

HYDROCARBONS IN GREAT LAKES SEDIMENTS

E. Nagy, J.H. Carey, J.H. Hart

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**Lakes Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6**

Environment Canada

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EXECUTIVE SUMMARY

Concentrations of polycyclic aromatic hydrocarbons (PAHs) were found to be higher near potential sources in Thunder Bay Harbour, the St. Mary's River, and Hamilton Harbour than in the main basins of Lake Erie or in selected cores in the St. Lawrence River.

Compositions (profiles) of PAHs near point sources were highly variable due to possible multiple sources or sediment movement. Pollutant surveys in such areas require careful planning and a fairly intensive sampling to accomodate the observed variability and to allow significant conclusions about specific pollutants.

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MANAGEMENT PERSPECTIVE

Polycyclic aromatic hydrocarbons (PAHs) were determined in six different locations in Great Lakes sediments. Their concentrations were significantly higher near potential sources than in "average" Great Lakes sediments. Similar concentrations were found in Thunder Bay and Hamilton Harbour and in the St. Mary's River.

The concentration and composition of the PAHs were quite variable around potential sources, showing the need of well thought out and intensive surveys at such locations.

PERSPECTIVES DE GESTION

On a mesuré la concentration d'hydrocarbures aromatiques polycycliques (HAP) dans les sédiments à six endroits différents dans les Grands Lacs. Les concentrations étaient sensiblement plus élevées près des sources possibles que dans les sédiments "typiques" des Grands Lacs. Des concentrations semblables ont été relevées dans le port de Thunder Bay et celui de Hamilton ainsi que dans la rivière St Mary's.

La concentration et la composition des HAP variaient considérablement près des sources possibles, d'où la nécessité de procéder à des relevés intensifs, bien planifiés, à de tels endroits.

RÉSUMÉ

Les concentrations d'hydrocarbures aromatiques polycycliques (HAP) relevées près des sources possibles dans le port de Thunder Bay, la rivière St Mary's et le port de Hamilton, étaient plus élevées que dans les principaux bassins du lac Erié ou dans des carottes prélevées à des endroits choisis dans le fleuve Saint-Laurent.

Les profils de composition des HAP près des sources ponctuelles variaient considérablement en raison de l'existence possible de sources multiples ou du mouvement des sédiments. On doit préparer avec soin les relevés de polluants à de tels endroits et effectuer un échantillonnage qui soit suffisamment intensif pour tenir compte de la variabilité observée et permettre des conclusions significatives au sujet de polluants particuliers.

RÉSUMÉ

La présence d'hydrocarbures aromatiques polycycliques (HAP) dans les sédiments a été déterminée à six endroits très éloignés les uns des autres dans le réseau des Grands Lacs. Les concentrations variaient de moins de 5 ug/g dans les bassins de sédimentation du lac Erié et dans des carottes prélevées à des endroits choisis dans le fleuve Saint-Laurent, à 20 à 30 ug/g (ou plus) à proximité des sources ponctuelles possibles.

La variation des concentrations de HAP et des profils de composition près des sources ponctuelles indique que la répartition des HAP pourrait être compliquée par les sources multiples ainsi que par la dynamique de l'eau et des sédiments. On doit donc apporter un grand soin aux relevés de sédiments à ces endroits et déployer les efforts nécessaires.

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ABSTRACT

The presence of polycyclic aromatic hydrocarbons (PAHs) in sediments was determined in six widely separated locations in the Great Lakes system. Concentrations varied from below 5 ug/g in the Lake Erie sedimentation basins and in selected St. Lawrence River cores to 20 - 30 ug/g (or higher) in the vicinity of potential point sources.

Variations in PAH concentration and composition (profiles) near point sources indicated that PAH distributions may be complicated by multiple sources and by water and sediment dynamics. Sediment surveys of such areas will therefore require careful planning and a "critical mass" of effort.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have been reported in airborne particulates, soils and freshwater and marine sediments in widely scattered geographic areas. They are regarded as significant environmental contaminants because of their carcinogenic or mutagenic properties (1-5).

PAHs produced by the combustion of various fuels in power production, space heating, industrial processes and in internal combustion engines are generally found on airborne particulate matter. They may be widely distributed in that form before deposition on land or water surface in precipitation. Rivers may concentrate PAHs from their drainage basins and may then accumulate them in lakes or oceans.

