Preliminary assessment of alkane and PAH data for sediment cores from six lakes in the Fraser River basin

DOE FRAP 1998-18

Prepared for:

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March 1997

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Abstract

Sediment cores were collected from six lakes in the Fraser drainage basin (Moose, Stuart, Kamloops, Nicola, Chilko and Harrison Lakes). Cores have been dated, primarily using ^{210}Pb and secondarily by counting varves or measuring ^{137}Cs where possible. Sections from the cores have been analyzed for a suite of hydrocarbon compounds including alkanes and polynuclear aromatic hydrocarbons (PAH). A preliminary examination of the data using down core profiles and multivariate techniques (Principal Components Analysis) reveals a complex pattern of hydrocarbons both in terms of history and compound distribution. All lake sediments contain detectable alkane and PAH compounds but there are differences between lakes and between sediment depths within lakes. The predominant signal in alkanes likely derives from natural sources including lake algae (e.g., nC_{17},) and terrestrial plant waxes (e.g., odd carbon alkanes between nC_{23} and nC_{33}) although, in the case of Kamloops Lake sediments, petroleum has also contributed alkanes. The algal alkanes show diagenetic loss on going down the cores. PAHs in the lake sediments derive from both natural and anthropogenic sources. Harrison and Nicola Lakes show increases in combustion PAHs in the early 1900s with decreases after about the 1950s consistent with changes from coal to liquid fuels. Kamloops Lake also shows clear PAH contamination probably from both combustion and petroleum inputs. Work is in progress toward a detailed assessment of hydrocarbons in the lake sediments in the context of local and regional sources and pathways.

Résumé

Des carottes de sédiments ont été prélevées dans six lacs du bassin hydrographique du Fraser (lacs Moose, Stuart, Kamloops, Nicola, Chilko et Harrison). On a effectué la datation au ^{210}Pb et, lorsque la chose était possible, on a compté les varves ou mesuré le ^{137}Cs. On a analysé des sections de carottes en vue d'y déceler une suite de composés à base d'hydrocarbures, notamment des alcanes et des hydrocarbures aromatiques polycycliques (HAP). Un examen préliminaire des données à l'aide des profils de carottes et de techniques multivariées (Analyse des composantes principales) révèle un modèle complexe d'hydrocrabures, tant en termes d'historique que de distribution du composé. Tous les sédiments lacustres contiennent des alcanes et des HAP décelables, mais il y a des différences entre les lacs et entre les profondeurs de sédiments dans un même lac. Le signal dominant chez les alcanes provient vraisemblablement de sources naturelles, notamment les algues (p. ex. nC_{17}) et les cires de plantes terrestres (p. ex. les alcanes de carbone impairs entre nC_{23} et nC_{33}) même si, dans le cas des sédiments du lac Kamloops, le pétrole a également contribué aux alcanes. À mesure qu'on descend le long de la carotte, on observe des pertes diagénétiques chez les alcanes qui tirent leur origine des algues. Les HAP trouvés dans les sédiments lacustres proviennent à la fois de sources naturelles et anthropiques. Les lacs Harrison et Nicola révèlent une augmentation des HAP de combustion vers le début du siècle, et une diminution vers la fins des années 50, ce qui correspond à l'abandon du charbon pour les combustibles liquides. Le lac Kamloops montre également une nette contamination par les HAP, probablement due à la combustion et à l'utilisation du pétrole. On s'affaire actuellement à une évaluation détaillée des hydrocarbures dans les sédiments lacustres dans le contexte de sources et de voies critiques locales et régionales.

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Introduction

This preliminary assessment compares alkane and PAH concentrations and profiles for sediment cores from six lakes in the Fraser River basin, suspended particulate samples from the Fraser River estuary and a sediment core from a reference location in the Strait of Georgia (Station A; Yunker *et al.*, submitted). Locations and sample collection dates are as follows:

Harrison Lake	November 1993
Nicola Lake	November 1993
Moose Lake	June 1994
Kamloops Lake	June 1994
Stuart Lake	June 1994
Chilko Lake	June 1994
Fraser River Estuary (suspended particulate)	February 1987
Strait of Georgia Core A	November 1993

Methods

All alkane (Table 1) and PAH (Table 2) analyses were performed by Axys Analytical Ltd. of Sidney B.C. Alkane and parent and alkyl PAH profiles for the lake samples are shown in Figures 1-4 and Appendices A and B. ^{210}Pb dates (mid-section) are shown on the right on the Figures.

Principal components analysis (PCA) was used to compare the composition of samples from the locations detailed above. The limit of detection was substituted when PAHs were undetectable. Samples were mid-range normalized, log transformed and autoscaled before PCA (Figure 5). With this procedure all samples and variables have equal importance, and PCA separates by sample profile.

The PCA results shown in Figure 5 should be regarded as preliminary. Most PAHs were undetectable for samples from the bottoms of the lake cores, and each sample must be vetted to ensure that detection limit artifacts are not influencing the PCA projections.

Alkanes

Surface sediments from all six lakes show a marked predominance of nC_{17} and of the odd carbon alkanes between nC_{23} and nC_{33} (with a maximum at nC_{27} or occasionally nC_{29}). These alkanes are naturally occurring biomarkers: the nC_{17} alkane has an algal origin, while the series of odd carbon nC_{23} to nC_{33} alkanes reflect plant waxes, typically from the surfaces of leaves (e.g., Meyers and Ishiwatari, 1993). The algal alkanes are less protected from degradation than the plant wax alkanes, and the proportion of nC_{17} (and of the lower alkanes) relative to the higher alkanes decreases rapidly downcore (Figure 1 and Appendix A).

Sediments from Kamloops Lake have an additional alkane envelope between nC_{17} and nC_{23}. While this likely indicates petroleum with an anthropogenic origin (particularly for the 5-6 cm section of core K2), these alkanes are also present in lower concentration in the bottom section of both cores (ca. 1860), and some natural contribution may be indicated. Further work is required to establish the source of these alkanes.

PAHs

Cores from all six lakes exhibit an increase in perylene concentration downcore (Figure 2). The sediment depth and year where the increase begins and the magnitude of the increase vary from core to core. Nevertheless in each case the increase reflects the natural production of perylene, likely from a precursor with a terrestrial, higher plant origin (Venkatesan, 1988; Meyers and Ishiwatari, 1993).

In Harrison and Nicola Lakes (the two lakes from the southern part of the basin with full PAH profiles) the Σ 178-278 parent PAH total (i.e., the sum of phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene and triphenylene, benzo[*b/j/k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and dibenz[*a,c/a,h*]anthracene) is low in the bottom part of the core, increases with the onset of anthropogenic activity at the turn of the century, peaks in the 1940s and 1950s, and decreases gradually to the present day (see Figure 2 and following Table). (The higher plant *n*-alkanes (nC_{23} to nC_{33}) exhibit similar increases in concentration.) Kamloops Lake, which is the other southern lake, is also low in the deepest section (ca. 1860) and exhibits a gradual PAH decrease from the late 1970s to the present, and likely will exhibit similar behavior when the full core has been analyzed. Of the northern lakes, Moose Lake shows little change in parent PAH concentration from 1890 to the present, and Stuart and Chilko Lakes show little change from the core bottom (about 1600 in Stuart Lake) to ca. 1930 to the present.

Location	Maximum Σ 178-278, ng/g	Year of Maximum	Baseline Σ 178-278, ng/g
Harrison Lake	200	1954	7.1
Nicola Lake	109	1943 - 1954	35
Moose Lake	52	1918	26
Kamloops Lake	232	1980	38
Stuart Lake	204	1991	130
Chilko Lake	33	1993	25
Strait of Georgia Core A	837	post 1980	620

The more volatile PAHs (naphthalene, phenanthrene, fluoranthene and pyrene) predominate in the surface section of the cores from Nicola, Moose and Chilko Lakes (Figure 3). The parent PAHs (marked C0 on the profiles) dominate the alkyl homologue series for the naphthalenes, dibenzothiophenenes, phenanthrene/anthracenes and fluoranthene/pyrenes, indicating both that combustion PAHs predominate, and that there has been little or no contribution from petroleum PAHs. (Note that the increase in concentration for C4 phenanthrene is due to the plant PAH, retene.) These profiles suggest that atmospheric inputs are the major source of PAHs to these lakes.

Harrison Lake has a much higher proportion of the molecular mass 252 and 276 PAHs (benzo[*b/j/k*]fluoranthene, benzo[*e*]- and -[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene) than Nicola, Moose and Chilko Lakes (Figure 3). However, while the alkyl substituted naphthalenes and phenanthrene/anthracenes make a greater contribution in Harrison Lake, the parent PAHs still generally predominate in the alkyl homologue series (Appendix B) and atmospheric inputs are likely to be the principal source of PAHs. The relative proportions of the three major groups of parent PAHs (m/z 202, 252 and 276) have changed little throughout the Harrison, Nicola and Moose Lake cores (Figure 4).

Stuart Lake has the highest Σ 178-278 baseline PAH concentration of any of the lakes (see table above). Like Harrison Lake, Stuart Lake has a high proportion of the molecular mass 252 and 276 PAHs. However, Stuart Lake sediments also have a high proportion of alkyl substituted PAHs, indicating significant inputs of petroleum PAHs. Perylene excluded, similar PAH profiles of parent and alkyl substituted PAHs are evident in all sections analyzed from the Stuart Lake cores, and the high baseline of parent and alkyl PAHs likely reflects a natural PAH source in eroded bitumens, shales, etc. To confirm this linkage more specific petroleum biomarkers (hopanes and steranes) need to be investigated and a more detailed examination of PAH profiles and is required in the sediments from Stuart Lake.

Parent PAH profiles in samples of suspended particulate from the Fraser River estuary and in a sediment core from a reference site in the Strait of Georgia (dating back to the 1930s) are most similar to the profiles in Kamloops Lake, while the alkyl PAH profiles in the estuary and strait are most similar to Stuart Lake.

PCA Results

Three major trends are evident in the PCA model (Figure 5). Samples with high proportions of perylene project in the upper right corner of the sample plot; samples with high amounts of alkyl PAHs project in the lower right corner; and, samples with high amounts of the higher molecular weight parent PAH project on the left.

Harrison Lake samples have high amounts of the higher molecular weight parent PAH and project on the left in Figure 5c; in deeper sections perylene dominates, and samples project on the upper right.

Samples from Nicola and Moose Lakes have similar compositions in most core segments (Figures 5d and 5c); the deepest sections are shifted to the upper right due to higher amounts of perylene.

Samples from the 5-6 and 9-10 cm sections of the two Kamloops Lake cores (Figure 5f) project on the lower right due to a higher proportion of alkyl substituted PAH, presumably from petroleum discharged into the Thompson River. Alkyl substituted PAHs make less of a contribution to the surface sections of the two cores.

Samples from Stuart Lake, Chilko Lake, the Fraser River estuary and Station A in the Strait of Georgia each cluster in a small group, indicating similar compositions downcore, and (for the Fraser River) throughout the estuary (Figures 5g to 5j). An exact match is not obtained between the lake samples and the samples from the estuary and strait, but the samples from Stuart Lake appear to be most similar in composition.

References

Meyers, P. A.; Ishiwatari, R. *Org. Geochem.* **1993**, *20*, 867-900.

Venkatesan, M. I. *Mar. Chem.* **1988**, *25*, 1-27.

Yunker, M. B.; Macdonald, R. W.; Goyette, D.; Paton, D. W.; Fowler, B. R.; Sullivan, D.; Boyd, J. *Sci. Total Environ*, submitted.

Tables

Table 1. Alkane parameters and abbreviations used in Appendix 1.

Alkane	Abbr.	Alkane	Abbr.
Dodecane	12	Heneicosane	21
2,6-Dimethylundecane	DMU	Docosane	22
Norfarnesane	NFr	Tricosane	23
Tridecane	13	Tetracosane	24
Farnesane	Far	Pentacosane	25
Tetradecane	14	Hexacosane	26
2,6,10-Trimethyltridecane	TMT	Heptacosane	27
Pentadecane	15	Octacosane	28
Hexadecane	16	Nonacosane	29
Norpristane	NPr	Triacontane	30
Heptadecane	17	Untriacontane	31
Pristane	Pr	Dotriacontane	32
Octadecane	18	Tritriacontane	33
Phytane	Ph	Tetratriacontane	34
Nonadecane	19	Pentatriacontane	35
Eicosane	20	Hexatriacontane	36

Table 2. PAH parameters and abbreviations used in Figure 5 and Appendix 2.

PAH	Abbr.
Naphthalene	Na
Fluorene	Fl
Phenanthrene + Anthracene	178
Fluoranthene + Pyrene	202
Benz[*a*]anthracene + Chrysene	228
Benzo[*b/j/k*]fluoranthene + Benzo[*e*]pyrene + Benzo[*a*]pyrene	252
Indeno[1,2,3-*cd*]pyrene + Benzo[*ghi*]perylene	276
Dibenz[*a,c/a,h*]anthracene	278
Perylene	Per
Naphthalene	N0
C1 naphthalenes	N1
C2 naphthalenes	N2
C3 naphthalenes	N3
C4 naphthalenes	N4
Dibenzothiophene	D0
C1 dibenzothiophenes	D1
C2 dibenzothiophenes	D2
C0 phenanthrene/anthracenes	P0
C1 phenanthrene/anthracenes	P1
C2 phenanthrene/anthracenes	P2
C3 phenanthrene/anthracenes	P3
C4 phenanthrene/anthracenes	P4
C0 fluoranthene/pyrenes	F0
C1 fluoranthene/pyrenes	F1
C2 fluoranthene/pyrenes	F2
C3 fluoranthene/pyrenes	F3
C4 fluoranthene/pyrenes	F4
Cadalene (4-isopropyl-1,6-dimethylnaphthalene)	Cd
Pimanthrene (1,7-dimethylphenanthrene)	Pm
Simonellite (1,1-dimethyl-1,2,3,4-tetrahydro-7-isopropyl phenanthrene)	Sm
Retene (1-methyl-7-isopropylphenanthrene)	Rt
3,3,7,12a-Tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene	gOHC
3,4,7,12a-Tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene	vOHC
Other Tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene	OHC
1-Methyl-isopropyl-7,8-cyclopentenophenanthrene	CPP
3,4,7-Trimethyl-1,2,3,4-tetrahydrochrysene	vTHC
3,3,7-Trimethyl-1,2,3,4-tetrahydrochrysene	gTHC
1,2,9-Trimethyl-1,2,3,4-tetrahydropicene	gTHP
2,2,9-Trimethyl-1,2,3,4-tetrahydropicene	gTHP

Notes: The black (left) bars at 202, 252 and 276 indicate the concentrations of fluoranthene, benzo[*b/j/k*]fluoranthene and indeno[*1,2,3-cd*]pyrene respectively and the grey (right) bars indicate pyrene, benzo[*e*]pyrene and benzo[*ghi*]perylene.

To date concentrations of the octa- and tetrahydrochrysenes and tetrahydropicenes have only been determined for Harrison and Nicola Lakes.

