
4) CD2 location 2
5) Fish Creek
6) Woods Camp
7) TL003
8) TL004
9) TL005
10) Trib 3 (two sediment cores also taken from this location and sectioned into 25% depths for each core and analyzed individually).
11) Ikpikpuk DL Camp
12) TLSB2
13) Tesh Offshore Camp
14) DANLE

Sediment PAH concentrations for the Teshekpuk Lake sites and the Ikpikpuk River stations were relatively low, ranging from 0.03 to 2.35 ug/g (dry wt.; **Table 2, Figure 5**). Much higher concentrations were measured in the eastern locations near and on the Colville River. These values ranged from 3.04 to 12.0 ug/g (dry wt.), with the highest levels found at the Uyagagvik Nigliq and Puvisuk sampling sites with 8.49 and 12.0 ug/g (dry wt.), respectively.

The individual PAH distributions found in the Teshekpuk Lake, Tesh Offshore Camp and Trib 3 sediments were dominated by the naphthalene series almost exclusively; however, two of the Tesh Offshore samples had trace amounts of some of the higher ringed PAHs (**Appendix I**). The profiles found at the Puvisuk and Uyagagvik Nigliq station locations were very different. These sediments had contributions of almost all homologs of each series of PAHs monitored, with a predominance of the phenanthrene/anthracenes, naphthalenes and fluoranthene/pyrenes followed closely by the fluorenes, dibenzothiophenes and the remaining targeted PAHs respectively. This general profile was also found in the sediments from Woods Camp and CD2; however there was little evidence of the fluorene and dibenzothiophene series of homologs in these samples, which were present in the Puvisuk and Uyagagvik Nigliq samples. Sediments from Fish Creek and Ikpikpuk DL Camp contained PAHs with relatively high amounts of the naphthalenes compared with the other PAHs in these samples. The less substituted homologs were the dominant members of those series. The distributions found in the DANLE and Trib 3 sediment core samples shared similar PAH profiles, with no measurable amounts of the naphthalene series and small amounts of the phenanthrene/anthracenes and fluoranthene/pyrenes. The parent compounds and the less substituted members of the homologous series predominated. The profiles did not change with depth in the sediment core samples with contributions mainly from the parent compounds (**Appendix I**).

Fish tissue and bile- Fish liver, meat and bile were collected from multiple fish and analyzed individually for PAHs (for tissue) and PAH metabolites (for bile) from the following locations (**Figures 6 and 7**):

1) Puvisuk
2) Ruth Nukapigak
3) CD2 location 1
4) CD2 location 2
5) Woods Camp
6) TL003
7) TLSB2
8) Ikpikpuk DL Camp
9) TLSB2
10) 600/611 and DANLE

No PAHs were detected in fish liver, meat, or bile.

Conclusion:

Aromatic hydrocarbons from petrochemical combustion or from direct petroleum inputs can be characterized by the extent of alkylation. Those aromatics originating from direct petroleum inputs have a high degree of alkylation and those from combustion sources, a lesser degree. This lower degree of alkylation results from the cleaving of the substituted side chains during high temperature combustion (Wetzel and Van Vleet 2003). These homolog distributions can be used to discriminate petrogenic sources of PAHs from combustion sources in sediments.

There were several different PAH profiles found in this study, suggesting different or a combination of sources for petroleum inputs. In sediments from several 2004 locations [Trib 3, Itta Camp, Joe Creek (two locations) and one location from Teshekpuk Lake] had signatures suggesting petrogenic inputs. Those samples from North and South Ikpikpuk River and the remaining Teshekpuk Lake sediments had signatures that were higher in the two-ringed naphthalene series, indicating perhaps contributions from boat fuel, and some of the higher ringed PAH parent compounds and less substituted members of those series' suggesting pyrogenic (combustion) sources.

This was the same type of profile found in the 2005 sediment samples taken from Trib 3 and Teshekpuk Lake. The highest concentrations of PAHs were found in samples from Puvisuk and Uyagagvik Nigliq with the presence of all homologs in a typical petroleum signature indicative of petroleum sources. Levels of contamination were comparatively moderate at CD2 and Woods Camp and the signatures were slightly different, lacking measurable amounts of the fluorene and dibenzothiophenes, suggesting that perhaps there may have been a different source of oil input to those areas. The Fish Creek and DL Camp sediments were similar in PAH signature to those found in most of the 2004 Teshekpuk Lake and Ikpikpuk River samples. The samples from DANLE and from the two cores taken from Trib 3 had characteristics of combustion sources of PAH contamination.

The Colville River, which drains a large part of the Brooks range, is the largest river which empties into the Beaufort Sea. The surrounding river area does not have well-developed soil and that soil transported via the Colville River carries with it fractions from coal and oil from natural seeps and oil-shale outcrops which occur in this watershed area (Steinhauer and Boehm 1992). This may help to explain in part the higher levels of PAH concentrations found in the Puvisuk, Uyagagvik Nigiq and CD2 locations.

Comparisons to previous sediment petroleum contamination studies can be made with the results from the current study to assess the degree of contamination that exists in this sensitive environment. This Arctic area is unique in its environmental characteristics, making it difficult to find suitable comparisons. However, the highest values found in this study are comparable to the lowest values found in more industrialized areas (Beg et al. 2002; Wetzel and Van Vleet 2003) and higher than PAH values found in a study of Beaufort Sea and Colville River mouth sediments (Steinhauer and Boehm 1992; Valette-Silver et al. 1999).

The assessment of sediments for evidence of contamination is a practical means of appraising the health of an environment. However, in general, this gives only a partial picture of the

complexities involved in a dynamic ecosystem. It is very important to assess biological contaminants loads of a system as well. In this case, the biota examined were broad whitefish, burbot, and lake trout. Overall, the body burdens of PAH contamination were very low and the main PAHs found in the 2004 tissues were from the highly soluble naphthalenes, although some liver samples from Trib 3 also had some of the parent compounds of a few of the higher ringed PAHs. There were no PAHs detected in the 2005 fish samples nor were any PAH metabolites found in any of the fish bile samples.

In order to put this into a biological assessment framework to evaluate possible effects on the environment, there are two guideline values that are commonly used for this kind of biological effects evaluation (Long et al. 1995). They are effects range-low (ERL) and effects range-median (ERM), which delineate concentration ranges for a particular chemical. The concentrations below the ERL value represent a minimal-effects range; a range intended to estimate conditions in which effects would be rarely observed. Concentrations equal to and above the ERL, but below the ERM, represent a possible-effects range within which effects would occasionally occur. Finally, the concentrations equivalent to and above the ERM value represent a probable-effects range within which effects would frequently occur (Long et al. 1995). In comparing the individual concentrations for each of the PAHs identified (**Appendix II**) there are several incidences in which some of the targeted PAHs have exceeded the ERL (**Table 4**). This is the minimum range where effects would rarely be observed. In no instance did any of the individual PAHs meet or exceed the ERM or probable effects limit.

The highest levels found in the consumable part of the fish, the meat, were much less than the levels found by the USEPA to produce some effects on rats (USEPA 1998). Therefore it appears that there may be no risk associated with the consumption of the broad whitefish, burbot, or lake trout based upon the samples taken and analyzed during this study. Food can be contaminated by environmental PAH that are present in air (by deposition), soil (by transfer) or water (by deposition and transfer), and during processing and cooking. The natural and anthropogenic sources of PAH in the environment are numerous. PAH compounds are emitted from a number of environmental sources, such as processing of coal, crude oil, petroleum, natural gas, production of aluminum, iron and steel, heating in power plants and homes (oil, gas, charcoal-fired stoves, wood stoves), burning of refuse, wood fires, and motor vehicle exhausts.

A 2002 report by the European Commission on Health and Consumer Protection on the risks to human health from PAHs in food states that except for naphthalene, there are only a limited number of studies available on the acute oral toxicity of PAHs. The LD_{50} values indicate that the acute oral toxicities of PAHs are moderate to low (European Commission Scientific Committee on Food 2002). The results of available oral short-term toxicity studies on PAHs are summarized in **Table 5**. A number of PAHs have been demonstrated to be genotoxic and carcinogenic. Therefore, the existence of a threshold cannot be assumed and the Committee could not establish a safe exposure limit. However, dietary assessment studies suggest that consumption of these PAHs is much less than the no observable adverse effects level (NOAEL). It recommended that exposures to PAH should be as low as reasonably achievable.
There will likely be an expansion of drilling in the NPR-A region in the future. Because of this and because of the sensitivity of these lands due to their subsistence and environmental importance, continued monitoring studies are recommended for the future. Establishing

comprehensive baselines in the near future will permit scientists to monitor changes in levels and sources of PAHs in sediments and in subsistence foods for Alaska Natives. Just as early detection of cancer is a key to successful treatment, early detection of contaminant problems and identification of likely sources can permit mitigation to protect a unique ecosystem, the wildlife that live there, and the Alaska Natives and others who depend on a healthy environment.

Products to date:

Activities related to this study have been described in a number of fora, ranging from international and national conferences to a local presentation to residents of Barrow, Alaska. To date, the following presentations have dealt, in part or entirely, with the results of this project:

Reynolds, J.E., III and D.L. Wetzel. 2005. Bowhead whales, bearded seals, and Alaska native health. Barrow Arctic Science Consortium Outreach Series (supported by National Science Foundation), Inupiat Heritage Center, 3 May.

Reynolds, J.E., III, D.L. Wetzel, C. Hanns, P. Mercurio, and T.M. O'Hara. 2005. Analyses of polycyclic aromatic hydrocarbons in sediments, fish and marine mammals from the North Slope of Alaska. Proc. International Symposium on Oil and Gas Activities in the Arctic. Organized by Arctic Monitoring and Assessment Programme (AMAP), 13-15 September 2005, St. Petersburg, Russia: 594-598.

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Figures
&
Tables

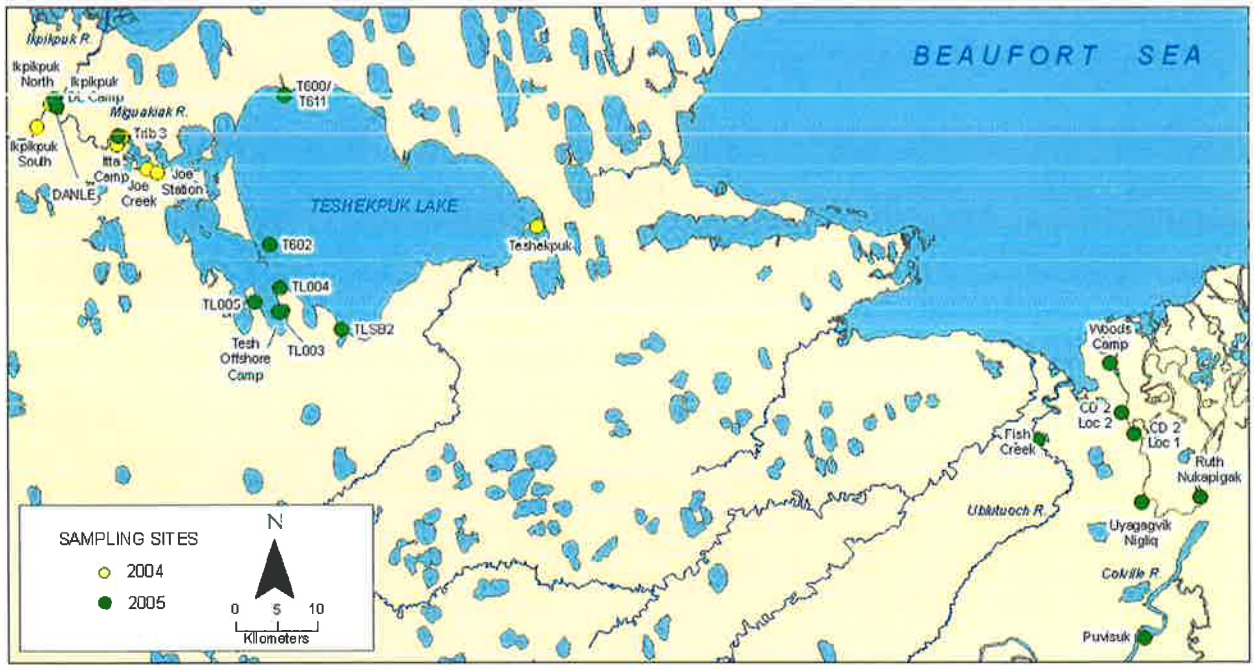


Figure 1. All sample station locations for the two year 2004/2005 NPRA fish and sediment study.