Another potential PAH source, petroleum, may enter marine or freshwater environments in oil spills, refinery wastes and in natural oil seeps.

This study of PAHs in Great Lakes surficial sediments was the continuation of an investigation, initiated in 1985, of these potential carcinogens in water systems of diverse geographic areas. In addition to examining possible inputs, accumulations and persistence of these substances, the goals of the study included the use of PAH profiles for the identification of the types of sources (energy production, space heating, etc).

The sampling strategy for 1986 relied on obtaining sediment samples from a number of ongoing studies in the Great Lakes that were designed to study metals or other organic contaminants in the sediments of selected areas.

EXPERIMENTAL METHODS

Study areas

Thunder Bay: The survey of PAHs was made in support of a continuing study of organic contaminants originating from Northern Wood Preservers, Inc., undertaken by E.P.S., Ontario Region (6). This plant is a known point source of creosote-related compounds to the lake. The location of the sampling sites is shown in Figure 1.

St. Mary's River: The PAH survey was again part of a larger study of inorganic and organic contaminants in the sediments of the St. Mary's River system. The location of the sampling sites in the river and in Little Lake George is shown in Figure 2. The sites are located downstream from several point sources of organics including a steel mill, a paper mill, and a sewage treatment plant. Surface sediments were collected with an Ekman dredge at the end of July, 1986. The sediments were fine brownish-to-grey silty clays, with some visible oil on the sediment surface.

Lake Erie: A surface sediment sample was collected, using a Shipek dredge, in each of the three sedimentation basins of Lake Erie, as shown in Figure 3.

Lake Ontario: Four surface sediment samples were collected off the Leslie Street spit in Toronto Harbour for PAH analysis, after a shallow-water sample, collected in 1985, appeared heavily coated with an oily material (7) and was found to contain extremely high PAH concentrations. The location is shown in Figure 4.

Hamilton Harbour: Sediment samples were obtained from two settling basins, designated N(orth) and S(outh) in Figure 5. The samples were collected with a grab sampler before and after a liming experiment in the South basin (8). Water samples were also collected for analysis at each sampling time.

St. Lawrence River: Four sediment cores were obtained from the sites shown in Figure 6, which were selected for the possibly different inputs from the St. Lawrence and the Ottawa rivers.

All sediment samples were frozen before shipping to the laboratory and were stored in a freezer before analysis.

Analyses

The sediment samples were extracted and fractionated according to the scheme shown in Figure 7. The base-neutral extract was separated into four fractions of increasing polarity, with normal alkanes and PAHs concentrated in the first two fractions. Fractions 3 and 4 contained few components that were

detected by gas chromatography.

Fractions 1 and 2 were analyzed by GC/FID for quantitation of n-alkanes (C₁₂ to C₂₆) and of 16 PAHs, listed in Table 1. Individual components were further identified by GC/MS. The latter technique was also used for the identification of additional polyaromatics or other organics in the extracts.

The water samples from Hamilton Harbour were filtered, then both suspended materials and the water phase were extracted with dichloromethane. The extracts were analyzed with the GC/FID and GC/MS techniques without fractionation.

The equipment and operating conditions for the analyses were:

GC/FID (quantitative):

Hewlett-Packard 5700A
Split injection (1:10)
30 m fused silica cap.column (DB-5)
Injection temp. 250°C
Detection temp. 250°C
Prog.: 90°C for 2 min - 4°C/min to 290°C,
290°C for 15 min.

GC/MS (qualitative):

Carlo-Erba system
On-column injection
30 m fused silica cap.column (DB-5)
Prog.: 70°C for 2 min - 5°C/min to 290°C
290°C for 15 min.

MS: Desi-Nermag system, electron ionization at 70 eV,
positive ion anode.

RESULTS AND DISCUSSION

Thunder Bay sediments

The concentrations of priority pollutant PAHs in the six sediment samples, as shown in Table 2, ranged from nondetectable levels to 11.6 micrograms/gram for individual compounds, and from about 9 to about 20 ug/g for the sum of the 16 compounds. In the whole set of samples, acenaphthene, anthracene, fluoranthene and pyrene were the predominant compounds. The PAH profiles, shown in Figure 8, varied significantly within the small sampling area, suggesting a variety of sources or some processes that may modify their composition.

In addition to the above suite of PAHs, the samples all contained a large number of methyl homologs, listed in Table 3.