Figures

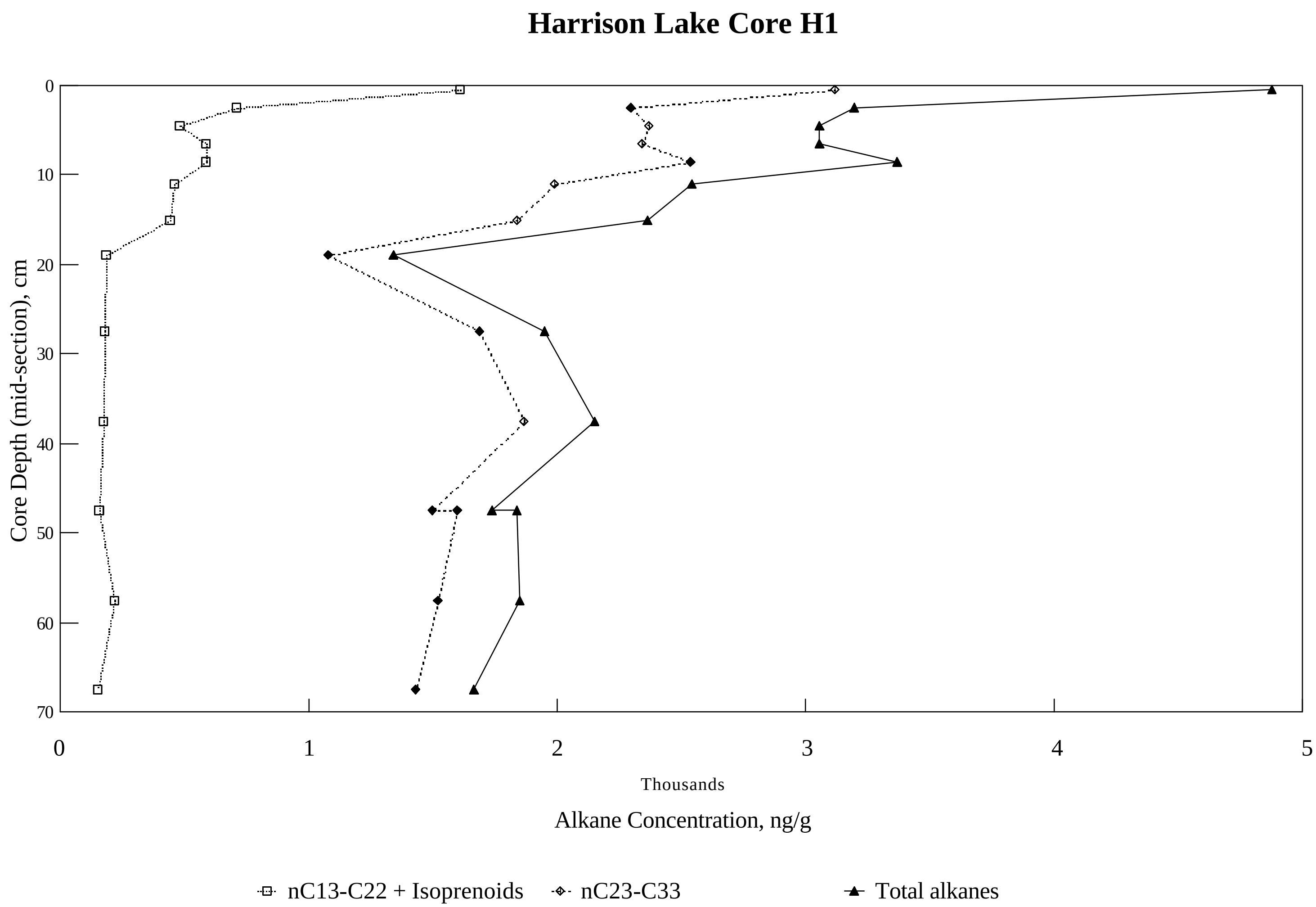

Figure 1a. Total alkane (solid line), and lower and higher alkane (dashed lines) concentrations for Harrison Lake.

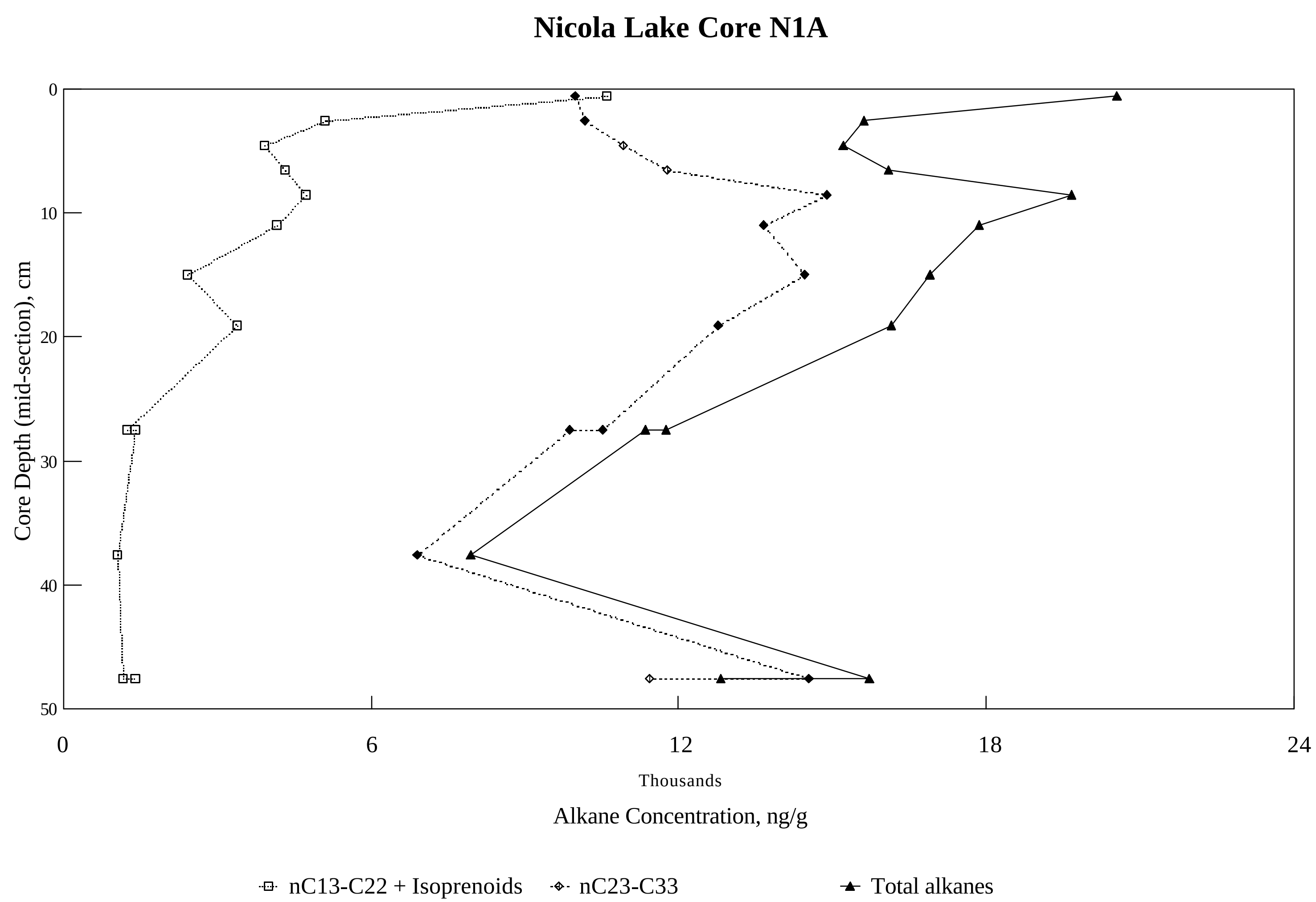

Figure 1b. Total alkane (solid line), and lower and higher alkane (dashed lines) concentrations for Nicola Lake.

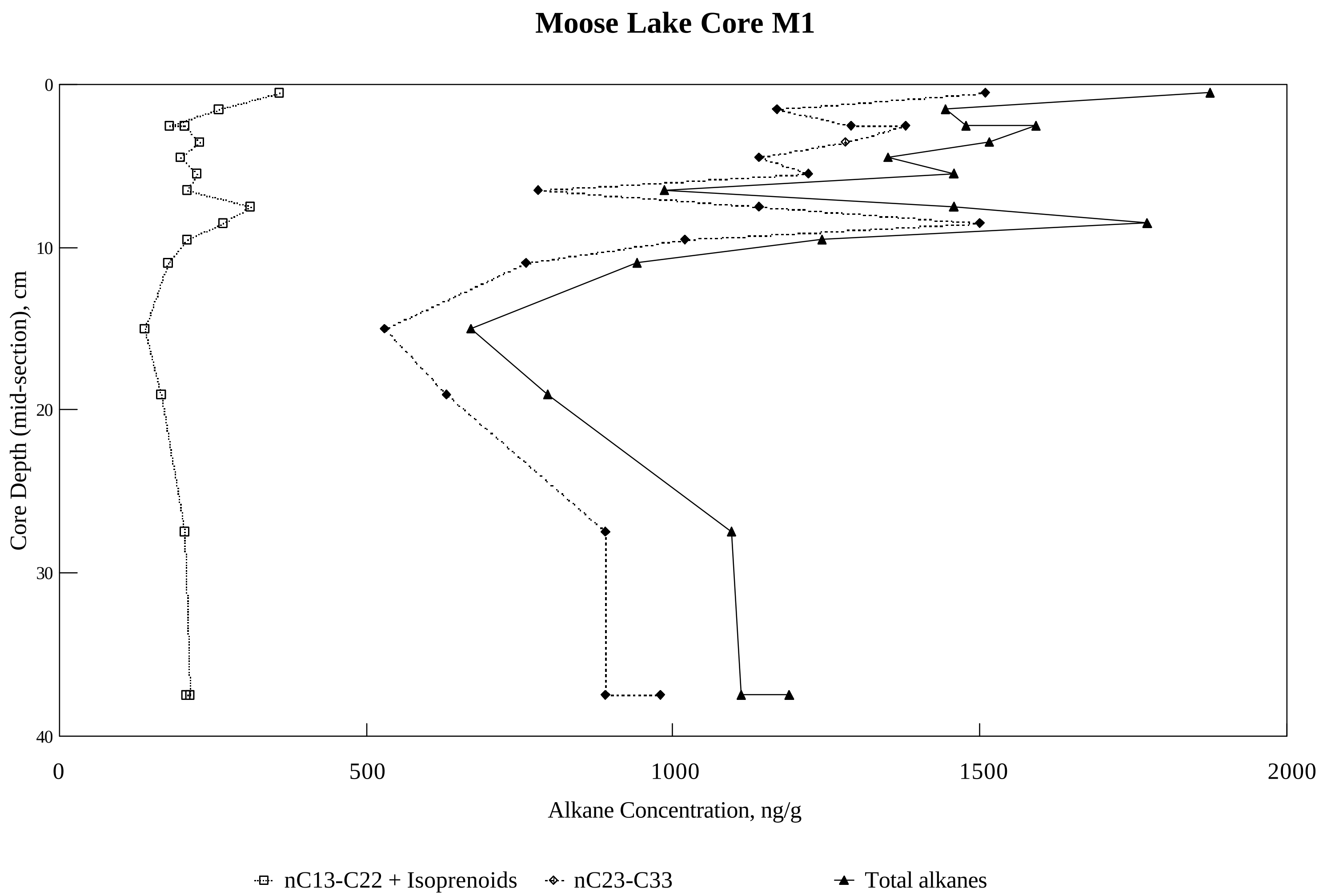

Figure 1c. Total alkane (solid line), and lower and higher alkane (dashed lines) concentrations for Moose Lake.

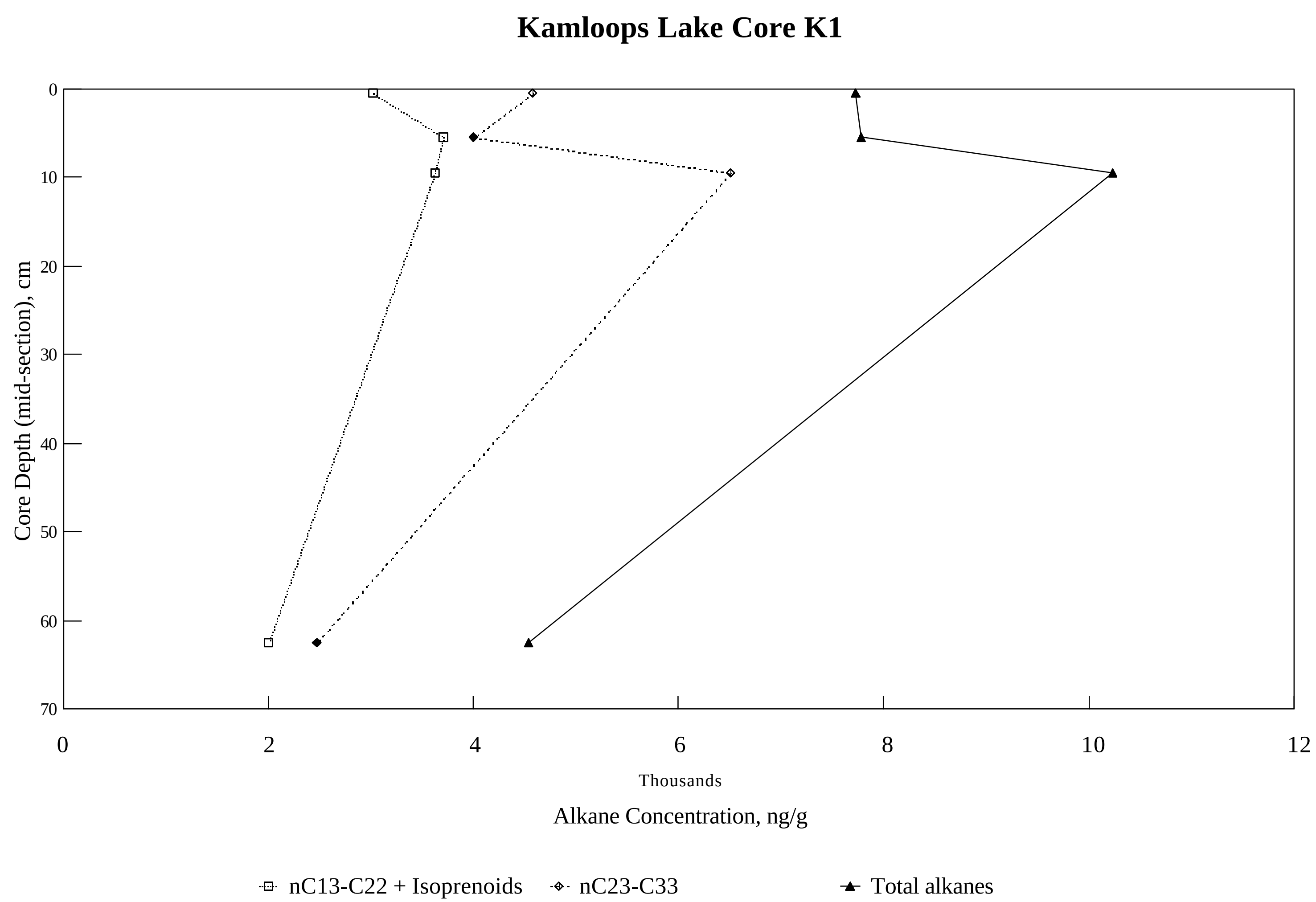

Figure 1d. Total alkane (solid line), and lower and higher alkane (dashed lines) concentrations for Kamloops Lake.