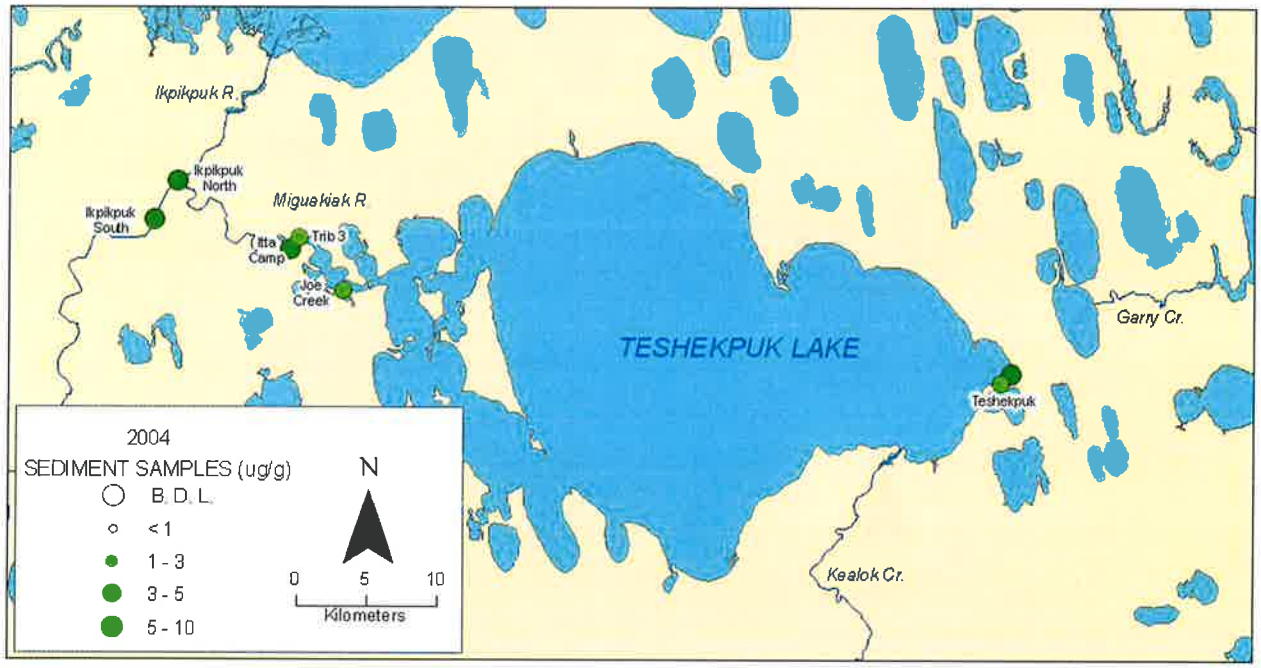


Figure 2. Total PAH concentrations and locations for sediment samples collected in 2004 for the NPRA fish and sediment study.

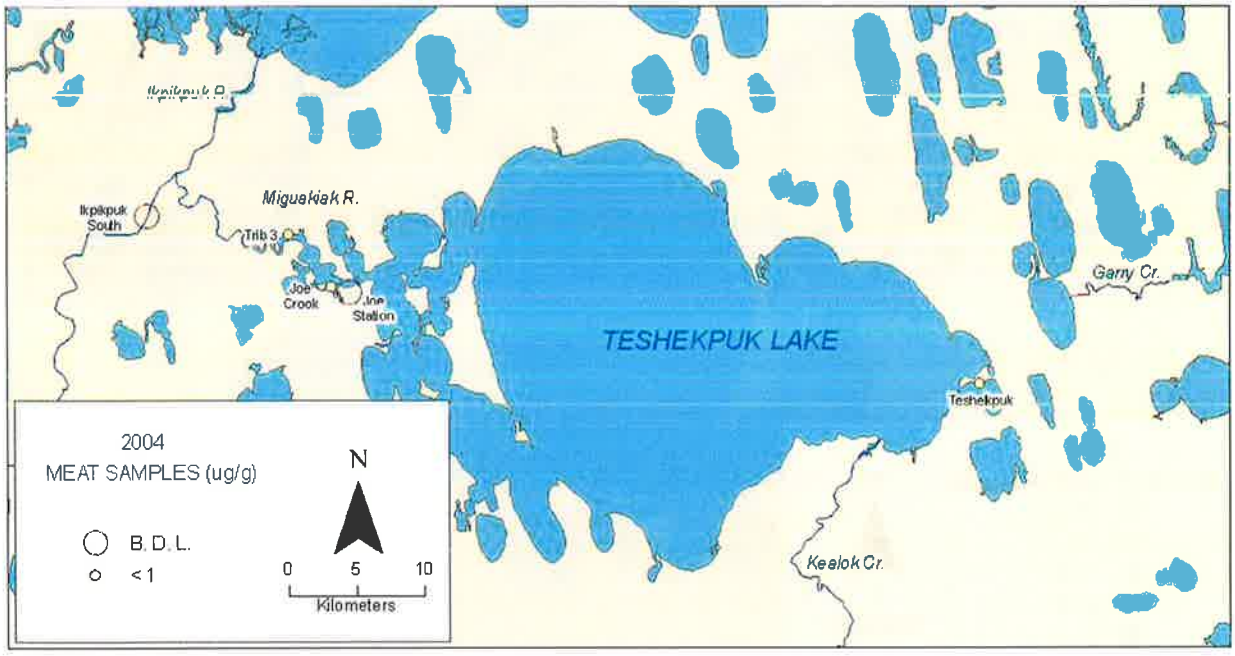


Figure 3. Total PAH concentrations and locations for fish meat samples collected in 2004 for the NPRA fish and sediment study

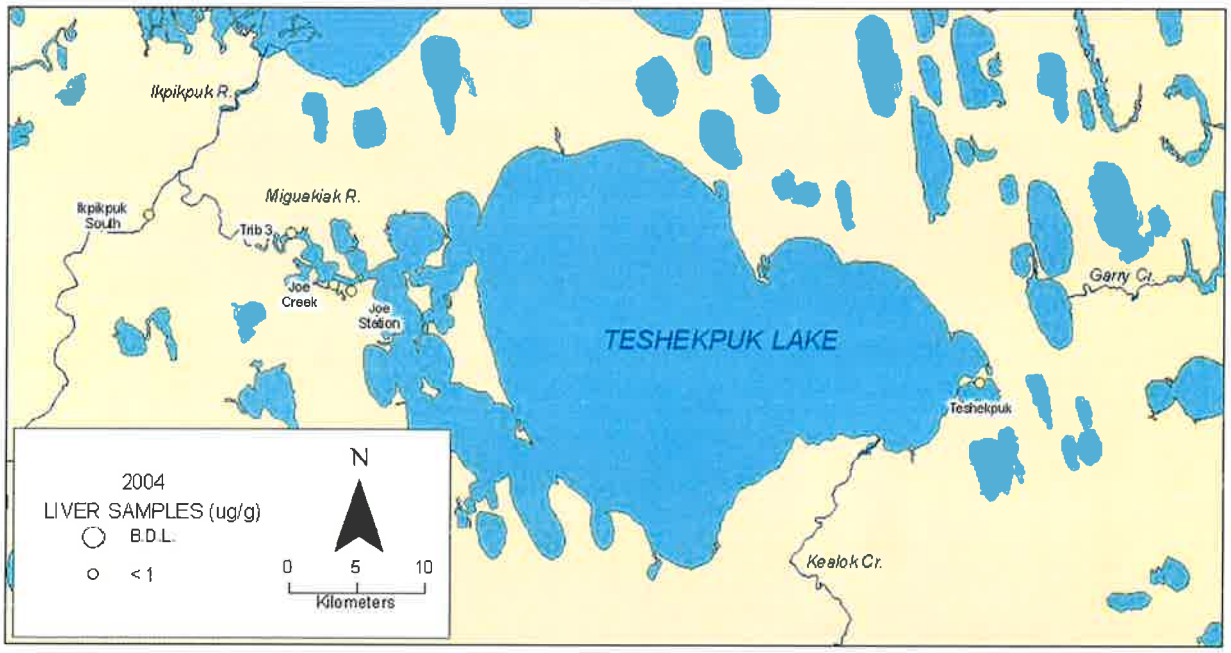


Figure 4. Total PAH concentrations and locations for fish liver samples collected in 2004 for the NPRA fish and sediment study

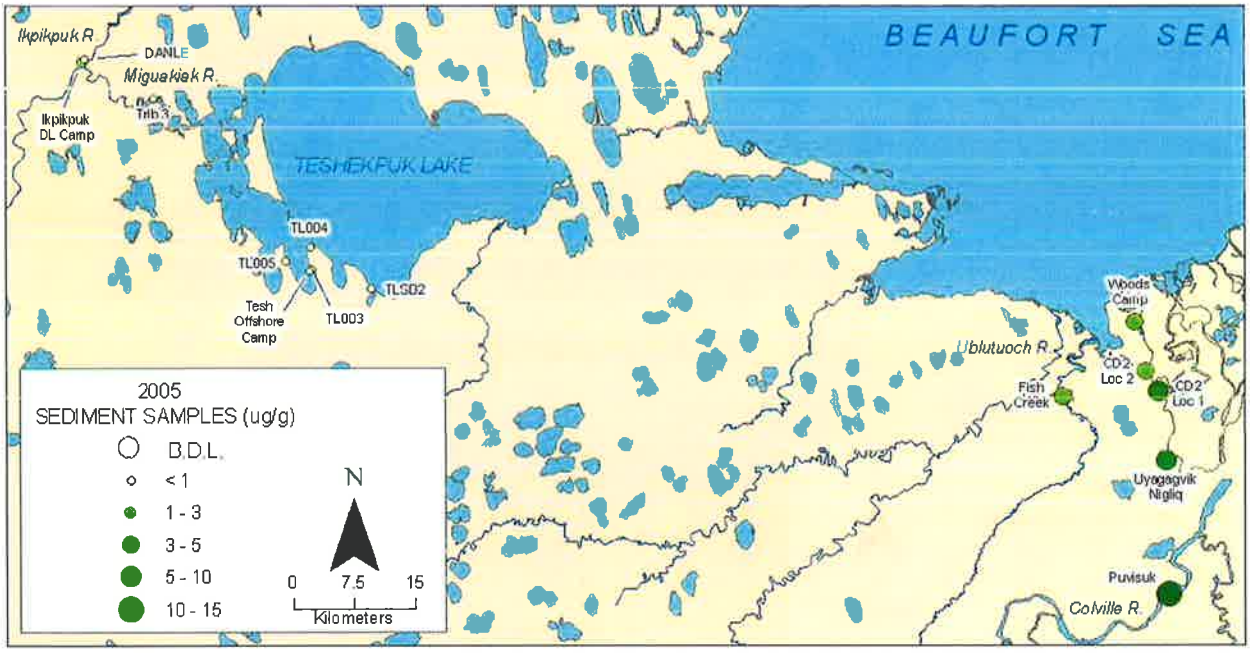


Figure 5. Total PAH concentrations and locations for sediment samples collected in 2005 for the NPRA fish and sediment study