Their concentrations, estimated from the GC/MS total ion chromatograms, were generally lower than those of their parent compounds, and diminished with increasing methyl substitution. The single exception from this behaviour was tetramethyl phenanthrene (or anthracene) which was often present at higher concentration than the lower homologs. Table 3 also lists the additional PAHs detected, of which biphenyl, dibenzofuran, and carbazole were seen in almost all samples at concentrations estimated to be similar to those of the major compounds of the priority list.

The analysis of normal alkanes was disturbed by broad peaks in the chromatograms. The GC/MS runs showed that the C₁₂ to C₂₆ homologs were all present at relatively low concentrations, estimated as about 5 ug/g for all 15 alkanes. Their concentrations were highest for the C₁₅ and C₁₇ members.

St. Mary's River sediments

The PAH concentrations in the three sediment samples (Table 4) showed that the St. Mary's River sample contained significantly higher PAH levels than the two sediment samples from Little Lake George, about 4 km downriver. The PAH profile in the river sample, shown in Figure 9, was also significantly different from those found in the lake sediments. Among the five predominant PAHs in the two locations, phenanthrene was the only common constituent:

river sediment:	lake sediments:
naphthalene	fluoranthene
benzo(a)anthracene	benzo(b)fluoranthene
phenanthrene	pyrene
benzo(k)fluoranthene	phenanthrene
dibenzo(ah)anthracene	benzo(a)pyrene

The n-alkane measurements and profiles were overwhelmed by the large PAH peaks in the chromatograms: estimated total n-alkane concentrations were about an order of magnitude below those of the PAHs.

Lake Erie sediments

The n-alkane and PAH concentrations in the sediments from the three lake basins are summarized in Table 5. The three lake basins get progressively deeper from west to east, the water depths at the three stations being 11, 26 and 66 m. The highest concentrations were found in the East basin for both compound types, possibly related to it being the deepest sink with the highest sedimentation rates.

The n-alkane profiles for the three sites are similar and all show some predominance of the C₁₅ and C₁₇ alkanes, indicating some biogenic origin (Figure 10).

The concentrations and the profiles of the priority pollutant PAHs are given in Table 6 and Figure 11. The significantly different compositions in the three basins suggest distinctive localized inputs of these materials, rather than a west-to-east transport in the lake.

Lake Ontario sediments

A 1985 sediment sample, collected about 1.5 km east of the Leslie Street Spit in Toronto Harbour, exhibited a black oily sheen on the sediment particles. On subsequent analysis, the sample was found to contain the highest PAH concentration (131 micrograms/gram) seen in this study. As the sample was obtained from the sloping nearshore bottom, and consisted of coarse sandy silt, the high organic content was thought highly unusual.

Subsequent sampling in the same area failed to locate the highly contaminated sediment: it is unclear whether this was due to inaccuracy in re-locating the site, or to dissipation (or movement) of the contamination from the original area. Table 7 shows the PAH analyses for the original "hot spot" and for two of the later samples.

The PAH profiles in the second set of samples, given in Figure 12, show two distinct types of composition, with neither matching the PAH profile of the original, highly contaminated sample. Such variability of concentration and composition in a small area must indicate multiple sources and a dynamic sediment environment.

An extensive search of the mass spectra of the original extract showed the presence of only a few PAHs other than those in the priority list, with biphenyl and dibenzofuran as the predominant ones. In addition, several methyl, dimethyl and tetramethyl homologs of naphthalene, biphenyl and anthracene were observed.

Hamilton Harbor samples

The settling lagoons in Hamilton Harbour contain dredged sediment from various areas of the harbour and is thought to be representative of sediment quality at a dredge disposal site.

Sediment samples were collected in the North and South settling lagoons before liming the South lagoon on Aug. 25, and again on Sept. 22, 1986. As indicated by the PAH concentrations in Table 8, the variability of the sediments in the two lagoons overwhelmed any possible changes that may be attributed to lime addition. The sediments in these lagoons, originating from various dredged areas of Hamilton Harbour, appear to be highly non-homogeneous.

The PAH and n-alkane profiles in these samples, shown in

Figures 13 and 14, further demonstrate the non-homogeneity of the lagoon sediments. The bars marked "x" in the alkane profiles indicate large interference peaks, while the large C₁₇ peaks show significant biological production of these alkanes. It should be noted that the alkane and PAH profiles in a Windermere Basin sediment sample (1.838 ug total alkanes and 5.849 ug total PAHs per g sediment), shown in Figure 14a, did not match those in the lagoons.