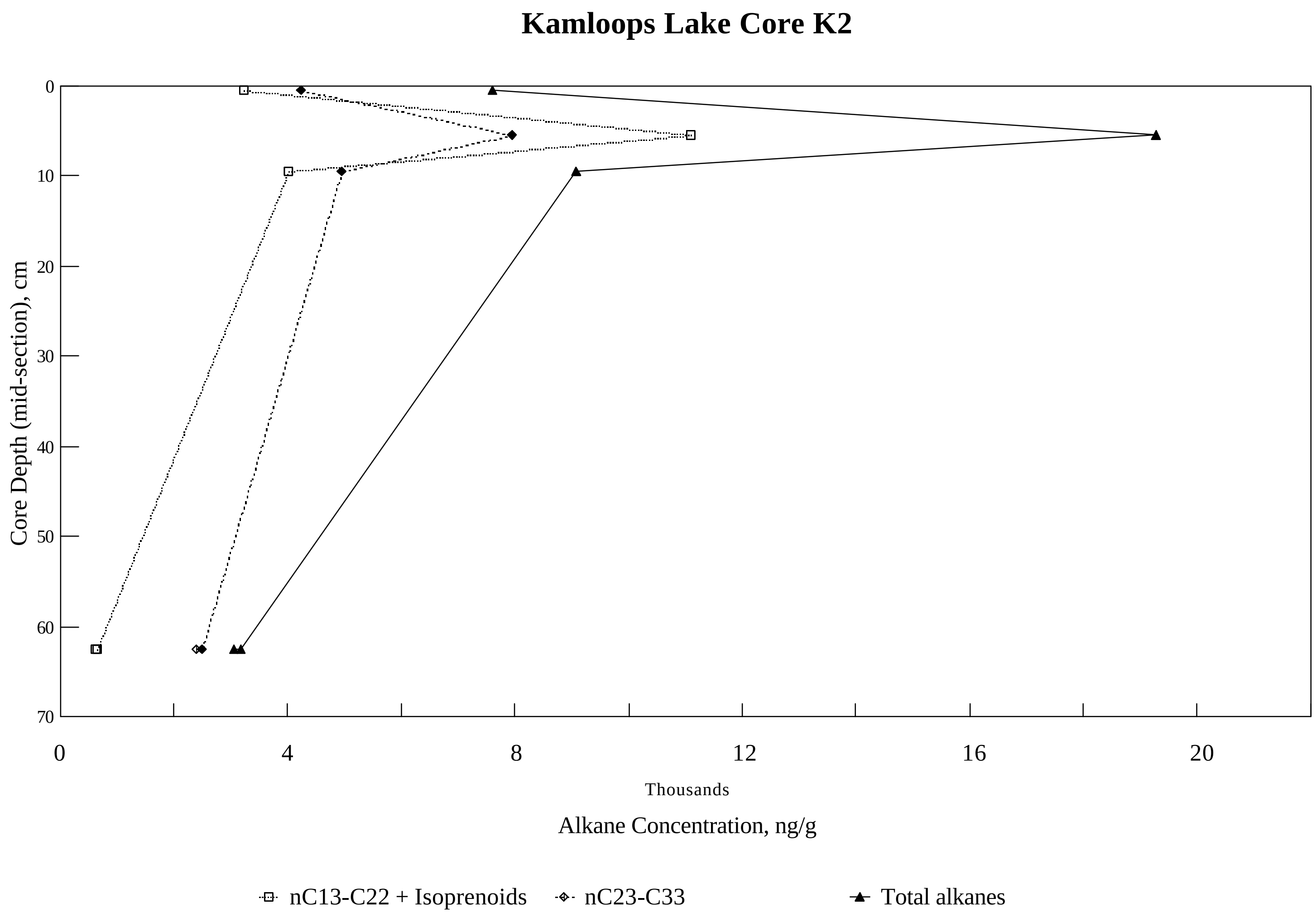

Figure 1e. Total alkane (solid line), and lower and higher alkane (dashed lines) concentrations for Kamloops Lake.

Stuart Lake Cores S2 and S1 Combined

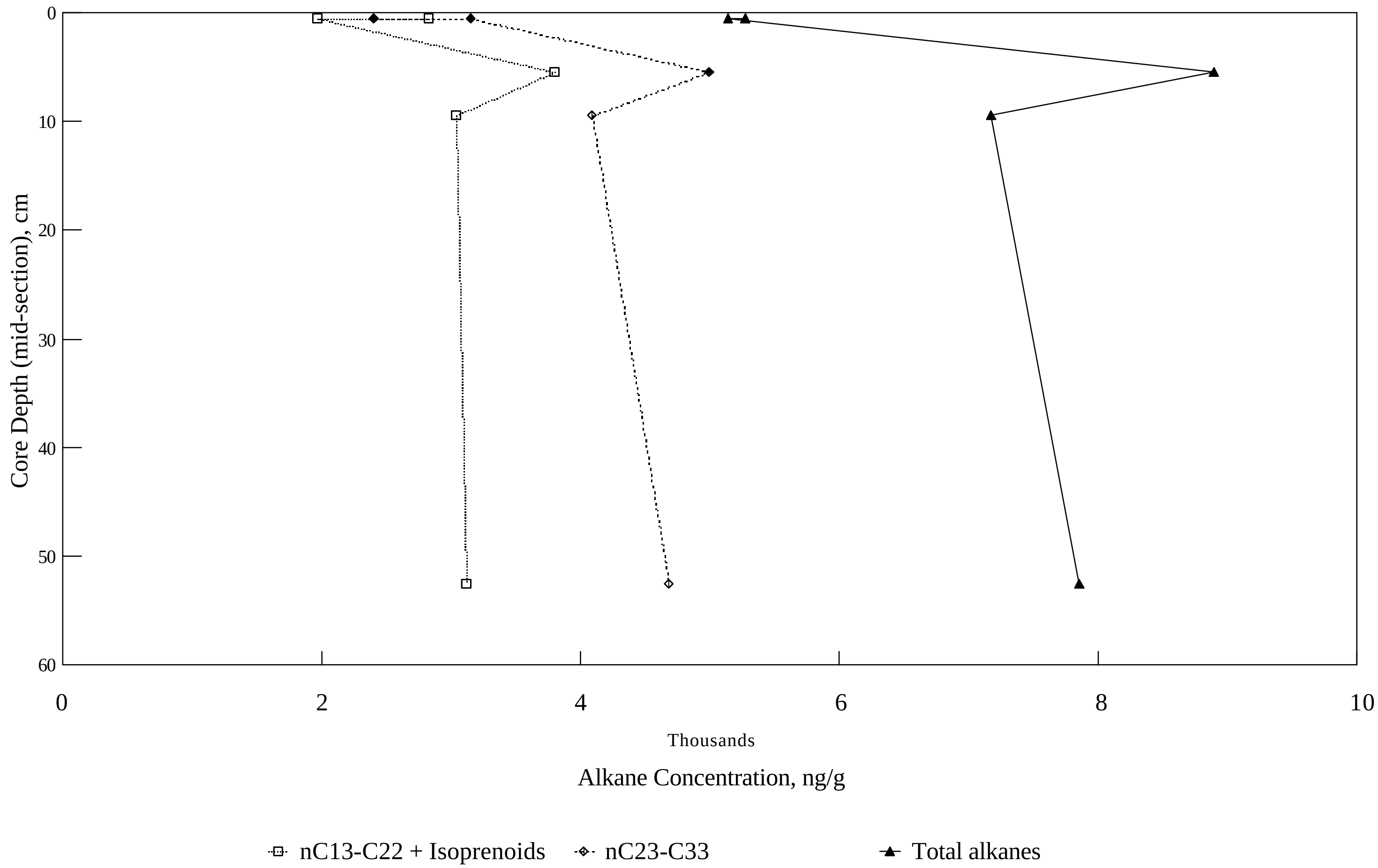

Figure 1f. Total alkane (solid line), and lower and higher alkane (dashed lines) concentrations for Stuart Lake.

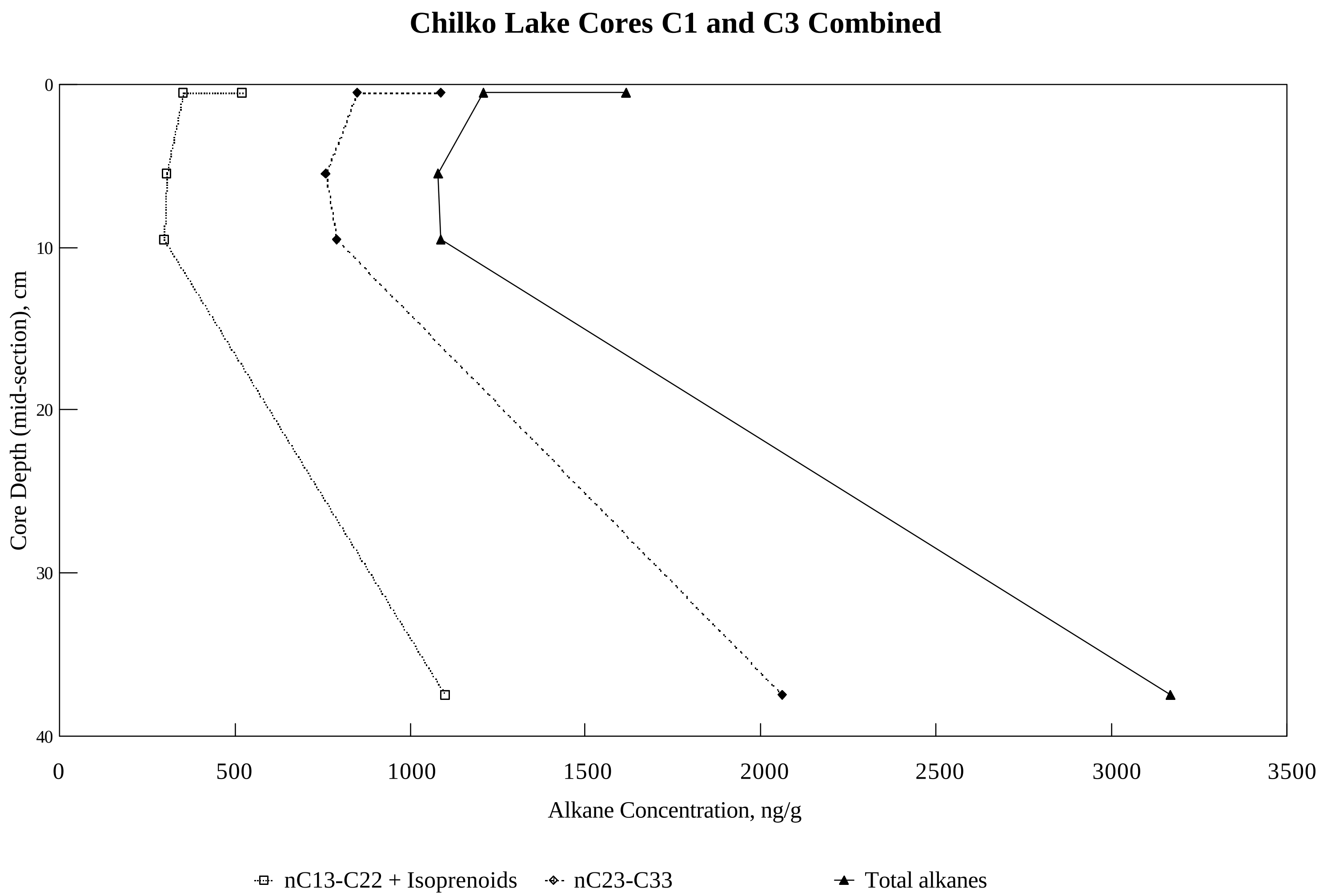

Figure 1g. Total alkane (solid line), and lower and higher alkane (dashed lines) concentrations for Chilko Lake.

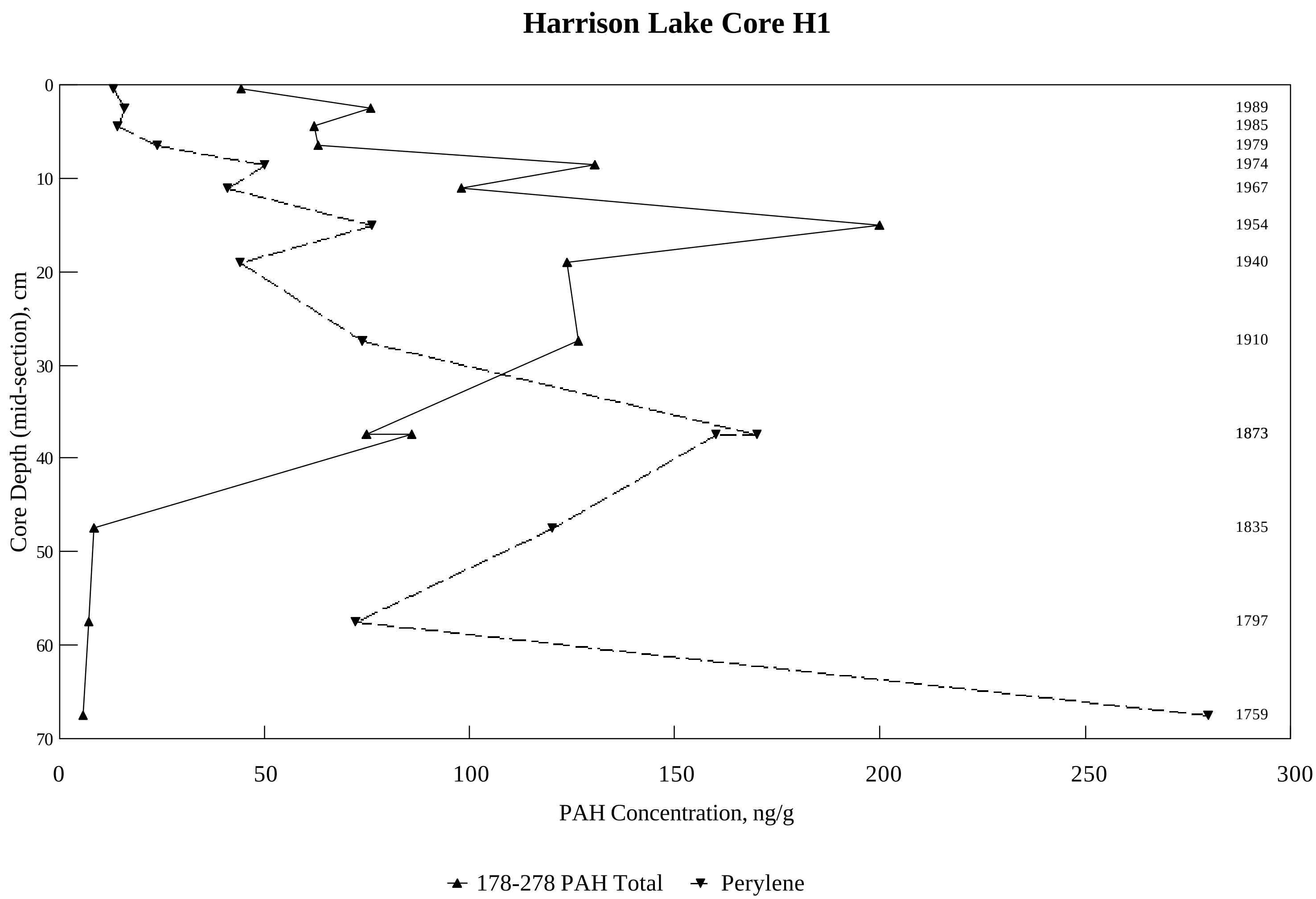

Figure 2a. Σ 178-278 parent PAH total (perylene excluded; solid line) and perylene (long dashed line) for Harrison Lake.