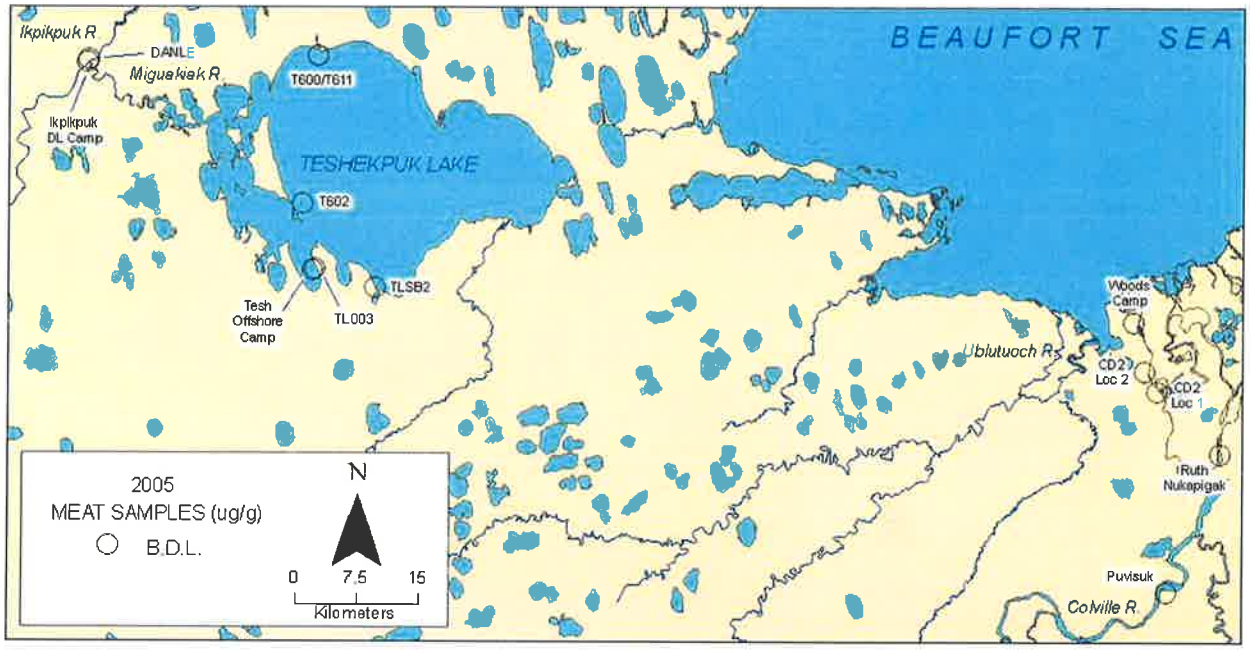


Figure 6. Total PAH concentrations and locations fish meat samples collected in 2005 for the NPRA fish and sediment study

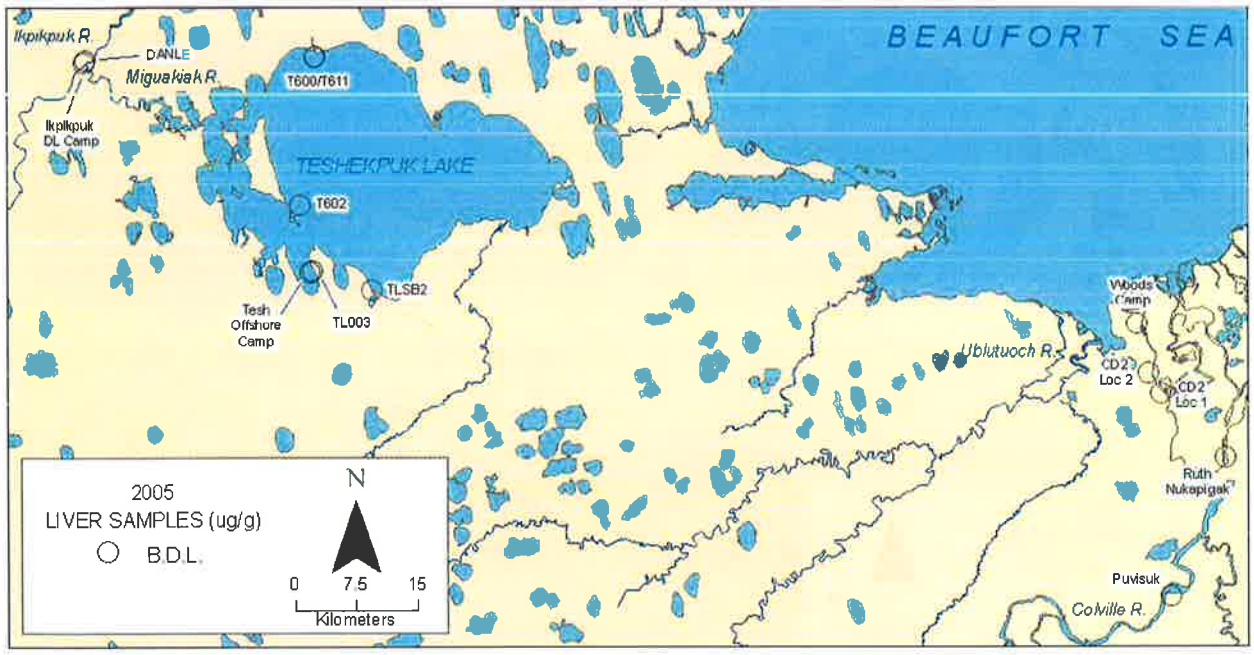


Figure 7. Total PAH concentrations and locations fish liver samples collected in 2005 for the NPRA fish and sediment study

Table 1. Selected polycyclic aromatic hydrocarbons monitored in this study
➢ naphthalene (C_0-C_4)
➢ fluorene (C_0-C_4)
➢ dibenzothiophene (C_0-C_4)
➢ anthracene*
➢ phenanthrene (C_0-C_4)
➢ fluoranthene*
➢ pyrene (C_0-C_4)
➢ benzo(a)anthracene*
➢ chrysene (C_0-C_4)
➢ benzo(a)pyrene
➢ benzo(e)pyrene
➢ benzo(k)fluoranthene
➢ benzo(b)fluoranthene

•The C_1-C_4 homologs of these PAHs are reported as combined C_1-C_4 homologs with the succeeding PAHs (e.g., C_1-C_4 homologs of phenanthrene reported as combined C_1-C_4 homologs for phenanthrene + anthracene). The unsubstituted parent homolog is C_0, and C_1-C_4 are the substituents containing from one to four carbon atoms in the attached side chains.

Table 2. Average polycyclic aromatic hydrocarbon concentrations (ug/g dry wt) per station location for the NPRA fish and sediment study.
(*--- = no sample taken at this location; n= the number of samples taken)

Year 1				
Location	**Sediment**	**Fish Meat**	**Fish Liver**	**Bile**
Ikpikpuk South	5.80 (n=3)	0.00 (n=1)	0.02 (n=1)	----
Ikpikpuk North	6.62 (n=3)	-----*	----	----
Joe Creek	3.59 (n=3)	0.07 (n=10)	0.17 (n=10)	----
Teshekpuk Lake Site 1	3.55 (n=3)	0.04 (n=3)	0.09 (n=3)	----
Teshekpuk Lake Site 2	5.89 (n=3)	----	----	----
Trib 3	4.69 (n=3)	0.03 (n=3)	0.27 (n=3)	----
Itta Camp	5.67 (n=1)	----	----	----
Joe Station	----	0.00 (n=2)	0.12 (n=2)	----
Year 2				
Location				
Puvisuk	12.00 (n=3)	0.00 (n=15)	0.00 (n=15)	0.00 (n=13)
Uyagagvik Nigilq	8.49 (n=3)	----	----	0.00 (n=12)
CD2 Loc 1	6.10 (n=4)	0.00 (n=9)	0.00 (n=9)	0.00 (n=8)
Fish Creek	3.04 (n=3)	----	----	----
Woods Camp	3.04 (n=3)	0.00 (n=7)	0.00 (n=7)	0.00 (n=10)
CD2 Loc 2	4.07 (n=3)	----	----	----
TL003	0.07 (n=3)	0.00 (n=13)	0.00 (n=13)	0.00 (n=14)
TL005	0.07 (n=3)	----	----	0.00 (n=2)
TL004	0.14 (n=3)	----	----	----
Trib 3	0.15 (n=3)	----	----	----
Ikpikpuk DL Camp	2.35 (n=3)	0.00 (n=7)	0.00 (n=7)	0.00 (n=5)
TLSB2	0.03 (n=3)	0.00 (n=11)	0.00 (n=11)	0.00 (n=9)
Tesh offshore Camp	0.34 (n=3)	0.00 (n=3)	0.00 (n=3)	0.00 (n=3)
DANLE	0.37 (n=3)	----	----	----
600/611, 602 and DANLE	----	0.00 (n=9)	0.00 (n=9)	0.00 (n=9)
Ruth Nukapigak Site	----	0.00 (n=11)	0.00 (n=11)	0.00 (n=9)

Table 3. GPS location for sampling sites for the NPRA fish and sediment study. GPS values reported in decimals.	
Year 1	
Joe Station	70.6308 -154.1625
Teshekpuk	70.5666 -152.9333
Ikpikpuk South	70.6812 -154.5580
Ikpikpuk North	70.7063 -154.5148
Joe Creek	70.6350 -154.1966
Trib 3	70.6700 -154.2800
Teshekpuk Lake Site 1	70.5666 -152.9333
Teshekpuk Lake Site 2	70.5666 -152.9333
Itta Camp	70.5016 -154.0533
Year 2	70.0884 -151.0312
Puvisuk	70.2387 -151.02008
Uyagagvik Nigliq	70.3160 -151.0338
CD 2 location 1	70.3950 -151.1012
Woods Camp	70.3149 -151.3404
Fish Creek	70.3403 -151.0734
CD 2 location 2	70.4767 -153.8485
TL003	70.4862 -153.8485
TL005	70.5018 -153.7670
TL004	70.6700 -154.2786
Trib 3	70.7095 -154.5061
Ikpikpuk DL camp	70.4557 -153.5712
TLSB2	70.4752 -153.7718
Tesh offshore Camp	70.5500 -153.8000
T602	70.7172 -153.7497
T600/T611	70.7126 -154.5026
DANLE	70.2416 -150.83667
Ruth Nukapigak Site	70.0884 -151.0312