GC/MS analysis of the extracts showed the presence of some phenols (M.W. 220, probably nonyl phenols - related to nonyl phenol ethoxylate surfactants), phthalate esters, and a limited number of methyl PAHs.

The analysis of duplicate water samples collected in the lagoons, presented in Table 9, showed too much variability between the duplicates to allow meaningful comparisons between the lagoons.

St. Lawrence River cores

Total n-alkane and PAH concentrations for all sections of four cores are given in Table 10. The concentration-depth profiles as well as the alkane and PAH profiles in each section are shown in three consecutive Figures for each core.

In Core 44, as shown in Figure 15, concentrations generally decreased with depth, with an unexplained increased concentration in the lowest section (30-32 cm). The high concentrations in the top section indicate increased present inputs. The alkane profiles are shifted toward the high molecular weight end of the spectrum, except in the surface sediment where the low end of the series is well represented, and a well-developed C₁₇ peak shows some biogenic character of the alkanes (Figure 16). The PAH profiles became "simplified" with depth: below 20 cm, the series consisted mainly of three compounds: benzo(a)anthracene, benzo(k)fluoranthene, and dibenzo(a,h)anthracene (Figure 17).

The concentration-depth curves for Core 54, in Figure 18, show greatly reduced present inputs. The n-alkane profiles shown in Figure 19 are dominated by interfering peaks in the high molecular-weight end and show generally decreasing concentrations with decreasing molecular weights. The latter characteristic may be the result of increasing resistance to biodegradation with increasing chain lengths. The PAH profiles are dominated by two benzofluoranthenes, with dibenzo(a,h)anthracene becoming the dominant compound in the deepest sections (Figure 20).

In Core 59, the downstream end of Lac St. Louis, the situation is reversed: as indicated in Figure 21, recent inputs have significantly increased. The n-alkane profiles are similar to those in Core 54, showing large interfering peaks, and gradually diminishing concentrations toward the short chain length end of the spectrum (Figure 22). The PAH profiles also

show a similar dominance by benzofluoranthenes and by dibenzo(a,h)anthracene (Figure 23). The latter compound was dominant in both the top and bottom sections of the core, but was not detected in the intermediate depths.

Core 62, possibly affected by inputs from the Ottawa River, exhibited reduced recent inputs, i.e. low concentrations in the surface sediment (Figure 24). The alkane profiles in Figure 25 show the same general characteristics as those in the other cores. The PAH profiles, however, are unique for the area: benzo(k)fluoranthene and dibenzo(a,h)anthracene are still dominant compounds, but most of the other members of the PAH series are present as well (Figure 26).

General remarks

PAH concentrations in the sediments away from known point sources, e.g. in the Lake Erie samples, are generally of the same order of magnitude reported elsewhere (9). It must be recognized, however, that reported "total" PAH concentrations do not necessarily represent the same suite of polyaromatics, making a comparison of PAH compositions difficult or impossible.

Although the present suite of priority pollutant PAHs may make the above comparisons easier, the authors suggest that the inclusion of some methyl PAHs and oxygen- and nitrogen-PAHs (OPAHs and NPAHs) in the analytical schemes would provide useful clues of the source and history of PAH assemblages in environmental samples.

The observed variability in PAH compositions indicate the dominance of specific point sources in each study area, where physical and chemical processes produce non-homogeneous distributions. A monitoring program of suspected point sources would require an intensive multi-disciplinary study of these compounds to provide useful information and to allow interpretation of the results.

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Table 1
Priority Pollutant PAHs

No.	Symbol	M.W.	Name
1	N	128	Naphthalene
2	AY	152	Acenaphthylene
3	AE	154	Acenaphthene
4	FL	166	Fluorene
5	PH	178	Phenanthrene
6	AN	178	Anthracene
7	F	202	Fluoranthene
8	PY	202	Pyrene
9	BaA	228	Benzo(a)anthracene
10	CH	228	Chrysene
11	BbF	252	Benzo(b)fluoranthene
12	BkF	252	Benzo(k)fluoranthene
13	BaP	252	Benzo(a)pyrene
14	IP	276	Indeno(123,cd)pyrene
15	DA	276	Dibenzo(a,h)anthracene
16	BP	276	Benzo(ghi)perylene

Table 2

Priority Pollutant PAHs in Thunder Bay Sediments
(micrograms/gram)