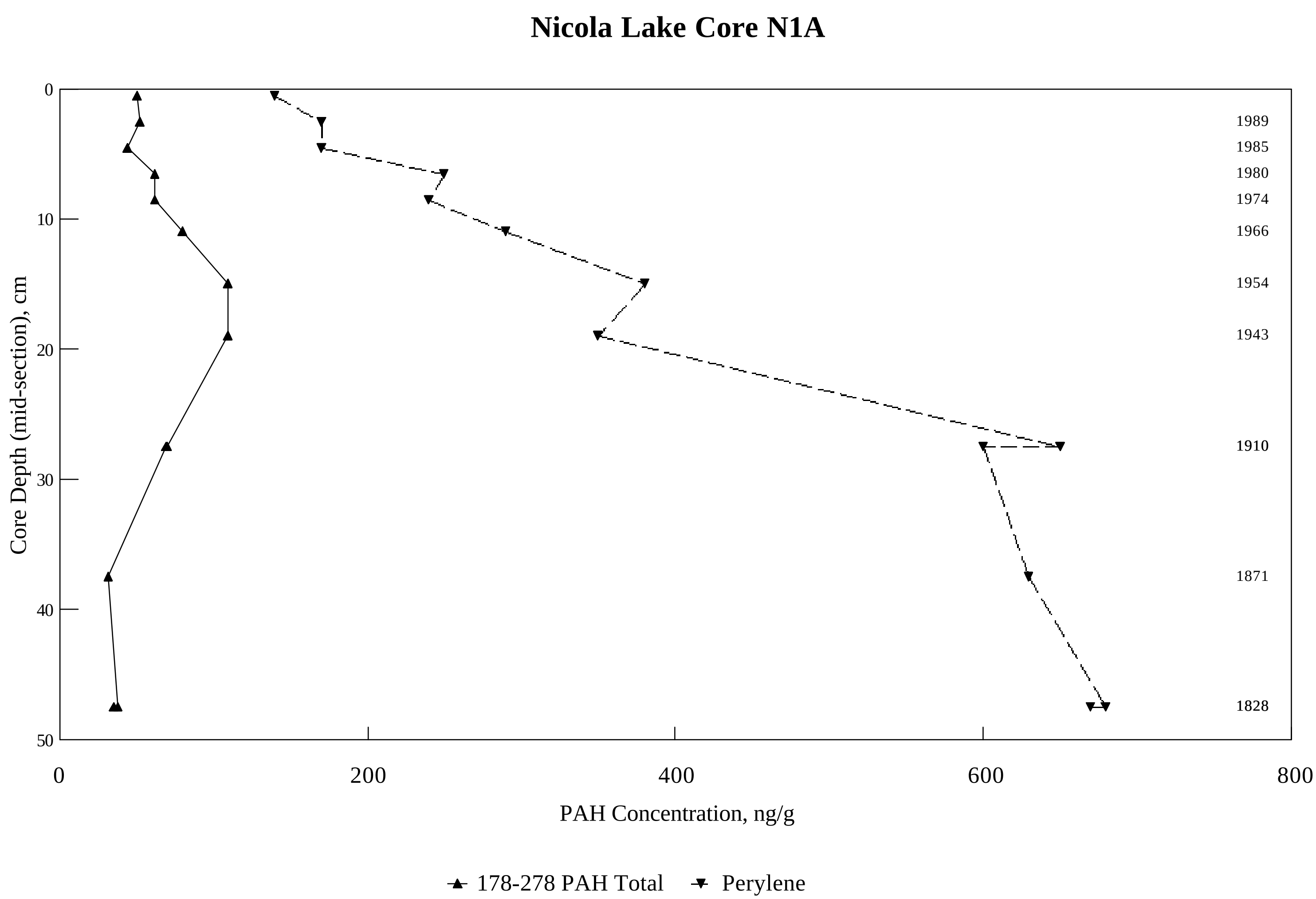

Figure 2b. Σ 178-278 parent PAH total (perylene excluded; solid line) and perylene (long dashed line) for Nicola Lake.

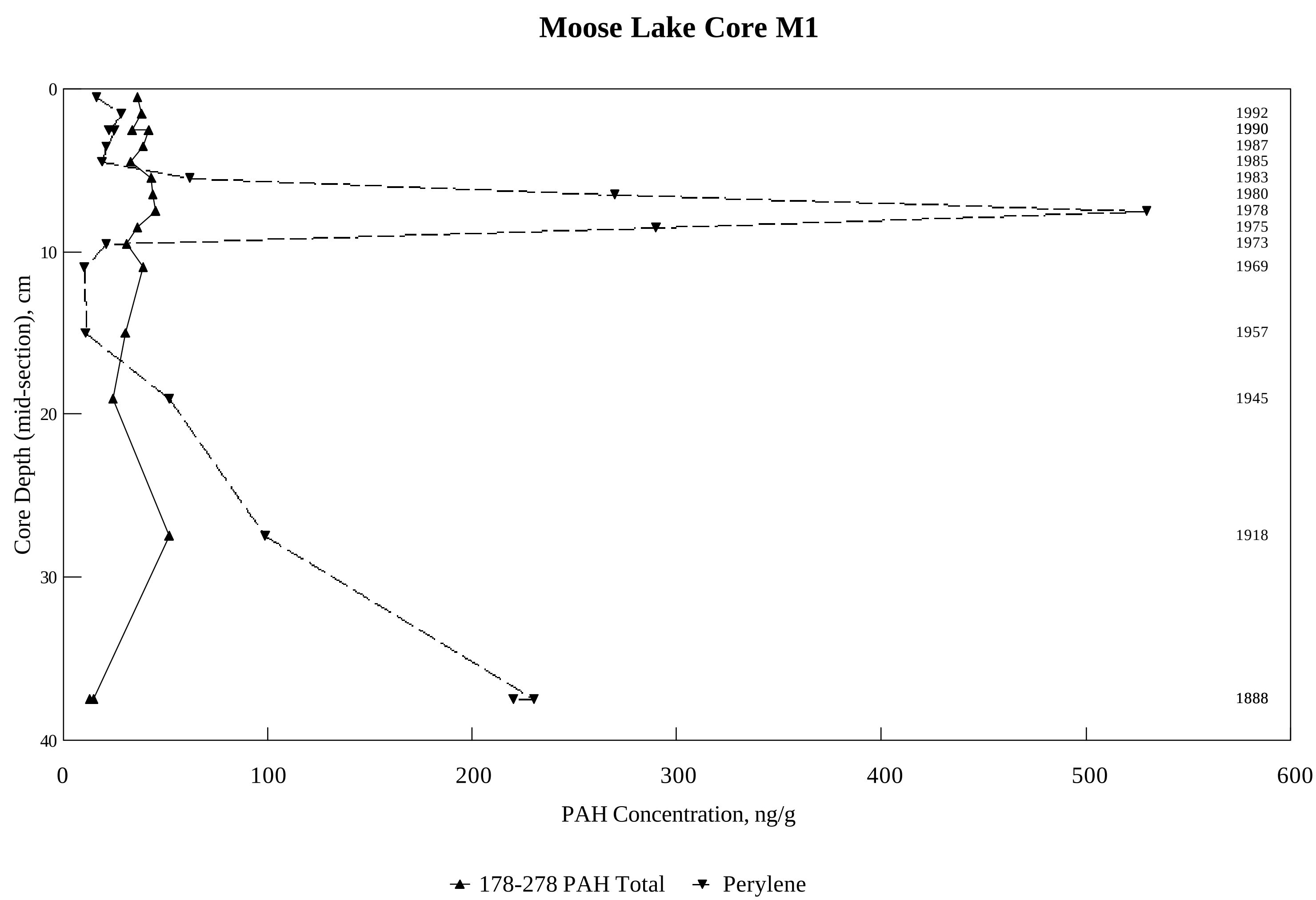

Figure 2c. Σ 178-278 parent PAH total (perylene excluded; solid line) and perylene (long dashed line) for Moose Lake.

Kamloops Lake Cores K1 and K2

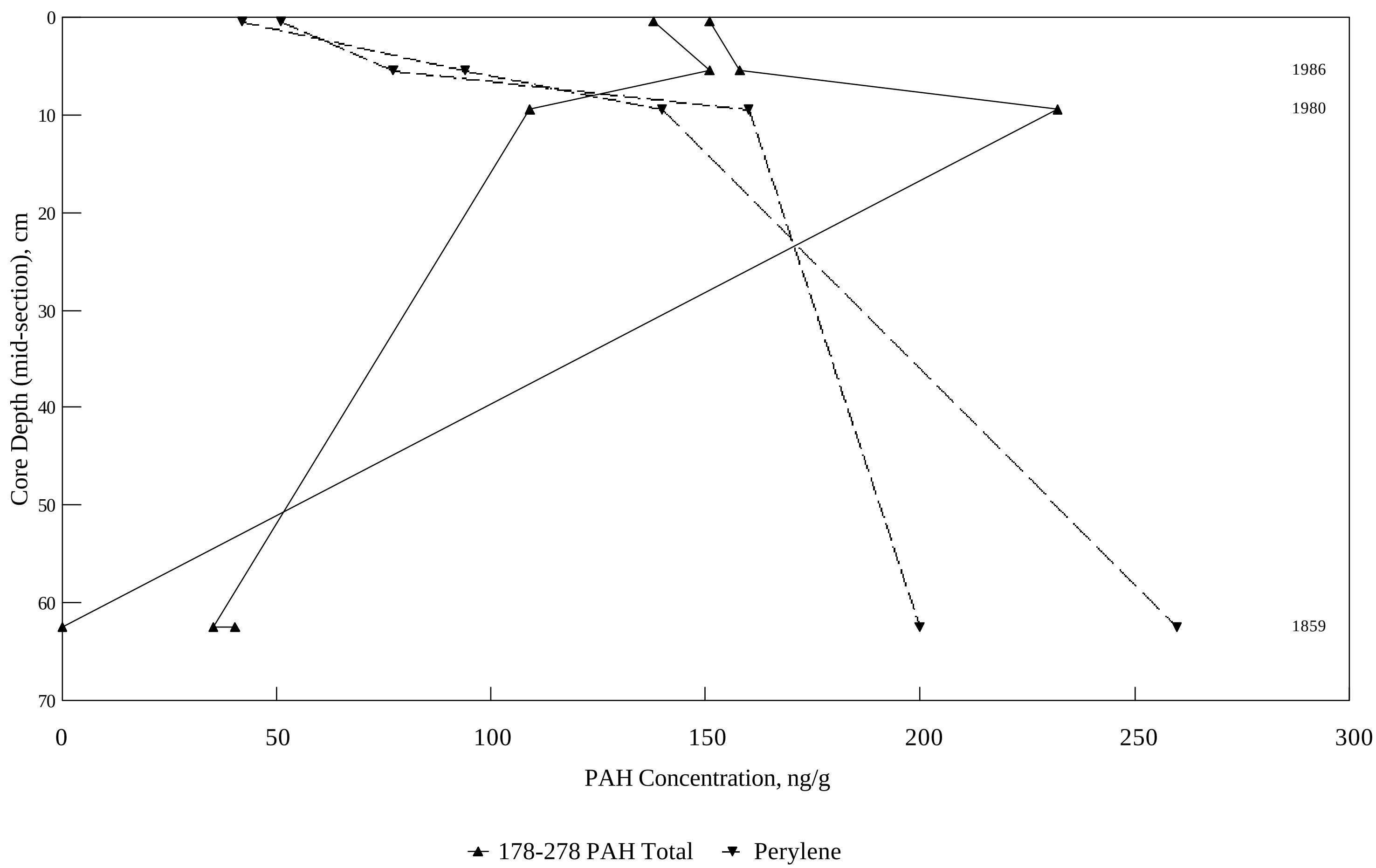

Figure 2d. Σ 178-278 parent PAH total (perylene excluded; solid line) and perylene (long dashed line) for Kamloops Lake.

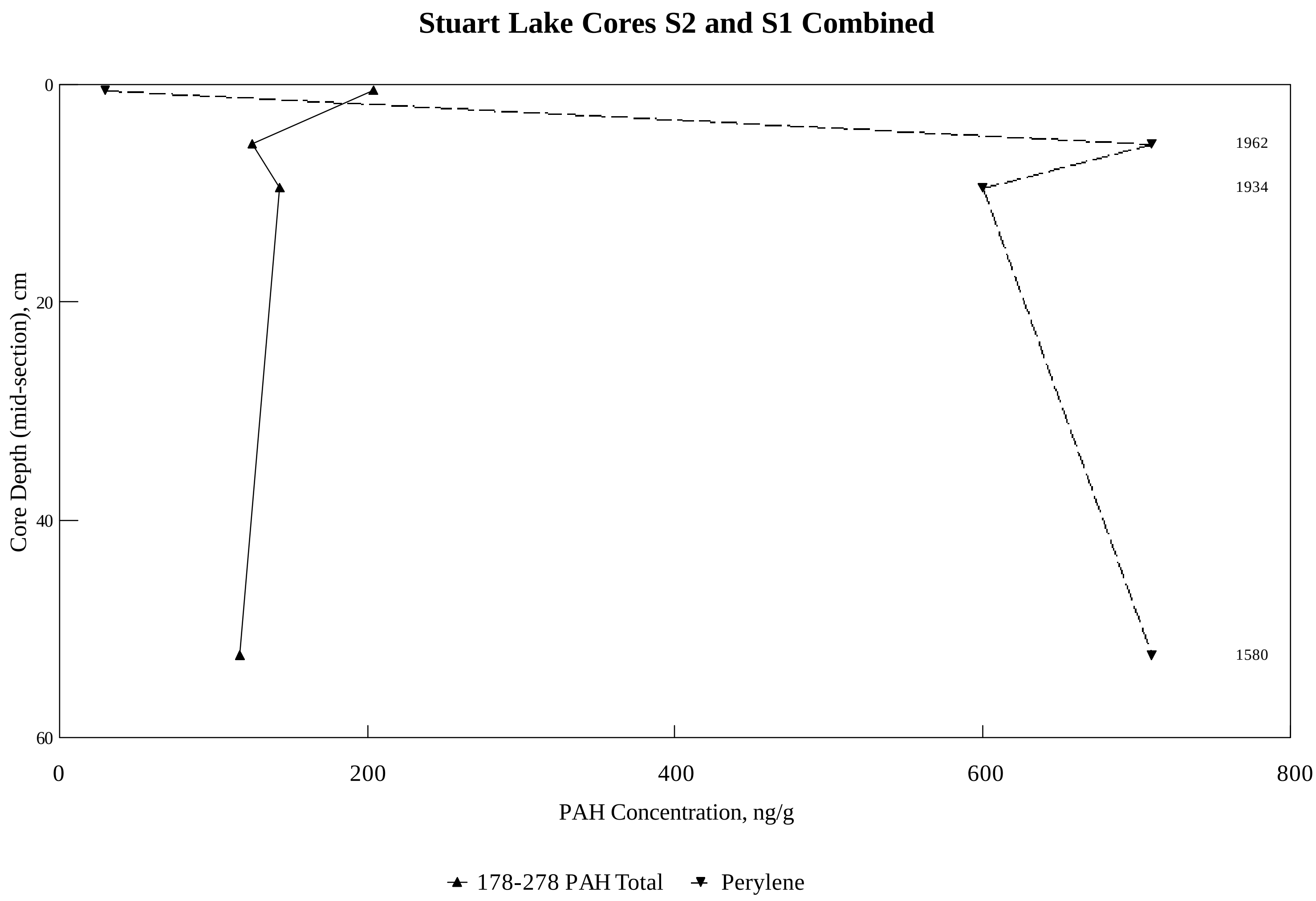

Figure 2e. Σ 178-278 parent PAH total (perylene excluded; solid line) and perylene (long dashed line) for Stuart Lake.