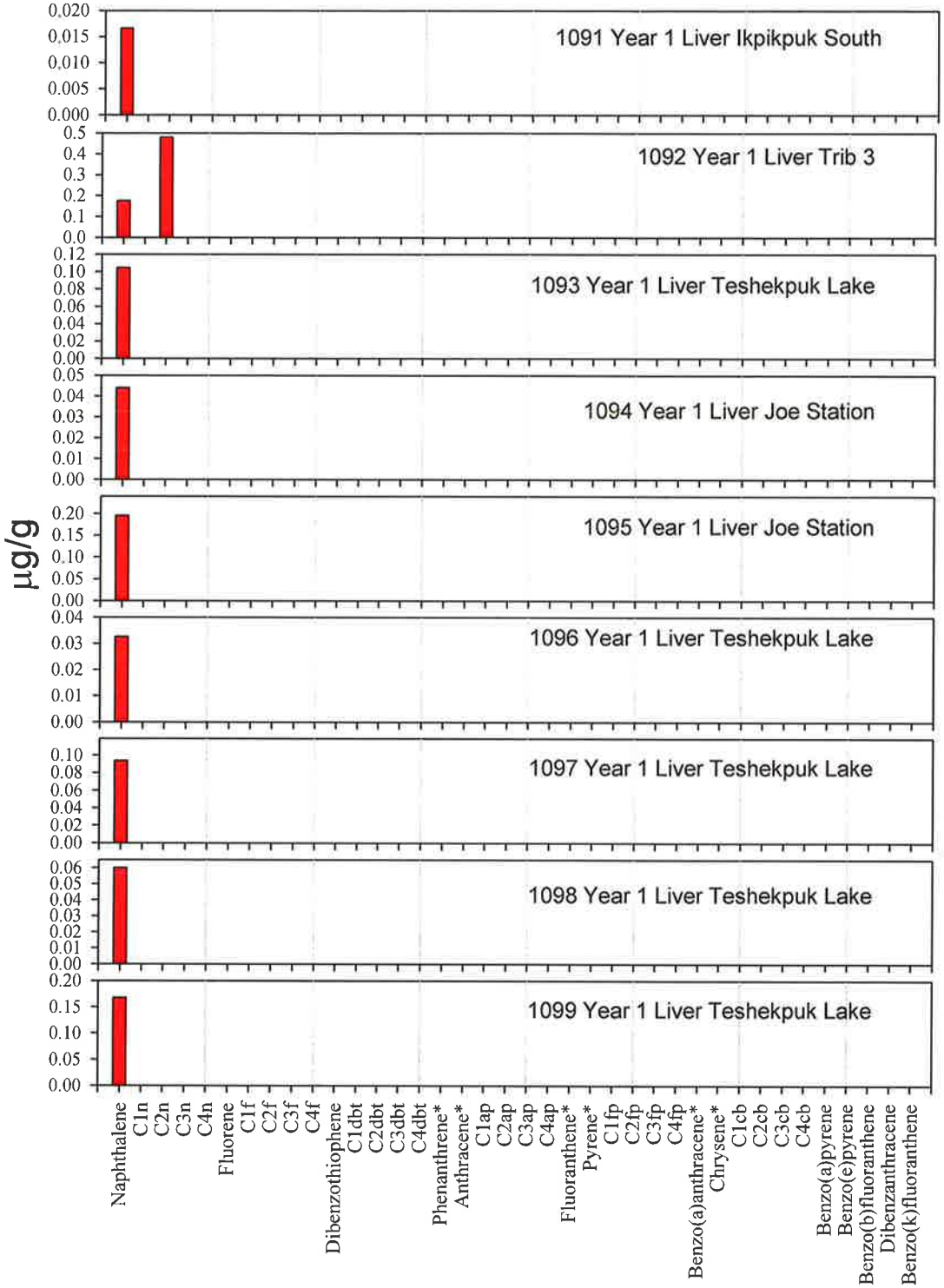
Table 4. Effects range low (ERL) and effects range median (ERM) guidelines of biological effects defined by Long et al. (1995).

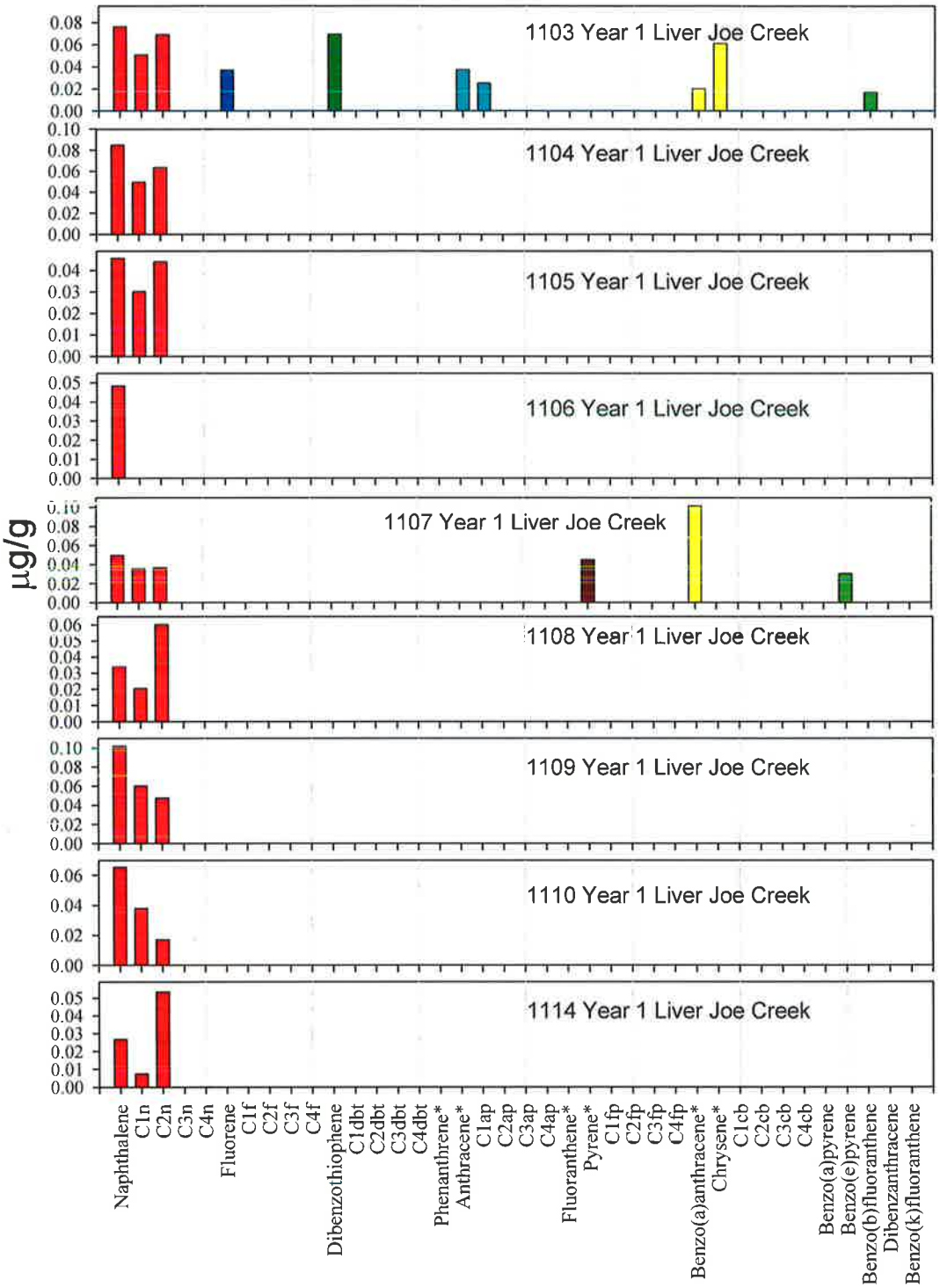
	Guidelines (ug/g dry wt)	
	ERL	ERM
naphthalene	0.16	2.10
2-methylnaphthalene	0.07	0.67
fluorene	0.02	0.54
phenanthrene	0.24	1.50
anthracene	0.85	1.10
fluoranthene	0.60	5.10
pyrene	0.67	2.60
benzo(a)anthracene	0.26	1.60
chrysene	0.38	2.60
benzo(a)pyrene	0.43	1.60
dibenzanthracene	0.63	2.60
Sum PAH	4.02	44.79

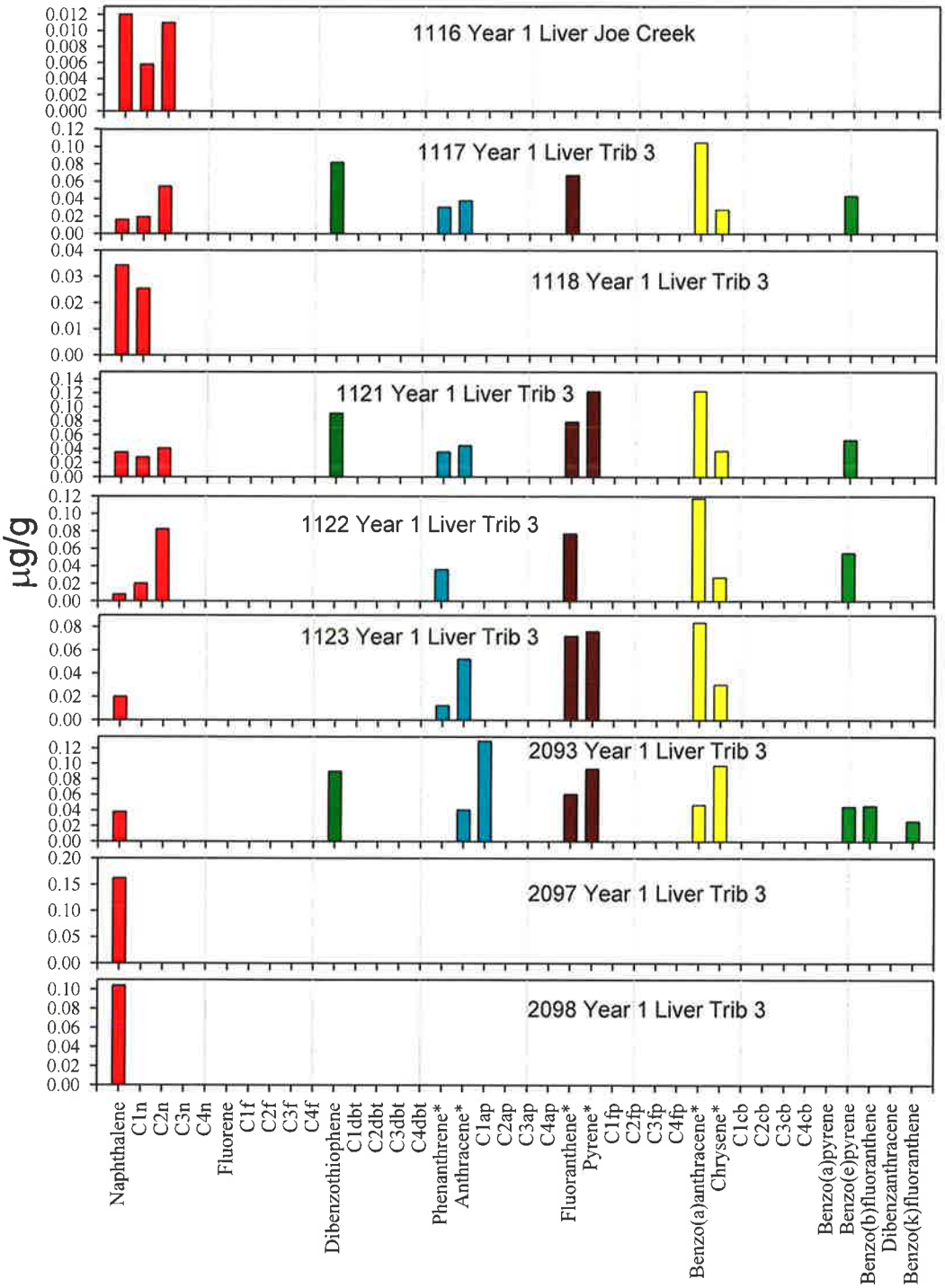
Table 5. Summary of short-term toxicity tests following oral administration for a number of polycyclic aromatic hydrocarbons (European Commission 2002).
No observable adverse effects level (NOAEL)