Compound	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
naphthalene	.030	.064	ND	ND	.058	.228
acenaphthylene	.124	.049	.468	.052	ND	ND
acenaphthene	3.318	7.558	11.682	.054	1.118	.677
flourene	.373	.265	.427	.636	.067	.095
phenanthrene	.894	.486	1.082	.539	.085	.050
anthracene	2.040	2.744	2.398	.638	4.316	ND
fluoranthene	3.116	.585	1.551	2.107	.441	9.065
pyrene	4.679	3.298	.986	3.874	ND	ND
benzo(a)anthracene	.256	.919	ND	3.669	.071	ND
chrysene	.867	1.629	ND	3.413	.567	.011
benzo(b)fluoranthene	.009	.400	.182	.062	ND	ND
benzo(k)fluoranthene	.010	.056	.235	ND	.055	.651
benzo(a)pyrene	.650	.265	.332	.011	.769	ND
indeno(123,cd)pyrene	.616	.509	.114	.053	1.275	.292
dibenzo(a,h)anthracene	ND	ND	.090	.352	.319	ND
benzo(g,h,i)perylene	1.701	.477	1.125	ND	.537	ND
Total	18.683	19.302	20.672	15.460	9.678	11.069

ND - not detected

Table 3

PAHs in Thunder Bay Sediments

Site	Methyl homologs	Other PAHs ^a
1	C1-naphthalene (2) C2-naphthalene (3) C1-phenanthrene (3) C4-phenanthrene	biphenyl dibenzofuran carbazole
2	C1-naphthalene (2) C2-naphthalene (2) C3-naphthalene (2) C1-phenanthrene C4-phenanthrene (3) C1-pyrene C1-carbazole	biphenyl dibenzofuran carbazole
3	C1-naphthalene (2) C2-naphthalene (3) C1-phenanthrene (2) C4-phenanthrene (3) C1-pyrene/fluoranthene C1-chrysene/BaA C1-carbazole	biphenyl dibenzofuran carbazole acridine/benzoquinoline 9-anthracenecarbonitrile
4	C1-naphthalene (2) C2-naphthalene (3) phenylnaphthalene C1-anthracene/phenanth. C2-anthracene/phenanth. C4-phenanthrene C1-pyrene/fluoranthene C1-fluorene C1-chrysene/BaA C1-biphenyl C1-carbazole C1-dibenzofuran	biphenyl dibenzofuran carbazole terphenyl acridine/benzoquinoline cyclopenta(def)phenanthr.
5	C1-naphthalene (2) C2-naphthalene (4) phenylnaphthalene C1-anthracene/phenanth. C4-phenanthrene C1-dibenzofuran	biphenyl dibenzofuran dibenzothiophene
6	C1-naphthalene (2) C2-naphthalene (3) C3-naphthalene phenylnaphthalene C4-phenanthrene	biphenyl dibenzofuran

a - In addition to priority pollutant PAHs

Table 4

Priority Pollutant PAHs in St. Mary's River Sediments
(micrograms/gram)

Compound	Site 5	Site 6	Site 7
naphthalene	6.724	.023	.053
acenaphthylene	ND	ND	ND
acenaphthene	ND	ND	ND
fluorene	.637	ND	.150
phenanthrene	4.371	.260	.517
anthracene	1.942	.059	.111
fluoranthene	ND	.379	.667
pyrene	.143	.290	.576
benzo(a)anthracene	4.855	ND	.317
chrysene	1.144	.183	.257
benzo(b)fluoranthene	.071	.311	.748
benzo(k)fluoranthene	2.707	.139	.339
benzo(a)pyrene	.089	.224	.373
indeno(123,cd)pyrene	ND	.067	.349
dibenzo(a,h)anthracene	2.196	.051	.134
benzo(ghi)perylene	ND	.160	.385
Total	24.879	2.146	4.976

ND - not detected

Table 5

N-alkanes and PAHs in Lake Erie sediments

Station	Concentration, micrograms/gram	
	N-alkanes(1)	PAHs(2)
357 (West)	0.979	1.768
84 (Central)	1.052	0.601
23 (East)	2.559	2.639

(1) Sum of C₁₂ to C₂₆ n-alkanes.

(2) Sum of 16 priority pollutants polyaromatics.