Chilko Lake Cores C1 and C3 Combined

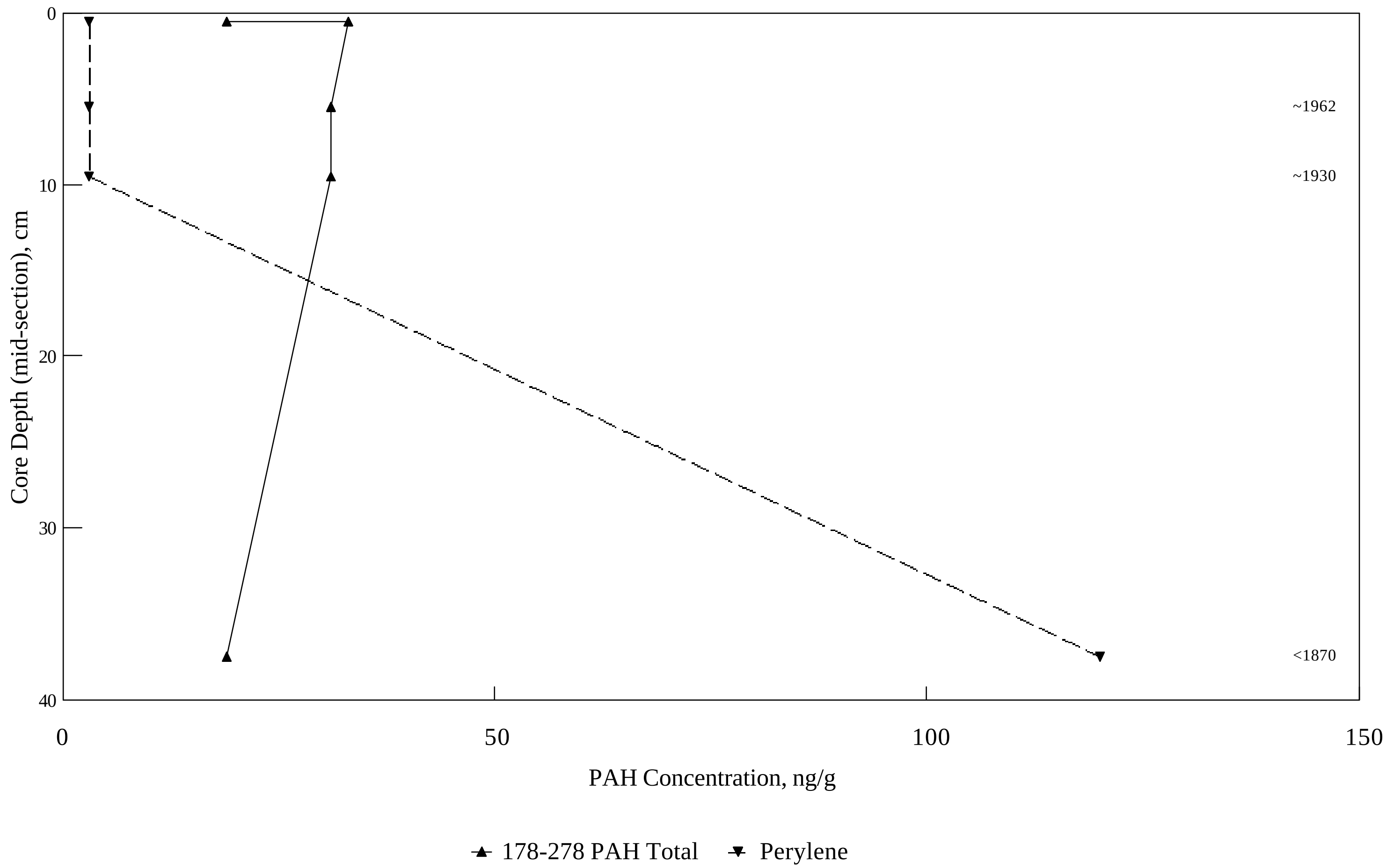

Figure 2f. Σ 178-278 parent PAH total (perylene excluded; solid line) and perylene (long dashed line) for Chilko Lake.

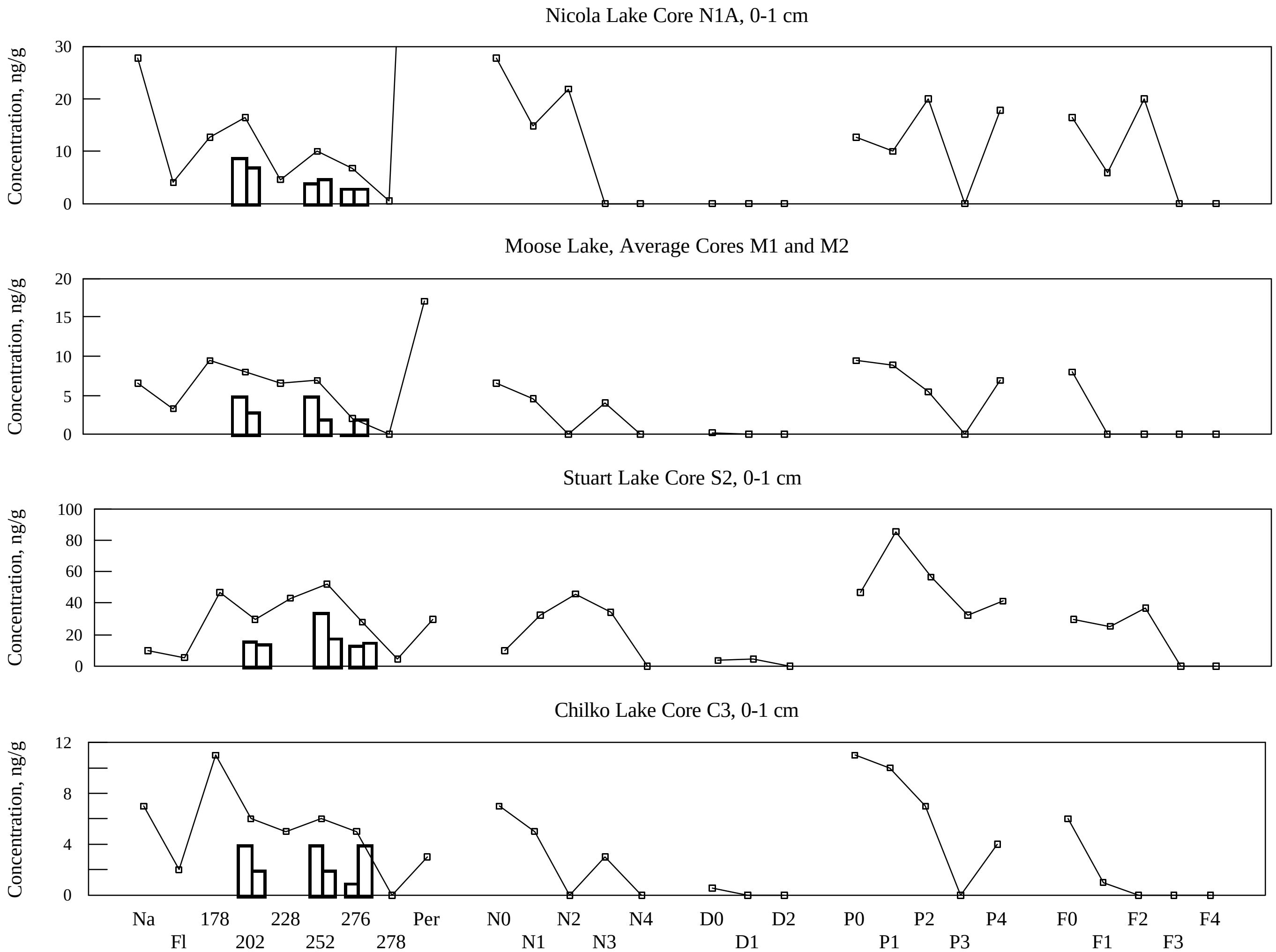

Figure 3a. PAH concentration profiles for parent and alkyl substituted PAHs (see Table 2 for abbreviations).

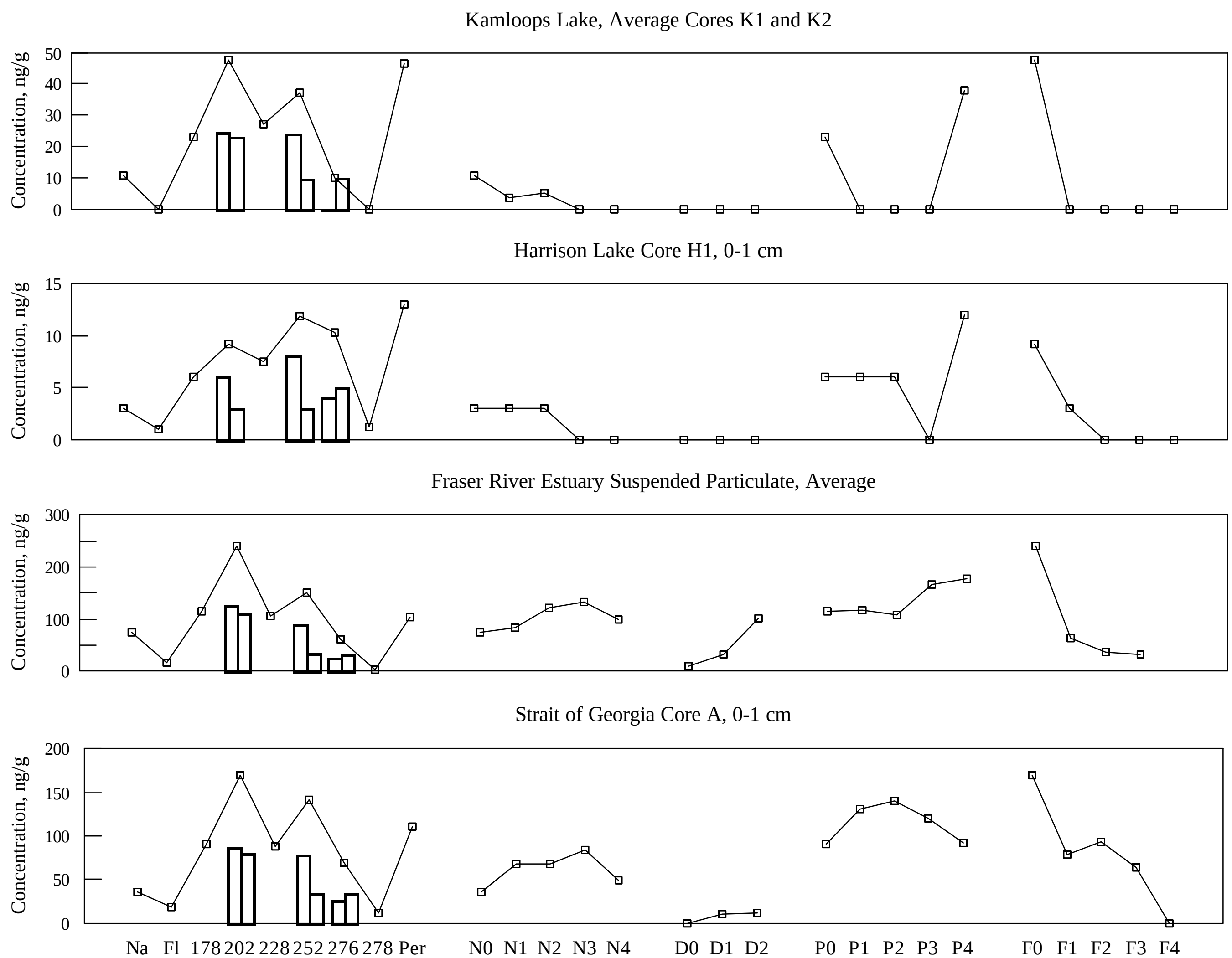

Figure 3b. PAH concentration profiles for parent and alkyl substituted PAHs (see Table 2 for abbreviations).

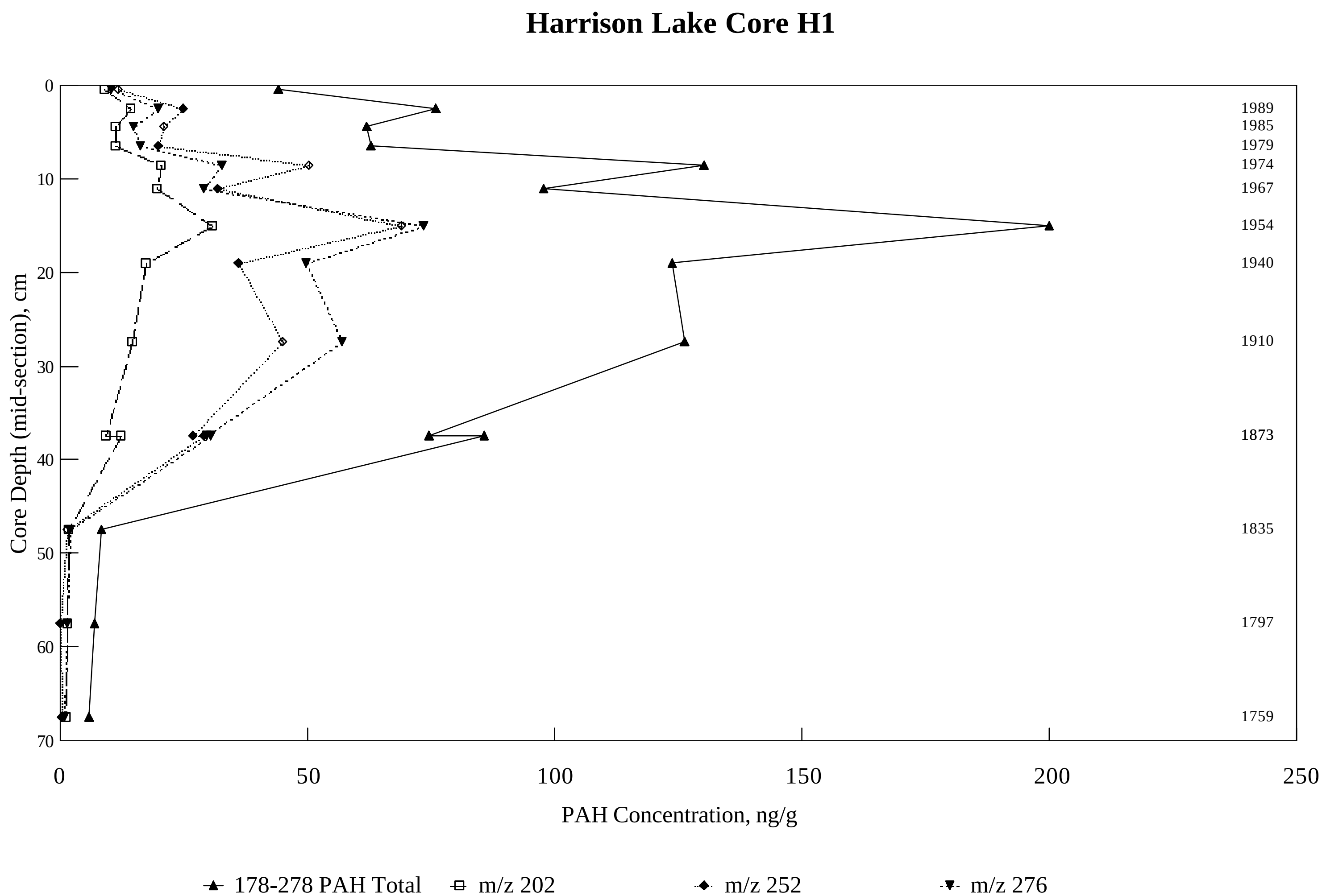

Figure 4a. Σ 178-278 parent PAH total (perylene excluded) and m/z 202, 252 and 276 concentrations for Harrison Lake.