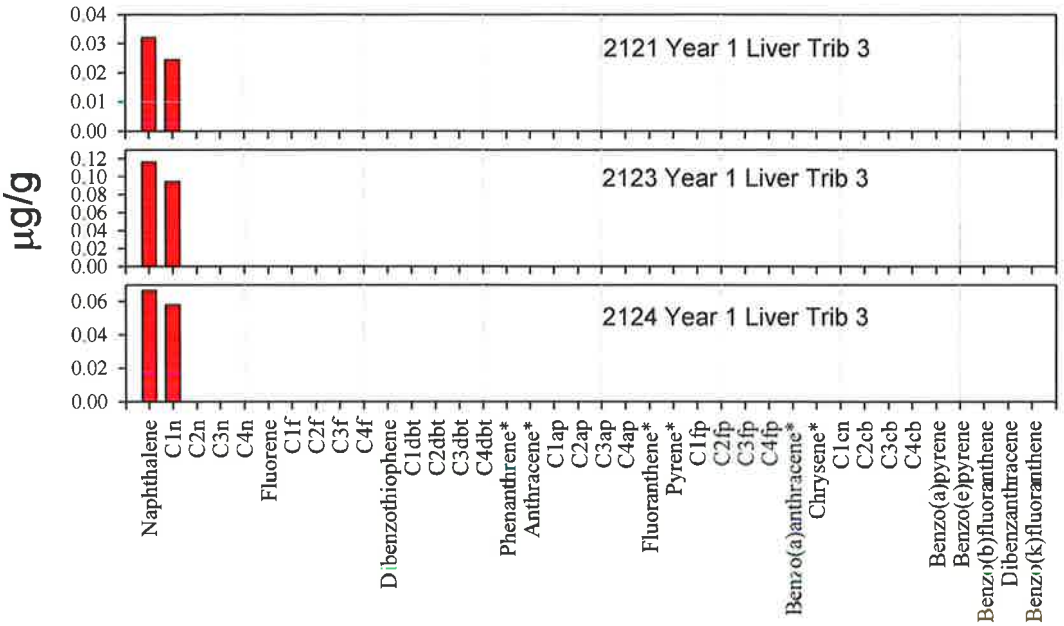
Compound	**Species**	**Duration**	**Critical Effect**	**NOAEL (mg/kg/bw)**	**Reference**
Acenaphthene	Mouse	90 days	Liver toxicity	175	USEPA 1989a
Anthracene	Mouse	90 days	None	1000	USEPA 1989a
Benzo(a)pyrene	Rat	90 days	Liver weight	3	Kroese et al. 2001
Fluoranthene	Mouse	13 weeks	Liver/kidney toxicity	125	USEPA 1988
Fluorene	Mouse	13 weeks	Organ weight, Haematology	125	USEPA 1989c
Naphthalene	Mouse	90 days	None	53	Shopp et al. 1984
"	Rat	13 weeks	Body weight, nephropathy	100 71	BCL 1980
"	Rat	11 weeks	Liver/kidney toxicity	150	Kawai 1979
"	Rabbit	4-13 weeks	cataract	500	Wells, et al, 1989
Pyrene	Mouse	13 weeks	Kidney toxicity	75	USEPA 1989d

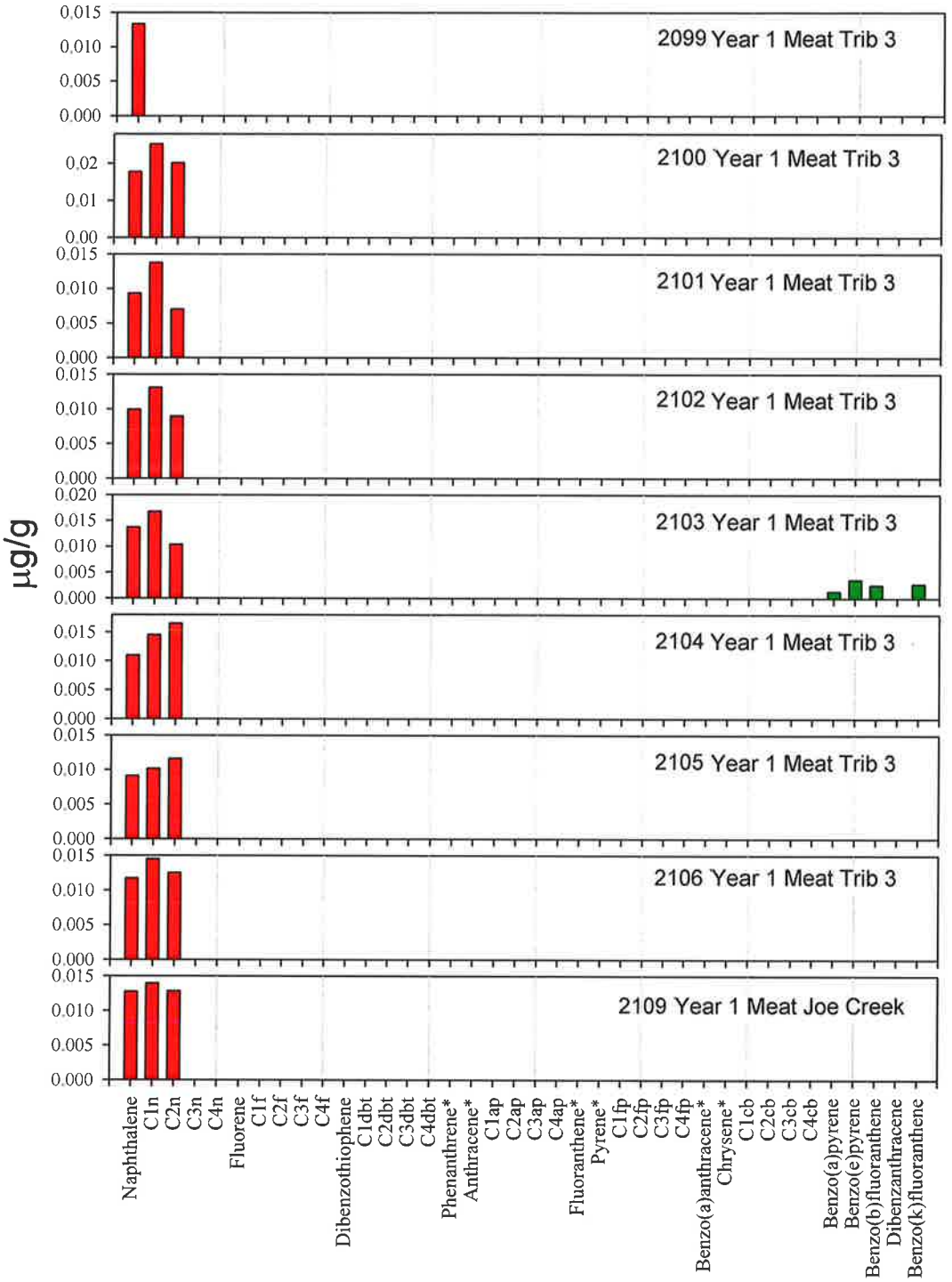
Appendix I
Polycyclic aromatic hydrocarbon component distribution for all samples with detectable amounts (amounts found in year 1 broad whitefish and some sediment samples from years 1 and 2)

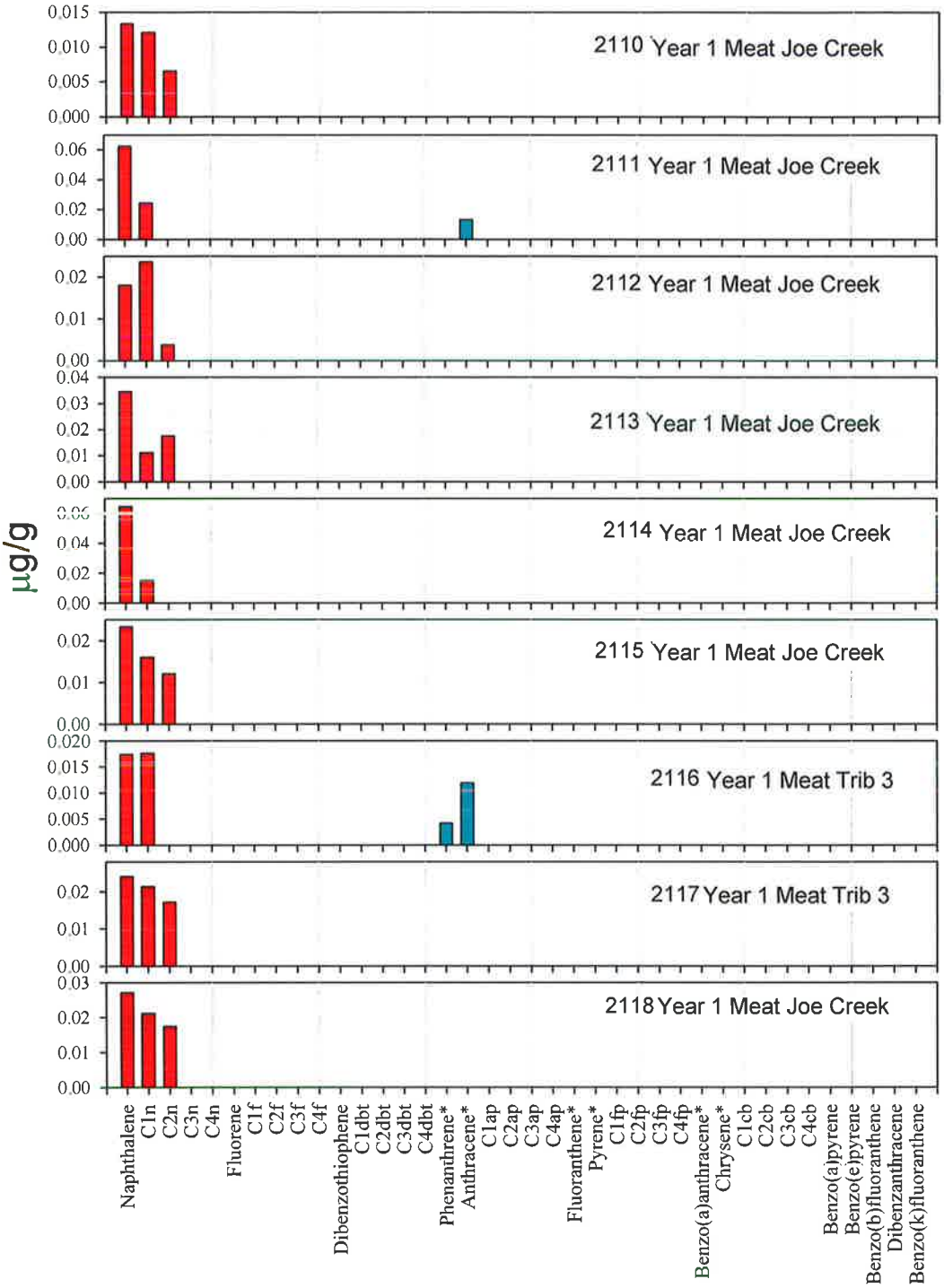

µg/g
1091 Year 1 Liver Ikpikpuk South
1092 Year 1 Liver Trib 3
1093 Year 1 Liver Teshekpuk Lake
1094 Year 1 Liver Joe Station
1095 Year 1 Liver Joe Station
1096 Year 1 Liver Teshekpuk Lake
1097 Year 1 Liver Teshekpuk Lake
1098 Year 1 Liver Teshekpuk Lake
1099 Year 1 Liver Teshekpuk Lake
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