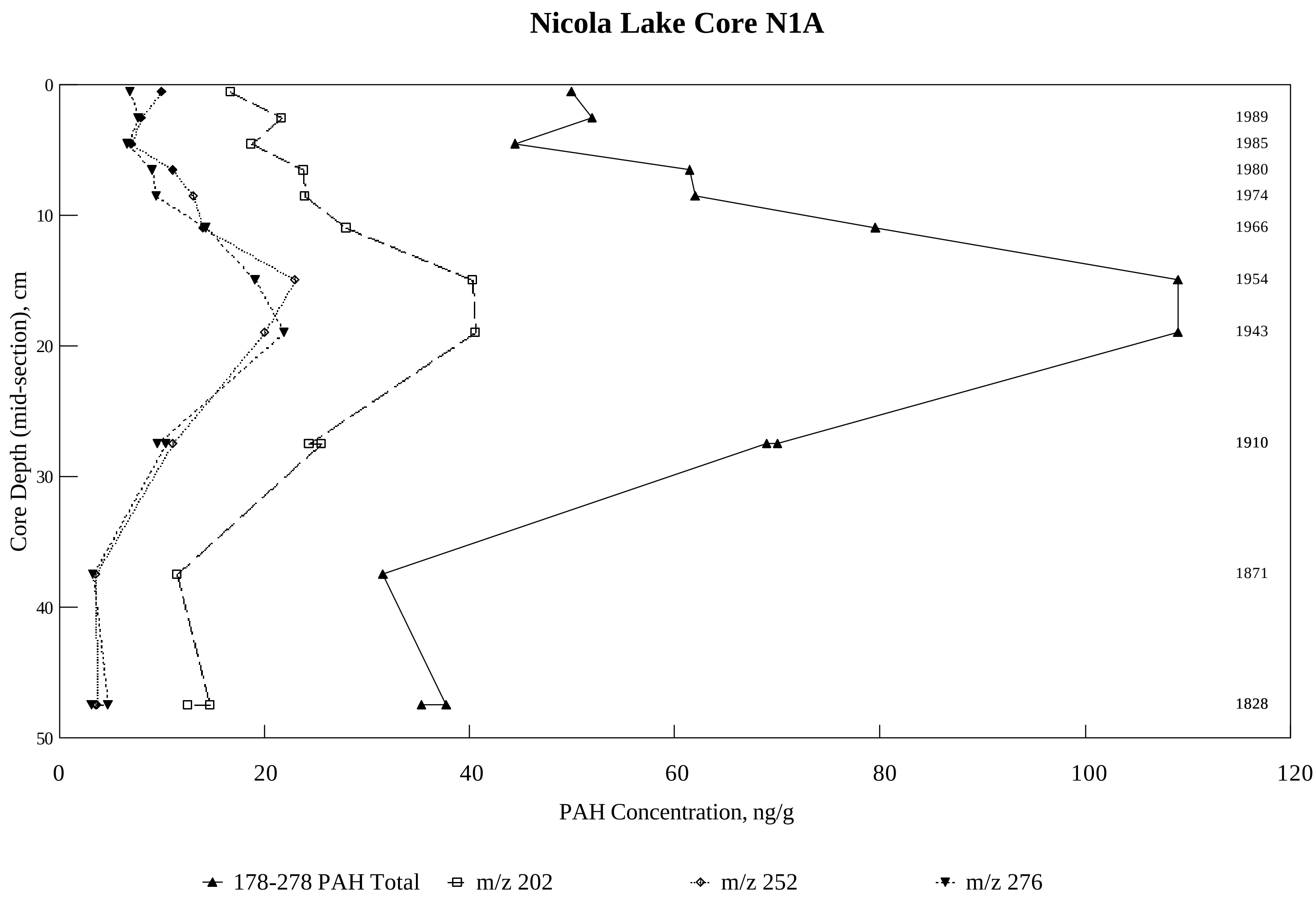

Figure 4b. Σ 178-278 parent PAH total (perylene excluded) and m/z 202, 252 and 276 concentrations for Nicola Lake.

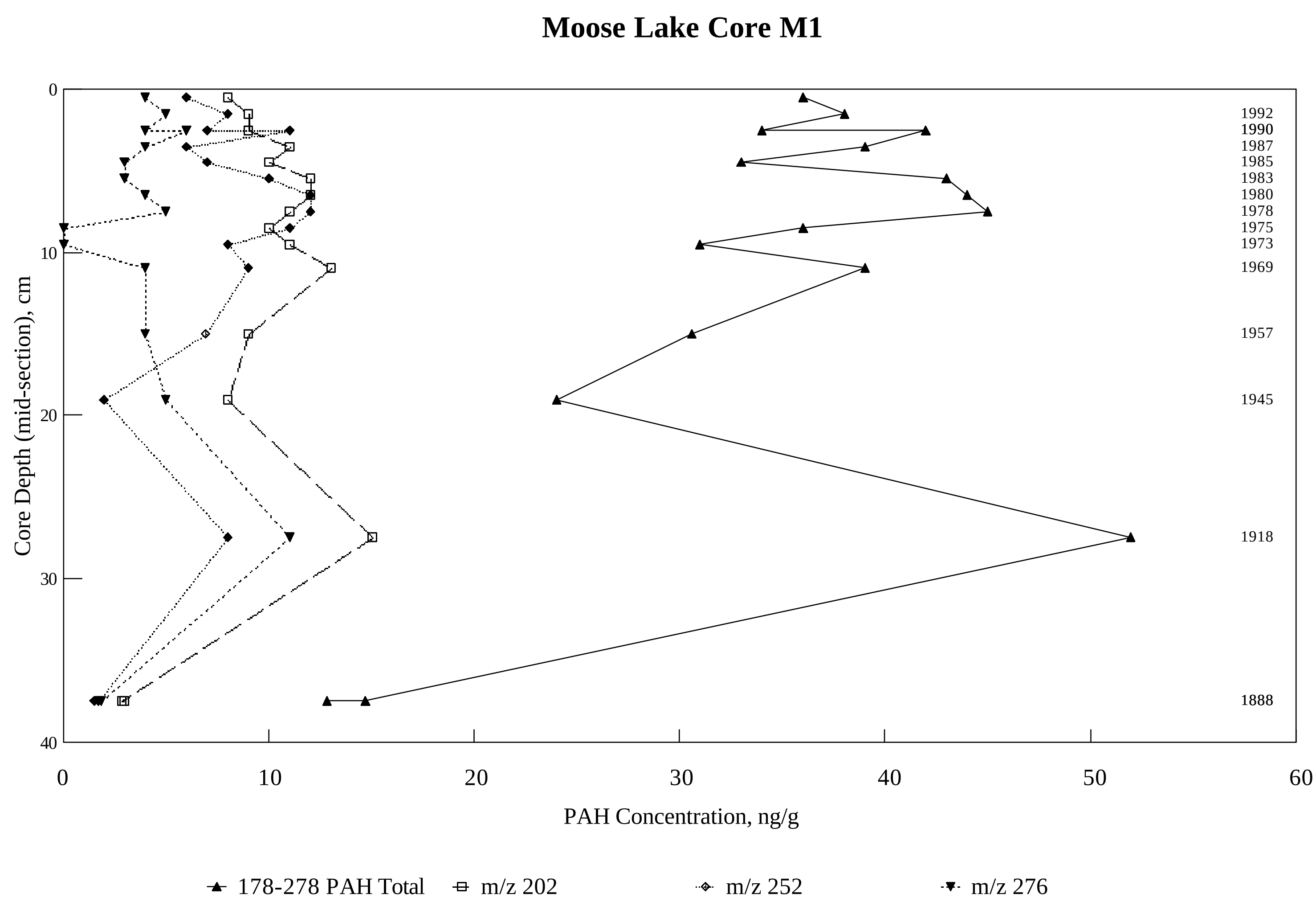

Figure 4c. Σ 178-278 parent PAH total (perylene excluded) and m/z 202, 252 and 276 concentrations for Moose Lake.

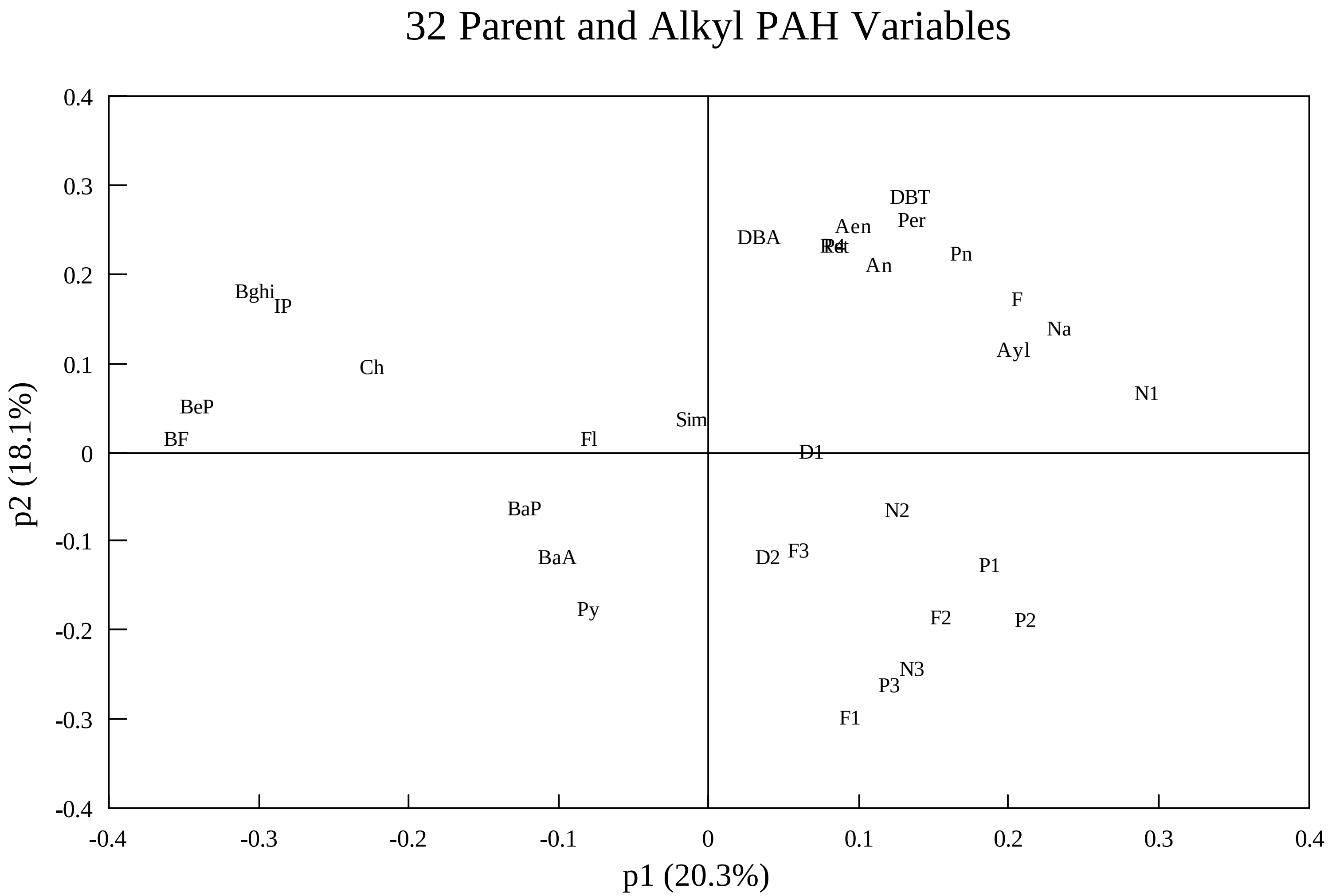

Figure 5a. PCA variable plot with data mid-range normalized, log transformed and autoscaled.

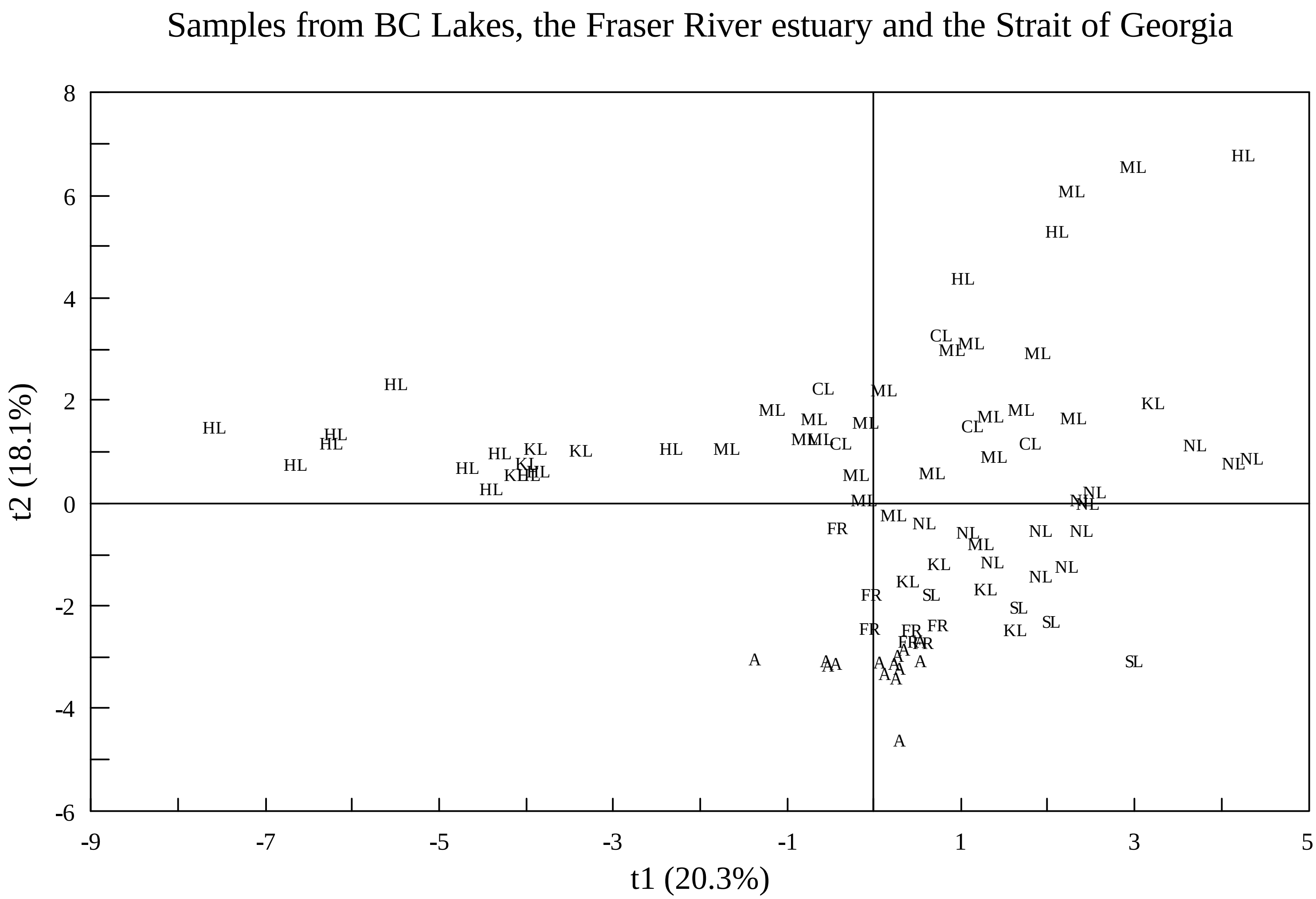

Figure 5b. PCA sample plot with data mid-range normalized, log transformed and autoscaled.