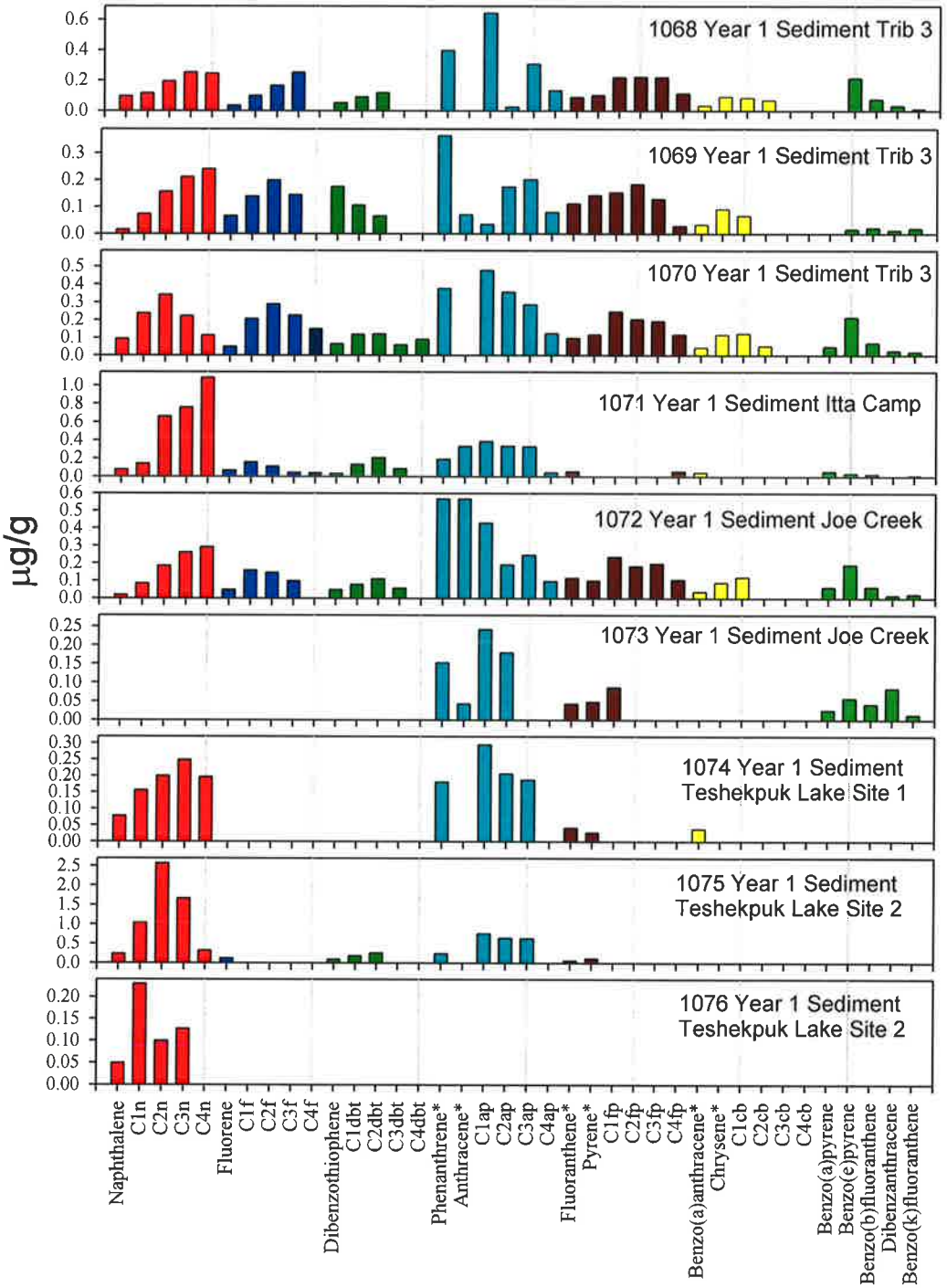

µg/g
1103 Year 1 Liver Joe Creek
1104 Year 1 Liver Joe Creek
1105 Year 1 Liver Joe Creek
1106 Year 1 Liver Joe Creek
1107 Year 1 Liver Joe Creek
1108 Year 1 Liver Joe Creek
1109 Year 1 Liver Joe Creek
1110 Year 1 Liver Joe Creek
1114 Year 1 Liver Joe Creek
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

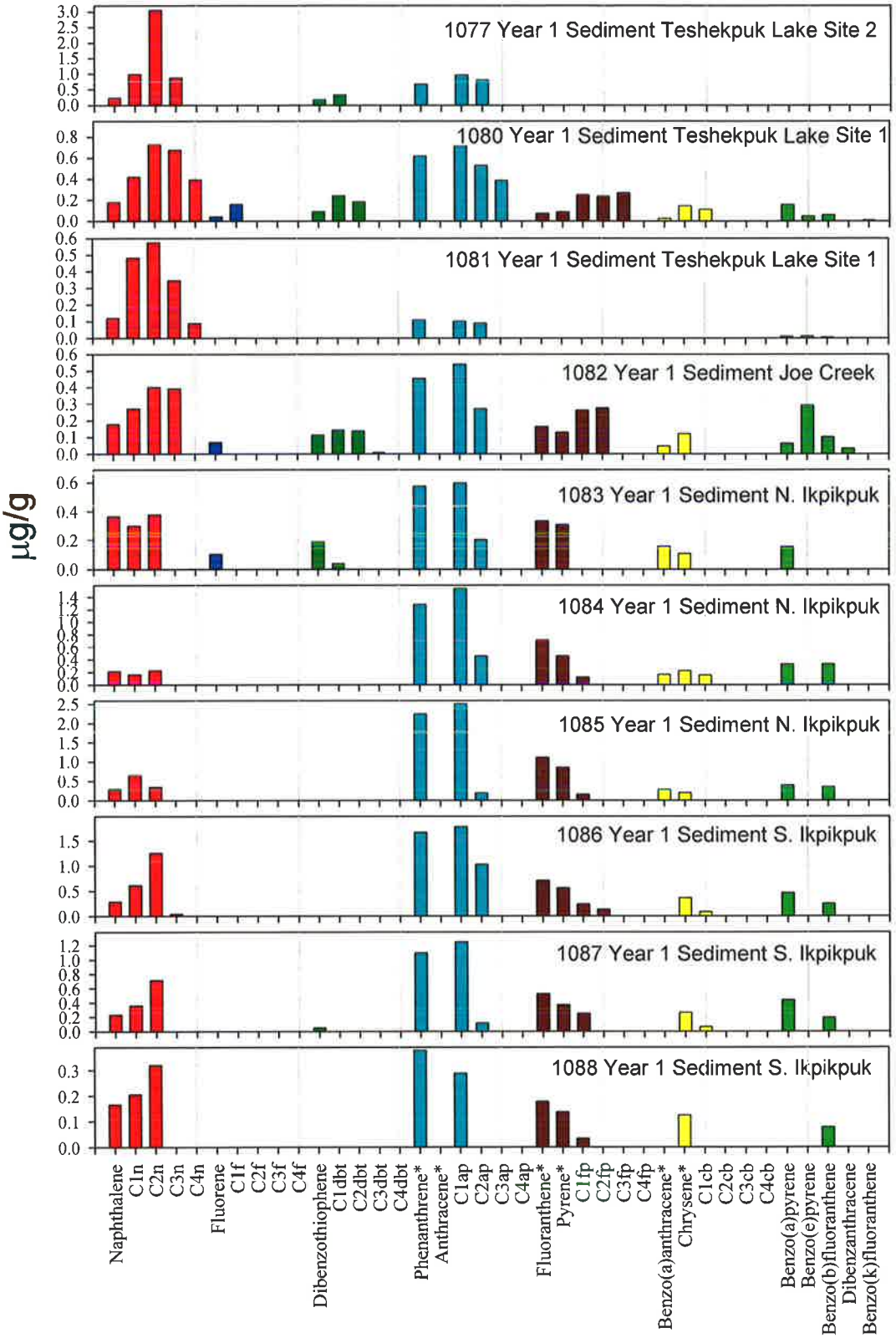

1116 Year 1 Liver Joe Creek
1117 Year 1 Liver Trib 3
1118 Year 1 Liver Trib 3
1121 Year 1 Liver Trib 3
1122 Year 1 Liver Trib 3
1123 Year 1 Liver Trib 3
2093 Year 1 Liver Trib 3
2097 Year 1 Liver Trib 3
2098 Year 1 Liver Trib 3
µg/g
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

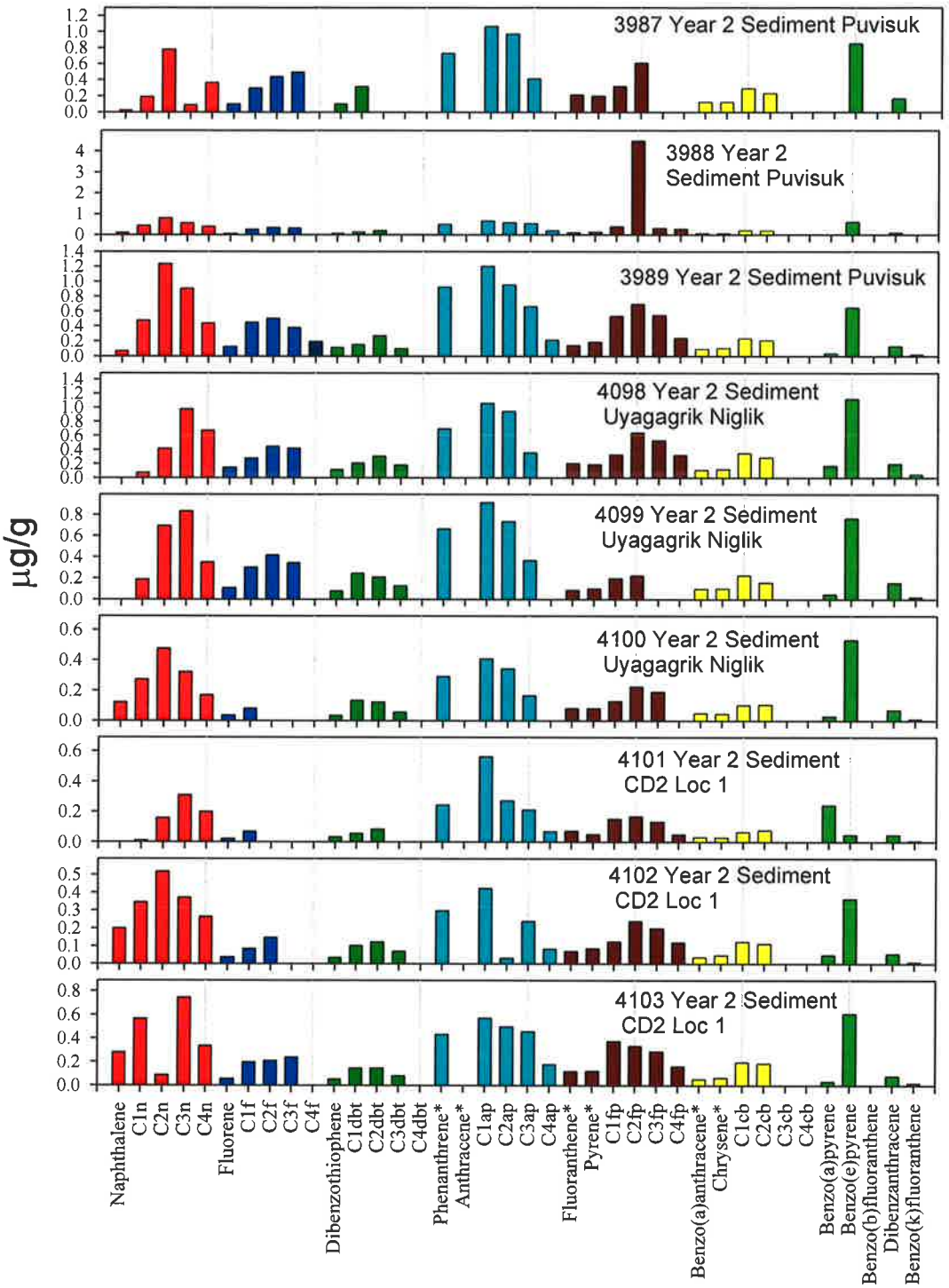

µg/g
2121 Year 1 Liver Trib 3
2123 Year 1 Liver Trib 3
2124 Year 1 Liver Trib 3
0.04
0.03
0.02
0.01
0.00
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.06
0.04
0.02
0.00
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cn
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

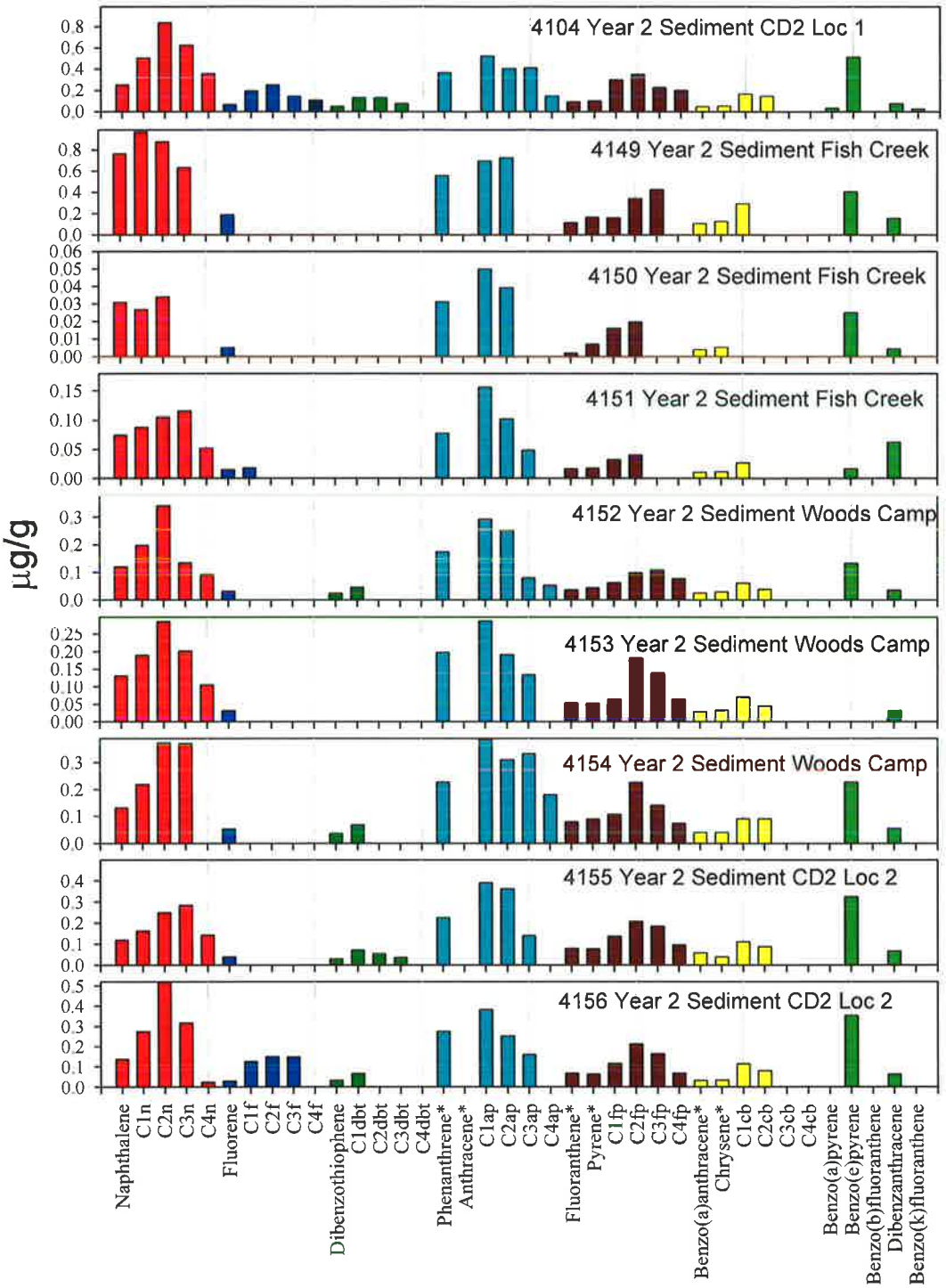

µg/g
2099 Year 1 Meat Trib 3
2100 Year 1 Meat Trib 3
2101 Year 1 Meat Trib 3
2102 Year 1 Meat Trib 3
2103 Year 1 Meat Trib 3
2104 Year 1 Meat Trib 3
2105 Year 1 Meat Trib 3
2106 Year 1 Meat Trib 3
2109 Year 1 Meat Joe Creek
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

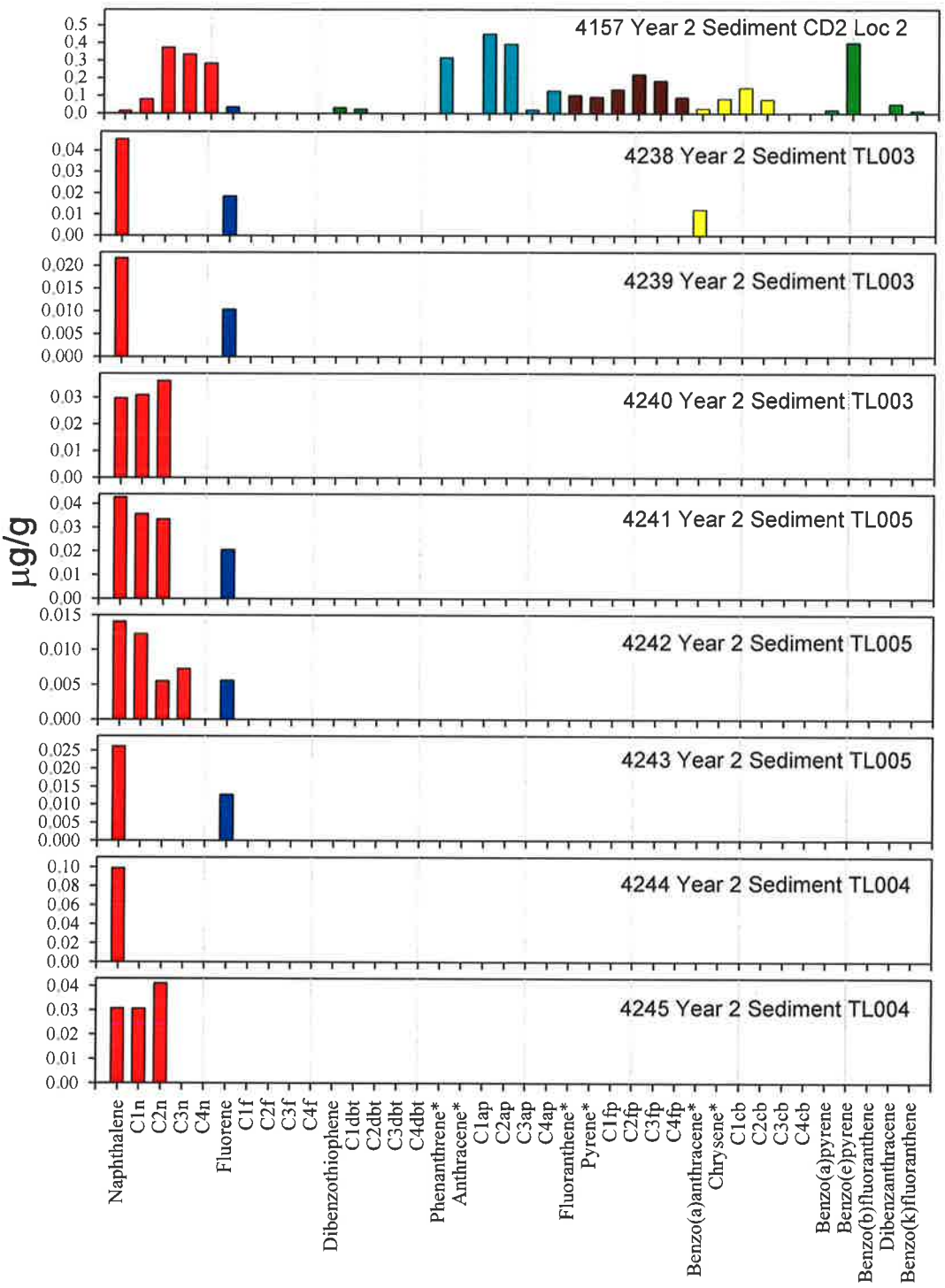

µg/g
2110 Year 1 Meat Joe Creek
2111 Year 1 Meat Joe Creek
2112 Year 1 Meat Joe Creek
2113 Year 1 Meat Joe Creek
2114 Year 1 Meat Joe Creek
2115 Year 1 Meat Joe Creek
2116 Year 1 Meat Trib 3
2117 Year 1 Meat Trib 3
2118 Year 1 Meat Joe Creek
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

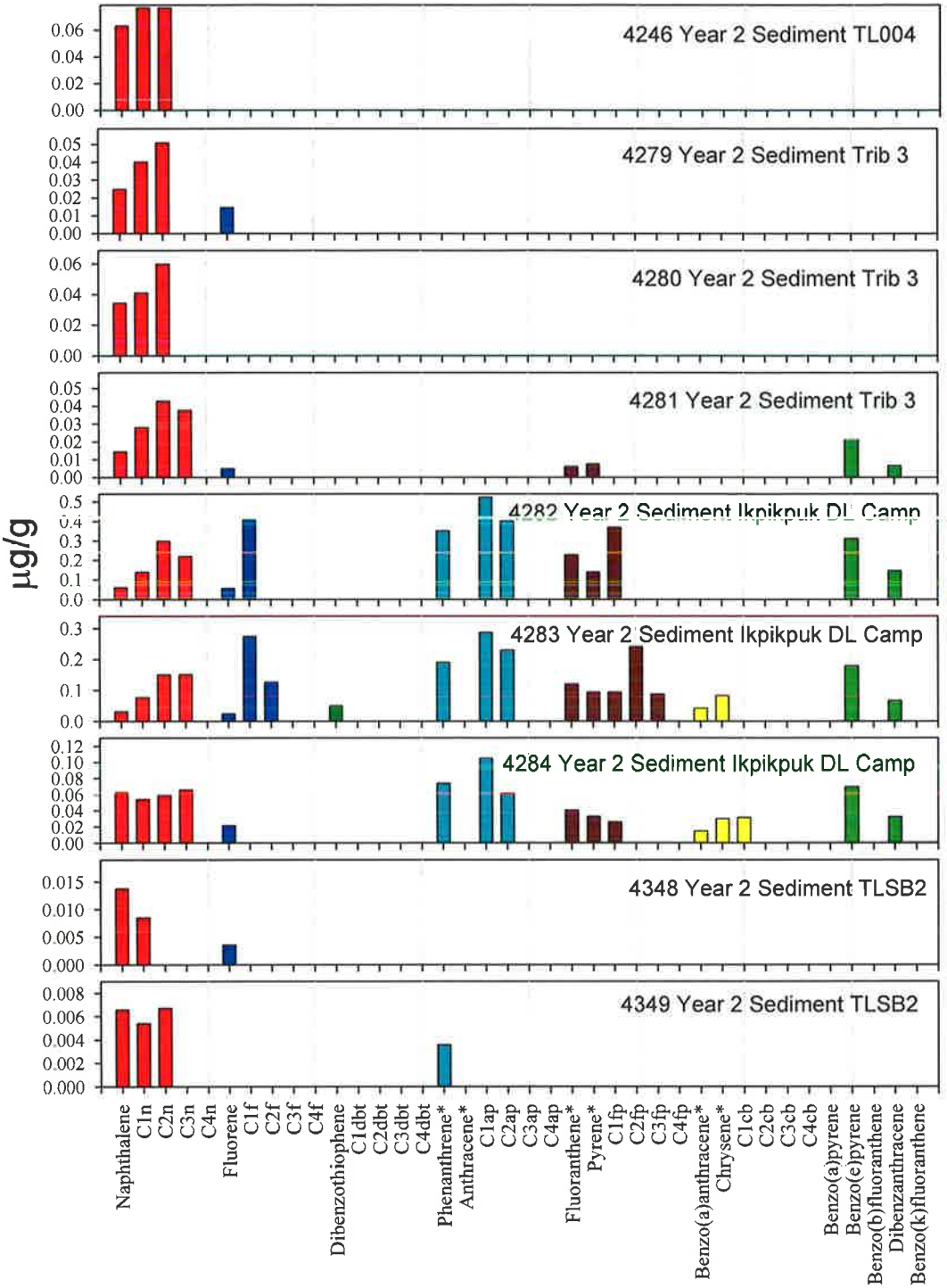

µg/g
1068 Year 1 Sediment Trib 3
1069 Year 1 Sediment Trib 3
1070 Year 1 Sediment Trib 3
1071 Year 1 Sediment Itta Camp
1072 Year 1 Sediment Joe Creek
1073 Year 1 Sediment Joe Creek
1074 Year 1 Sediment Teshekpuk Lake Site 1
1075 Year 1 Sediment Teshekpuk Lake Site 2
1076 Year 1 Sediment Teshekpuk Lake Site 2
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