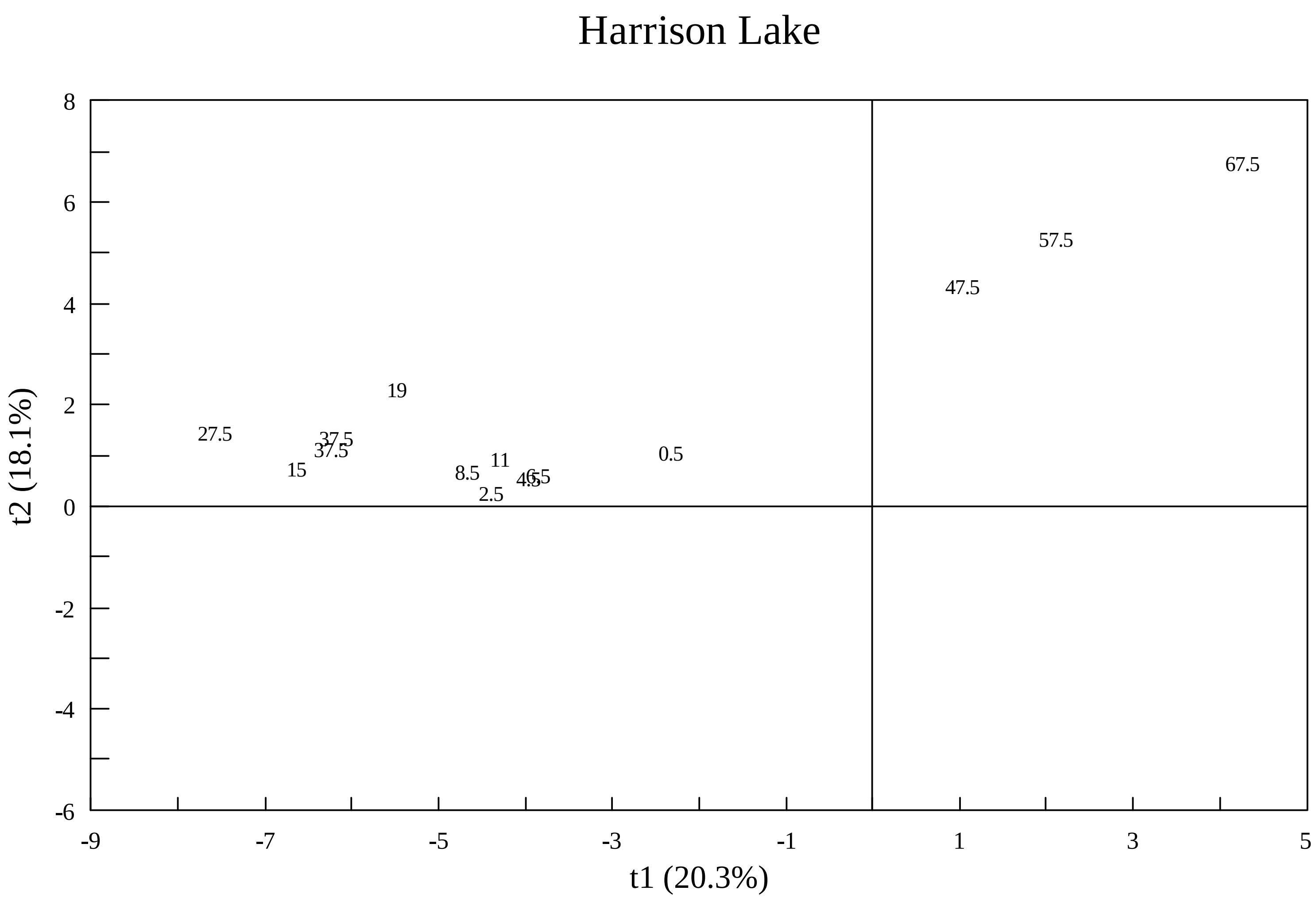

Figure 5c. PCA sample plot showing Harrison Lake samples by core depth (mid-section, in cm).

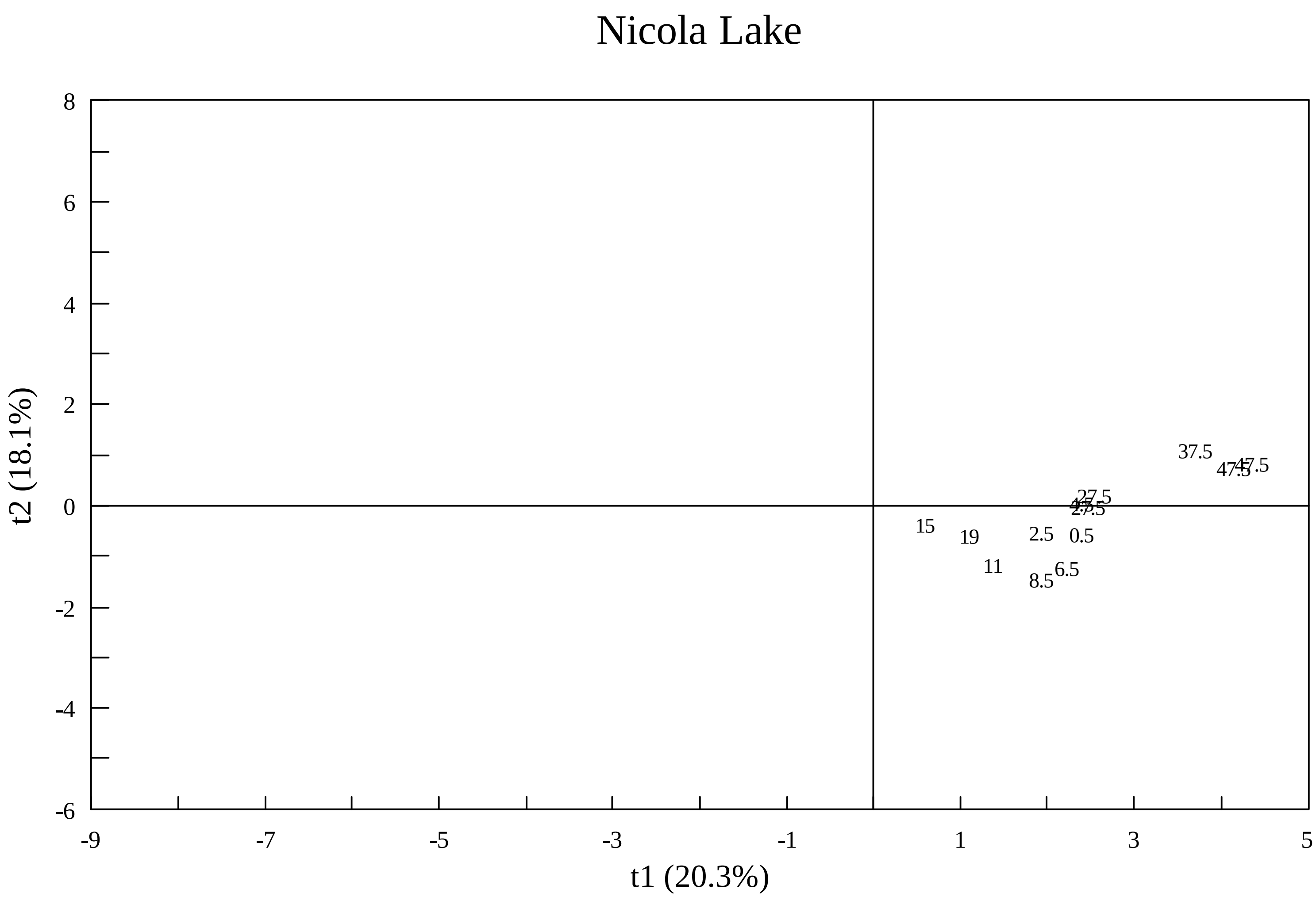

Figure 5d. PCA sample plot showing Nicola Lake samples by core depth (mid-section, in cm).

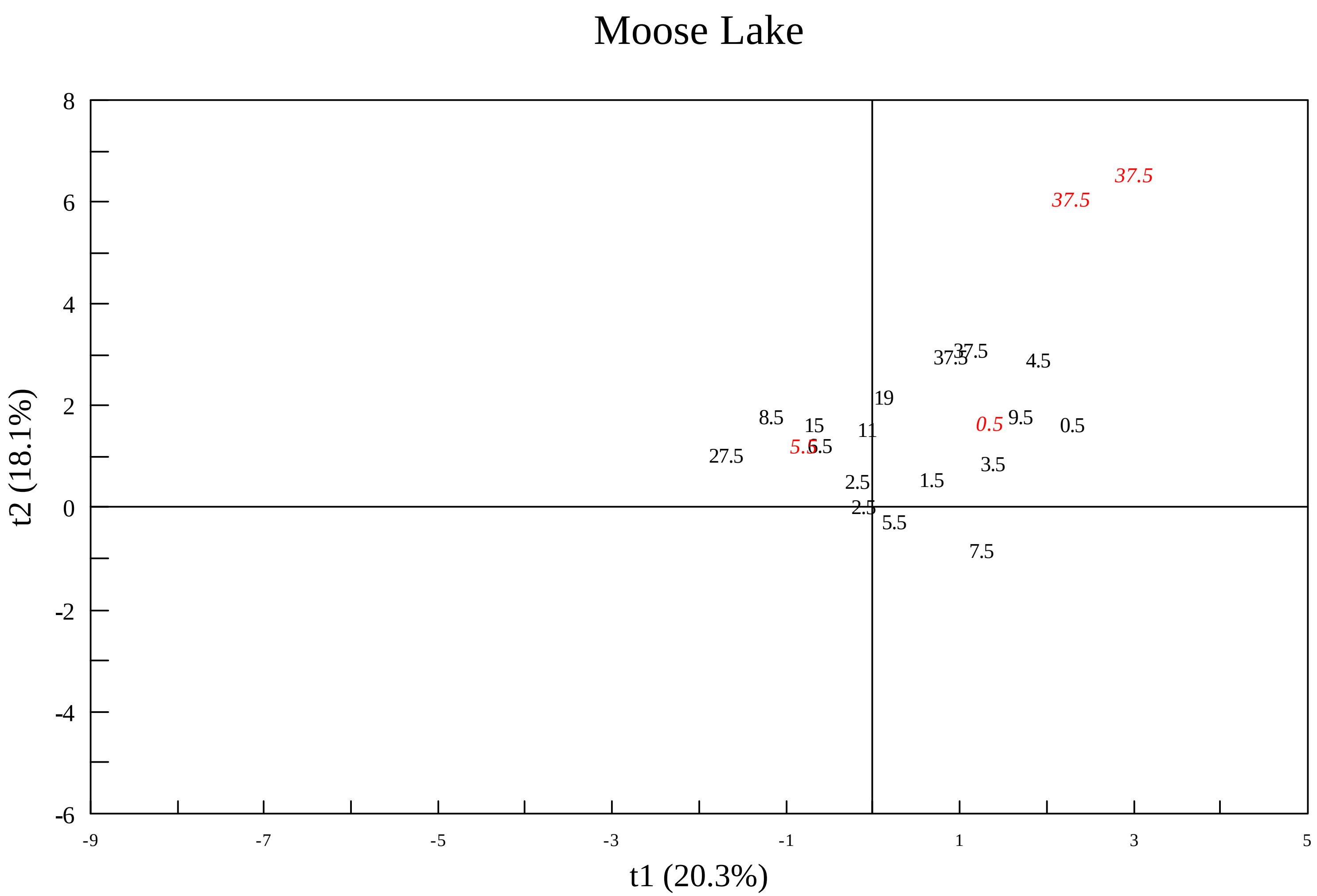

Figure 5e. PCA sample plot showing Moose Lake samples by core depth (mid-section, in cm; core 2 is in italics).

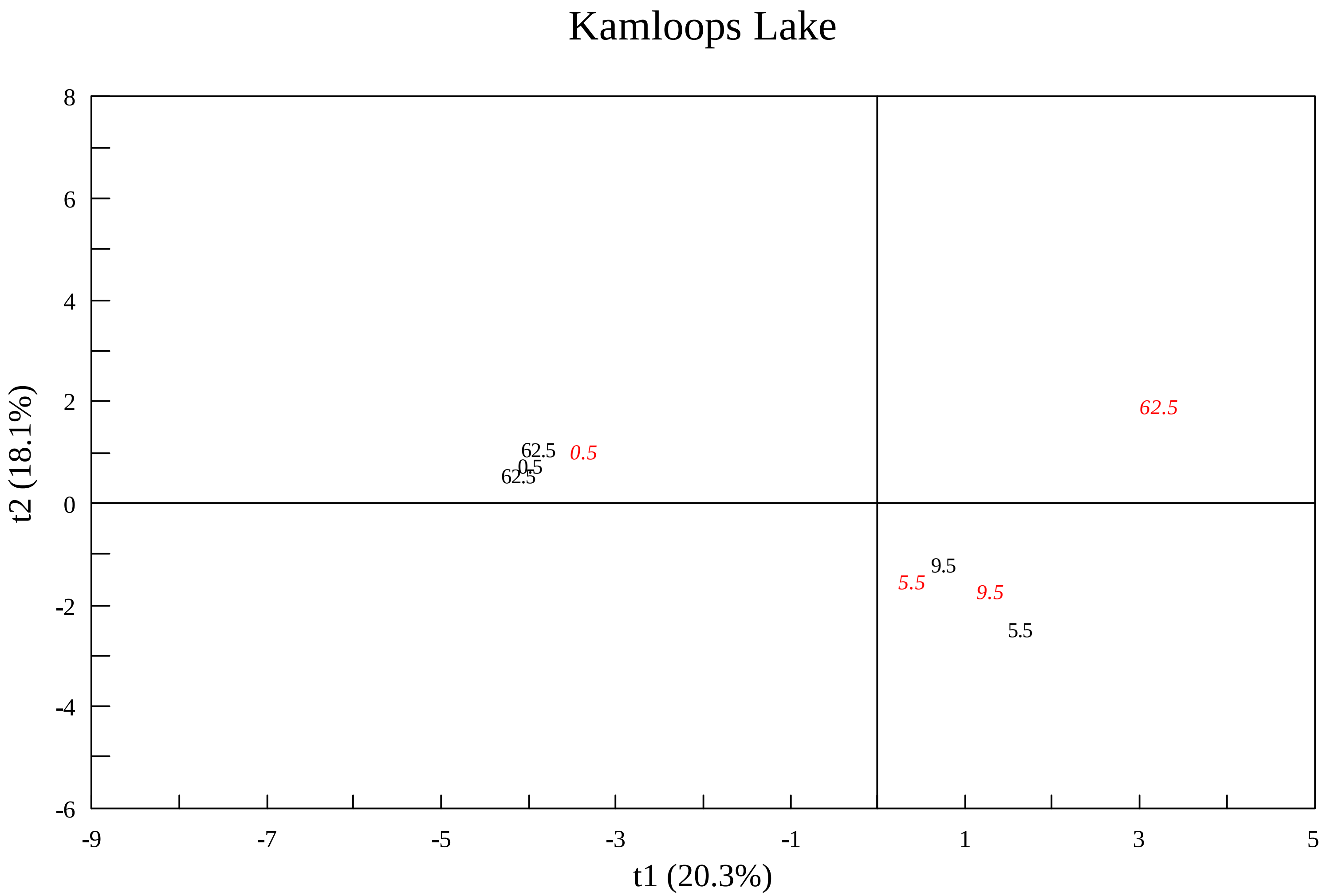

Figure 5f. PCA sample plot showing Kamloops Lake samples by core depth (mid-section, in cm; core 2 is in italics).