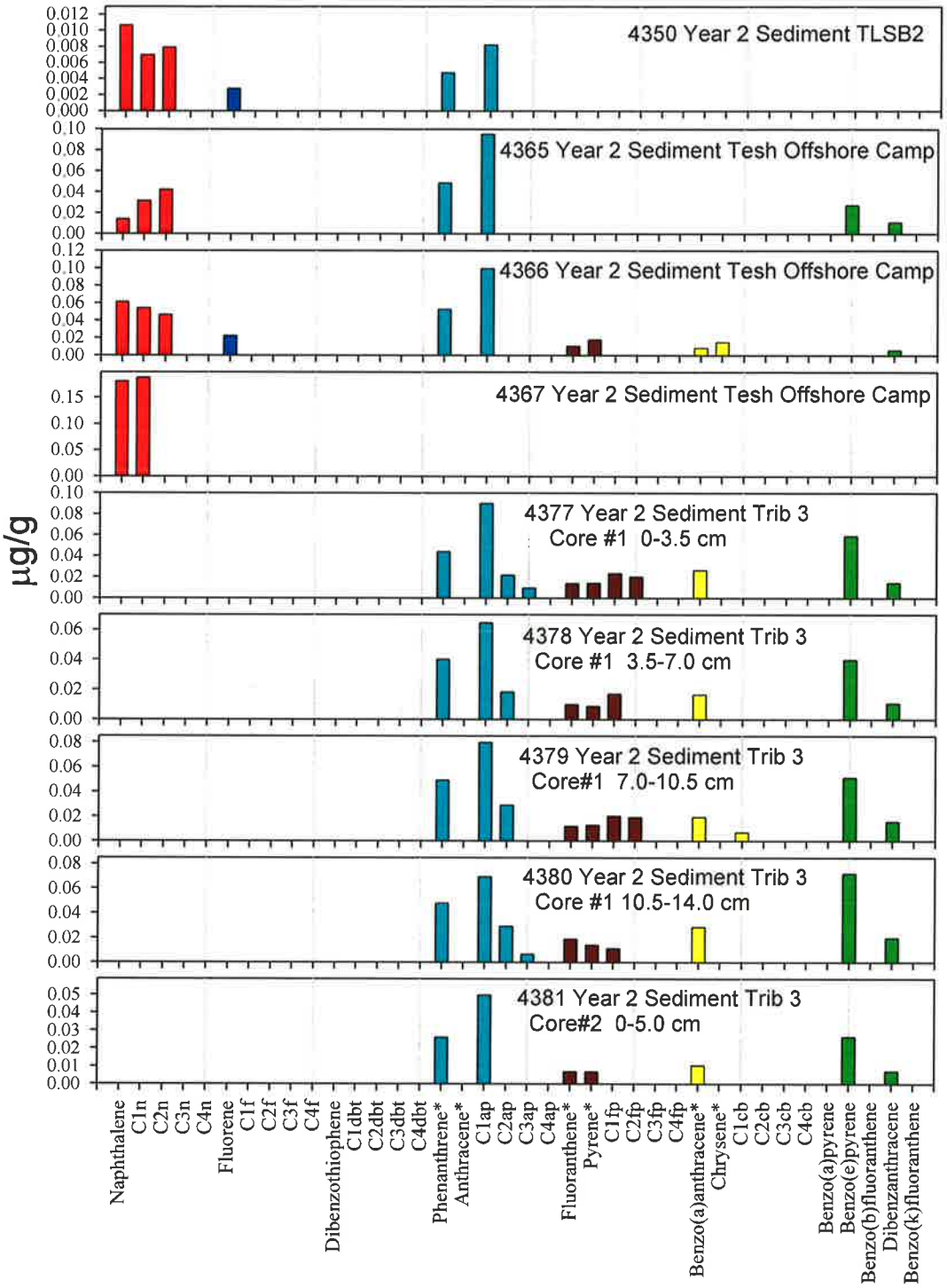

µg/g
1077 Year 1 Sediment Teshekpuk Lake Site 2
1080 Year 1 Sediment Teshekpuk Lake Site 1
1081 Year 1 Sediment Teshekpuk Lake Site 1
1082 Year 1 Sediment Joe Creek
1083 Year 1 Sediment N. Ikpikpuk
1084 Year 1 Sediment N. Ikpikpuk
1085 Year 1 Sediment N. Ikpikpuk
1086 Year 1 Sediment S. Ikpikpuk
1087 Year 1 Sediment S. Ikpikpuk
1088 Year 1 Sediment S. Ikpikpuk
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

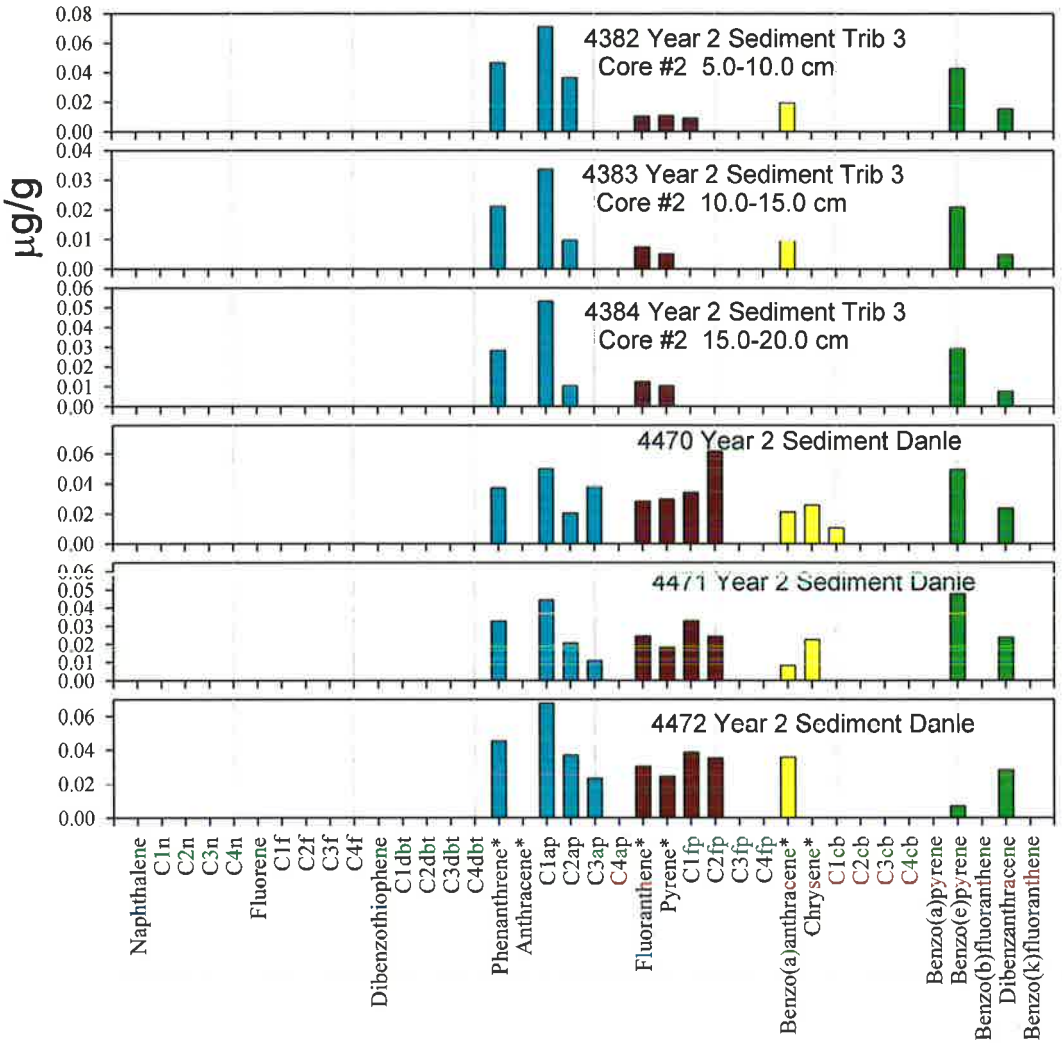

3987 Year 2 Sediment Puvisuk
3988 Year 2 Sediment Puvisuk
3989 Year 2 Sediment Puvisuk
4098 Year 2 Sediment Uyagagrik Niglik
4099 Year 2 Sediment Uyagagrik Niglik
4100 Year 2 Sediment Uyagagrik Niglik
4101 Year 2 Sediment CD2 Loc 1
4102 Year 2 Sediment CD2 Loc 1
4103 Year 2 Sediment CD2 Loc 1
µg/g
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene


4104 Year 2 Sediment CD2 Loc 1
4149 Year 2 Sediment Fish Creek
4150 Year 2 Sediment Fish Creek
4151 Year 2 Sediment Fish Creek
4152 Year 2 Sediment Woods Camp
4153 Year 2 Sediment Woods Camp
4154 Year 2 Sediment Woods Camp
4155 Year 2 Sediment CD2 Loc 2
4156 Year 2 Sediment CD2 Loc 2
µg/g
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene


4157 Year 2 Sediment CD2 Loc 2
4238 Year 2 Sediment TL003
4239 Year 2 Sediment TL003
4240 Year 2 Sediment TL003
4241 Year 2 Sediment TL005
4242 Year 2 Sediment TL005
4243 Year 2 Sediment TL005
4244 Year 2 Sediment TL004
4245 Year 2 Sediment TL004
µg/g
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene


µg/g
4246 Year 2 Sediment TL004
4279 Year 2 Sediment Trib 3
4280 Year 2 Sediment Trib 3
4281 Year 2 Sediment Trib 3
4282 Year 2 Sediment Ikpikpuk DL Camp
4283 Year 2 Sediment Ikpikpuk DL Camp
4284 Year 2 Sediment Ikpikpuk DL Camp
4348 Year 2 Sediment TLSB2
4349 Year 2 Sediment TLSB2
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene


µg/g
4350 Year 2 Sediment TLSB2
4365 Year 2 Sediment Tesh Offshore Camp
4366 Year 2 Sediment Tesh Offshore Camp
4367 Year 2 Sediment Tesh Offshore Camp
4377 Year 2 Sediment Trib 3
Core #1 0-3.5 cm
4378 Year 2 Sediment Trib 3
Core #1 3.5-7.0 cm
4379 Year 2 Sediment Trib 3
Core#1 7.0-10.5 cm
4380 Year 2 Sediment Trib 3
Core #1 10.5-14.0 cm
4381 Year 2 Sediment Trib 3
Core#2 0-5.0 cm
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene


µg/g
4382 Year 2 Sediment Trib 3
Core #2 5.0-10.0 cm
4383 Year 2 Sediment Trib 3
Core #2 10.0-15.0 cm
4384 Year 2 Sediment Trib 3
Core #2 15.0-20.0 cm
4470 Year 2 Sediment Danle
4471 Year 2 Sediment Danle
4472 Year 2 Sediment Danle
Naphthalene
C1n
C2n
C3n
C4n
Fluorene
C1f
C2f
C3f
C4f
Dibenzothiophene
C1dbt
C2dbt
C3dbt
C4dbt
Phenanthrene*
Anthracene*
C1ap
C2ap
C3ap
C4ap
Fluoranthene*
Pyrene*
C1fp
C2fp
C3fp
C4fp
Benzo(a)anthracene*
Chrysene*
C1cb
C2cb
C3cb
C4cb
Benzo(a)pyrene
Benzo(e)pyrene
Benzo(b)fluoranthene
Dibenzanthracene
Benzo(k)fluoranthene

Appendix II
Individualized polycyclic aromatic hydrocarbon component concentrations for all samples collected for the two year NPRA study