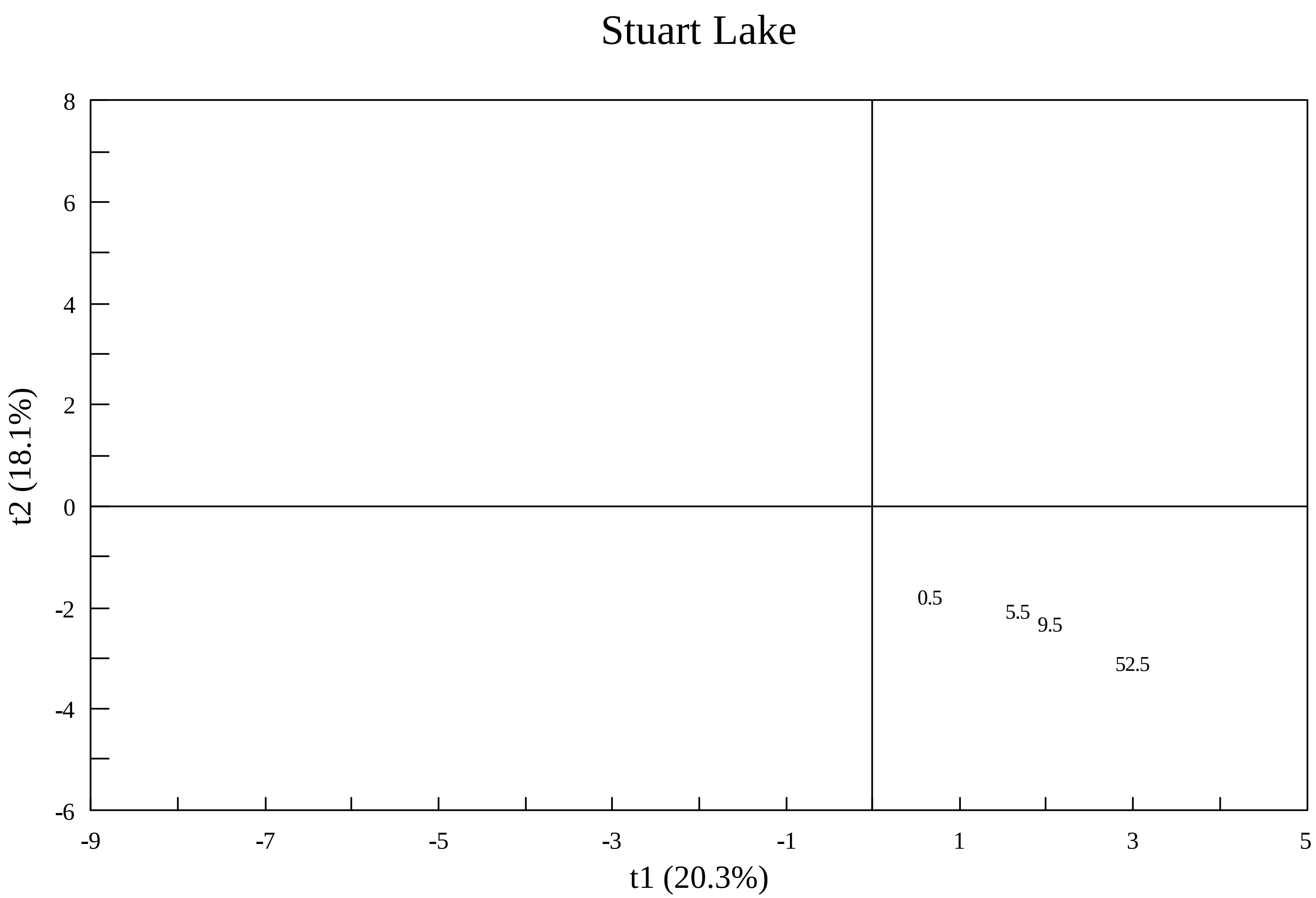

Figure 5g. PCA sample plot showing Stuart Lake samples by core depth (mid-section, in cm).

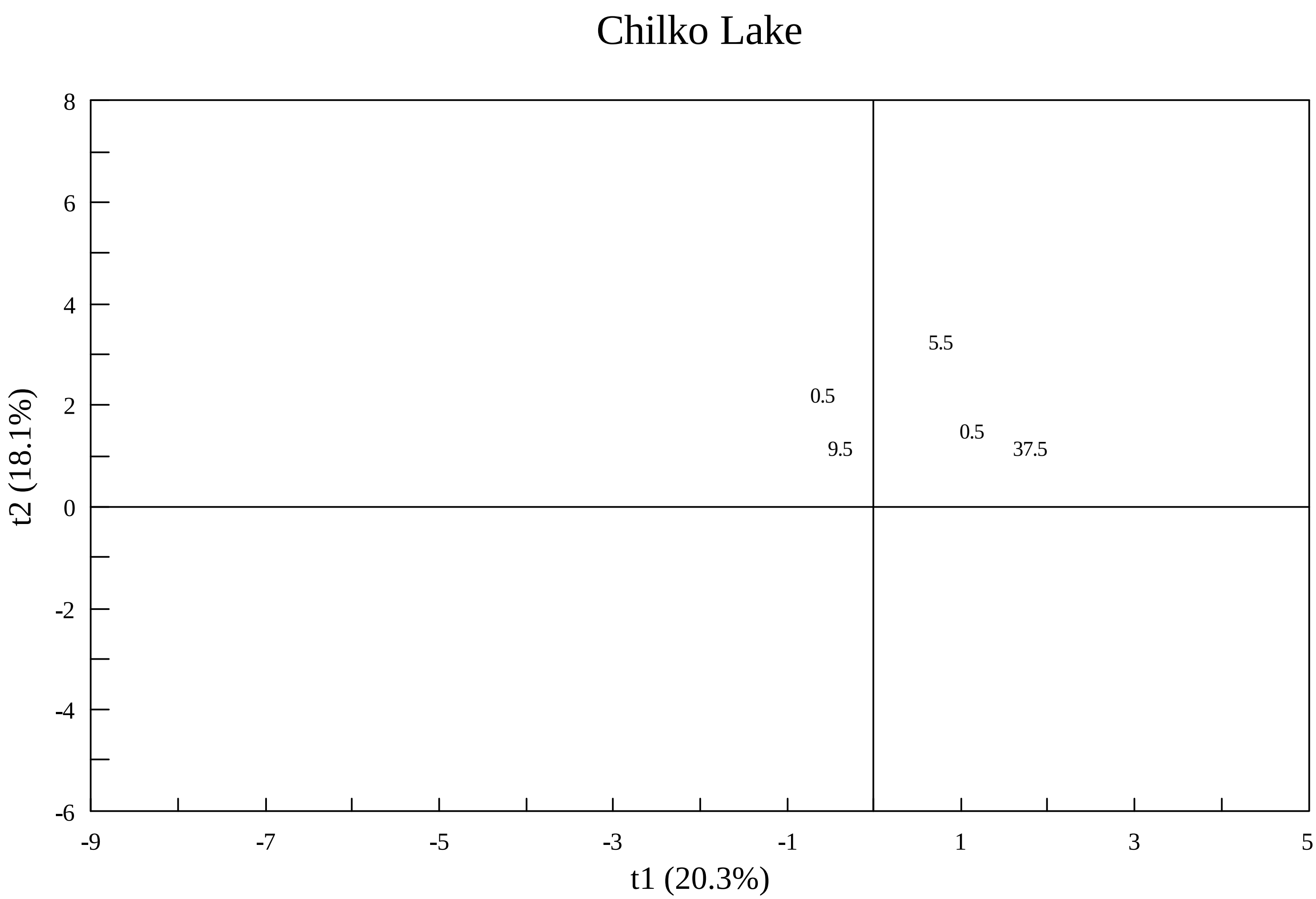

Figure 5h. PCA sample plot showing Chilko Lake samples by core depth (mid-section, in cm).

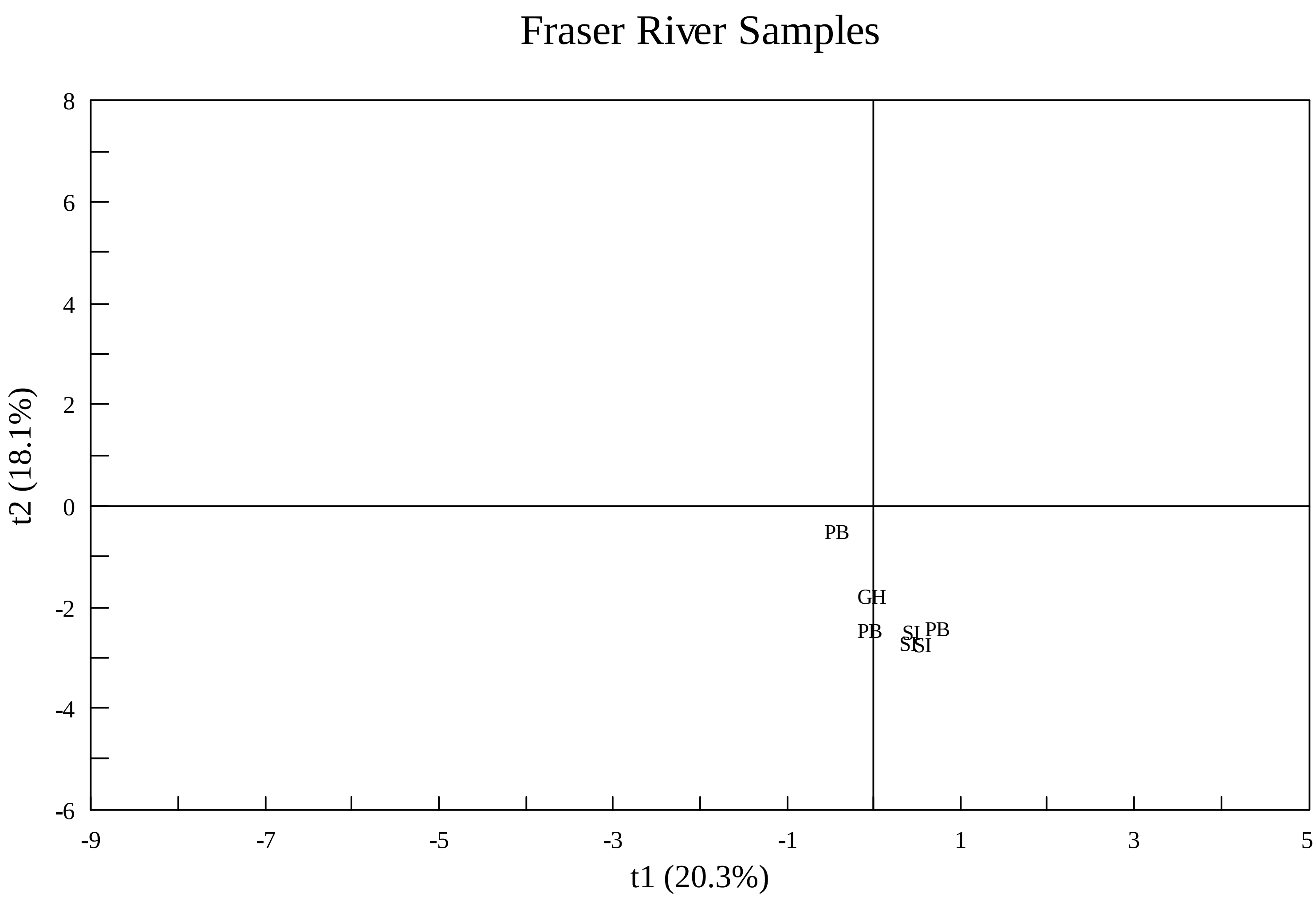

Figure 5i. PCA sample plot showing Fraser River estuary (Pattullo Bridge, PB; Steveston Island, SI) and Ganges Harbour (GH) samples.

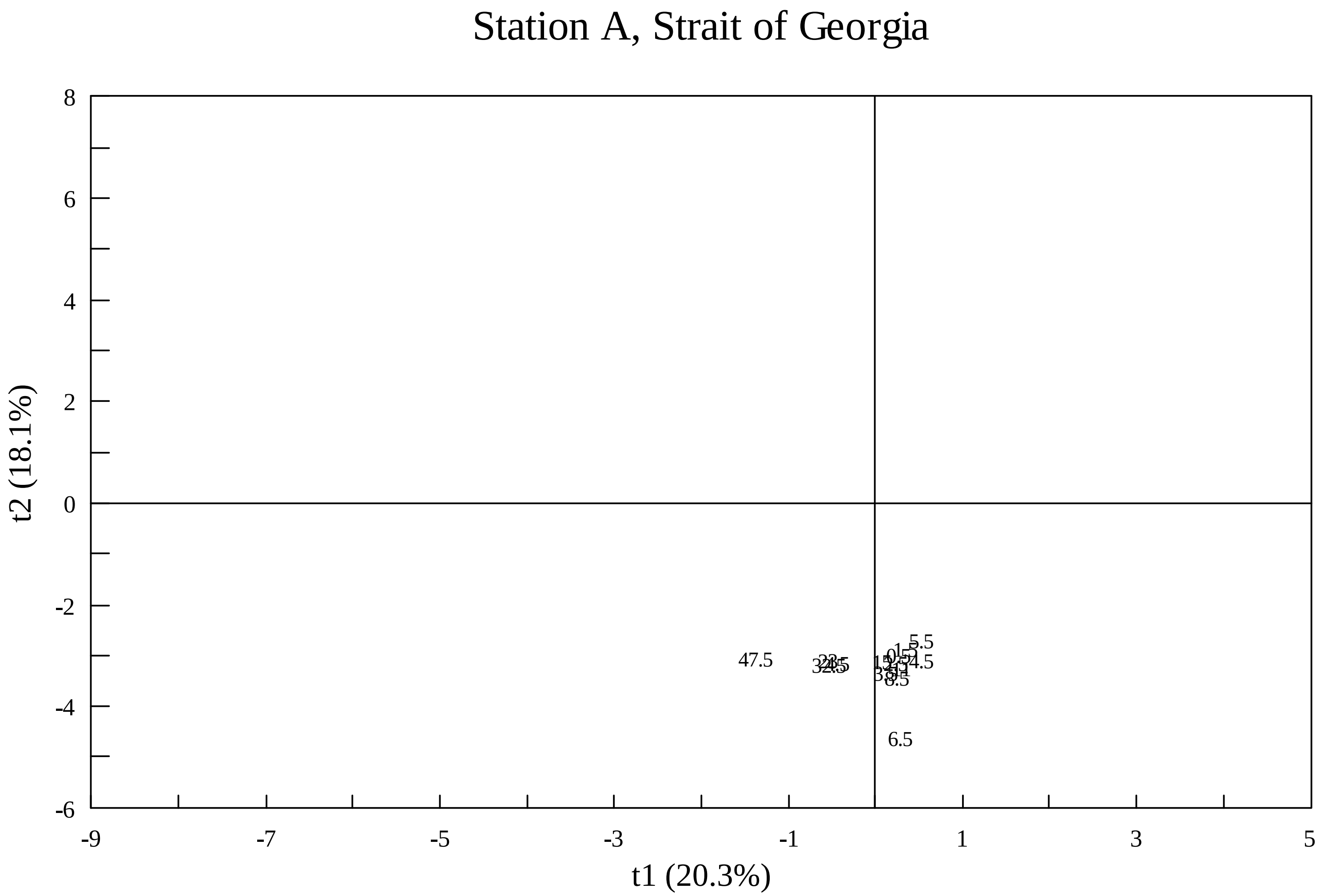

Figure 5j. PCA sample plot showing samples by core depth (mid-section, in cm) from Station A in the Strait of Georgia.

Appendix A

Appendix B