Table 6

Priority Pollutant PAHs in Lake Erie Sediments
(micrograms/gram)

Compound	Western basin	Central basin	Eastern basin
napthalene	ND	ND	.100
acenaphthylene	ND	ND	.006
acenaphthene	ND	ND	ND
fluorene	.160	ND	.086
phenanthrene	.163	ND	.136
anthracene	.047	ND	.032
fluoranthene	.108	ND	.152
pyrene	.198	ND	.120
benzo(a)anthracene	.019	ND	.028
chrysene	.104	ND	.099
benzo(b)fluoranthene	.321	.189	ND
benzo(k)fluoranthene	.158	.126	.697
benzo(a)pyrene	.136	.197	.102
indeno(123,cd)pyrene	ND	ND	.096
dibenzo(a,h)anthracene	.122	.089	.729
benzo(ghi)perylene	.232	ND	.274
Total	1.768	.601	2.639

ND - not detected

Table 7

Priority Pollutant PAHs in Lake Ontario Sediments
(micrograms/gram)

Compound	Special site	Site 40	Site 41
naphthalene	35.665	.089	.057
acenaphthylene	4.574	ND	ND
acenaphthene	17.861	.142	ND
fluorene	ND	.239	ND
phenanthrene	ND	.809	.046
anthracene	13.934	.080	ND
fluoranthene	6.174	.566	.037
pyrene	.827	.440	.036
benzo(a)anthracene	3.505	.290	ND
chrysene	11.706	.302	ND
benzo(b)fluoranthene	.084	.638	.023
benzo(k)fluoranthene	ND	.160	.242
benzo(a)pyrene	11.008	.332	.050
indeno(123,cd)pyrene	ND	1.228	ND
dibenzo(a,h)anthracene	25.853	ND	ND
benzo(ghi)perylene	ND	ND	ND
Total	131.191	5.315	.491

Note: The PAH concentrations and profiles at sites 81 and 82 were similar to those of 41 and 40, respectively.

Table 8

Priority Pollutant PAHs in Hamilton Harbour Sediments
(micrograms/gram)

Cpd.	before liming*		after liming*	
	South	North	South	North
N	ND	2.827	1.937	.212
AY	.131	ND	.584	ND
AE	ND	1.189	1.217	.036
FL	1.265	1.143	.505	.043
PH	4.004	4.231	.143	.203
AN	.818	.936	ND	.058
F	6.363	ND	1.026	.260
PY	4.804	ND	.327	.189
BaA	1.801	2.842	1.847	.118
CH	7.041	2.297	2.280	.105
BbF	4.522	3.407	ND	.508
BkF	1.667	1.634	1.715	.299
BaP	1.702	2.358	ND	.213
IP	1.757	1.291	4.134	.683
DA	.777	.461	ND	ND
BP	1.689	1.258	ND	.572
Total	32.439	25.874	15.715	3.499

* - only the South lagoon was treated.

Table 9

N-alkanes and PAHs in Hamilton Harbour water
(microgram/L¹)

Sampling time	Location (lagoon).	Alkanes ²	PAHs ³
before liming ⁴	North ⁵	14.422	2.196
	North	7.753	2.642
	South	0.979	2.044
	South	6.602	2.058
after liming	North	9.585	2.111
	North	9.944	2.088
	South	2.987	0.916
	South	2.978	1.788

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- 1 - concentrations in total sample (water + suspended particulates)
 - 2 - sum of C₁₂ to C₂₆ normal alkanes
 - 3 - sum of 16 priority pollutant PAHs
 - 4 - only the South lagoon was limed
 - 5 - duplicate water samples were collected

Table 10

N-alkanes and PAHs in St. Lawrence River cores
(micrograms/gram)

Core No.	Depth (cm)	N-alkanes	PAHs
44	1- 5	1.232	1.513
	6- 9	1.266	2.210
	10-12	.558	1.585
	14-16	.539	.600
	18-20	.369	.230
	20-22	.540	.370
	25-27	.567	.396
	30-32	1.481	1.074
54	0- 5	1.829	1.164
	6- 9	5.117	4.418
	10-12	5.150	5.051
	14-16	4.791	4.994
	18-20	2.414	5.722
	20-22	1.899	4.512
59	2- 5	.855	1.719
	6- 9	.506	.414
	10-12	.546	.400
	14-16	.458	.180
	18-20	.555	.527
62	1- 5	1.041	2.150
	6- 9	2.090	4.446
	10-16	1.989	4.217
	18-22	1.137	2.895
	25-29	.542	2.227

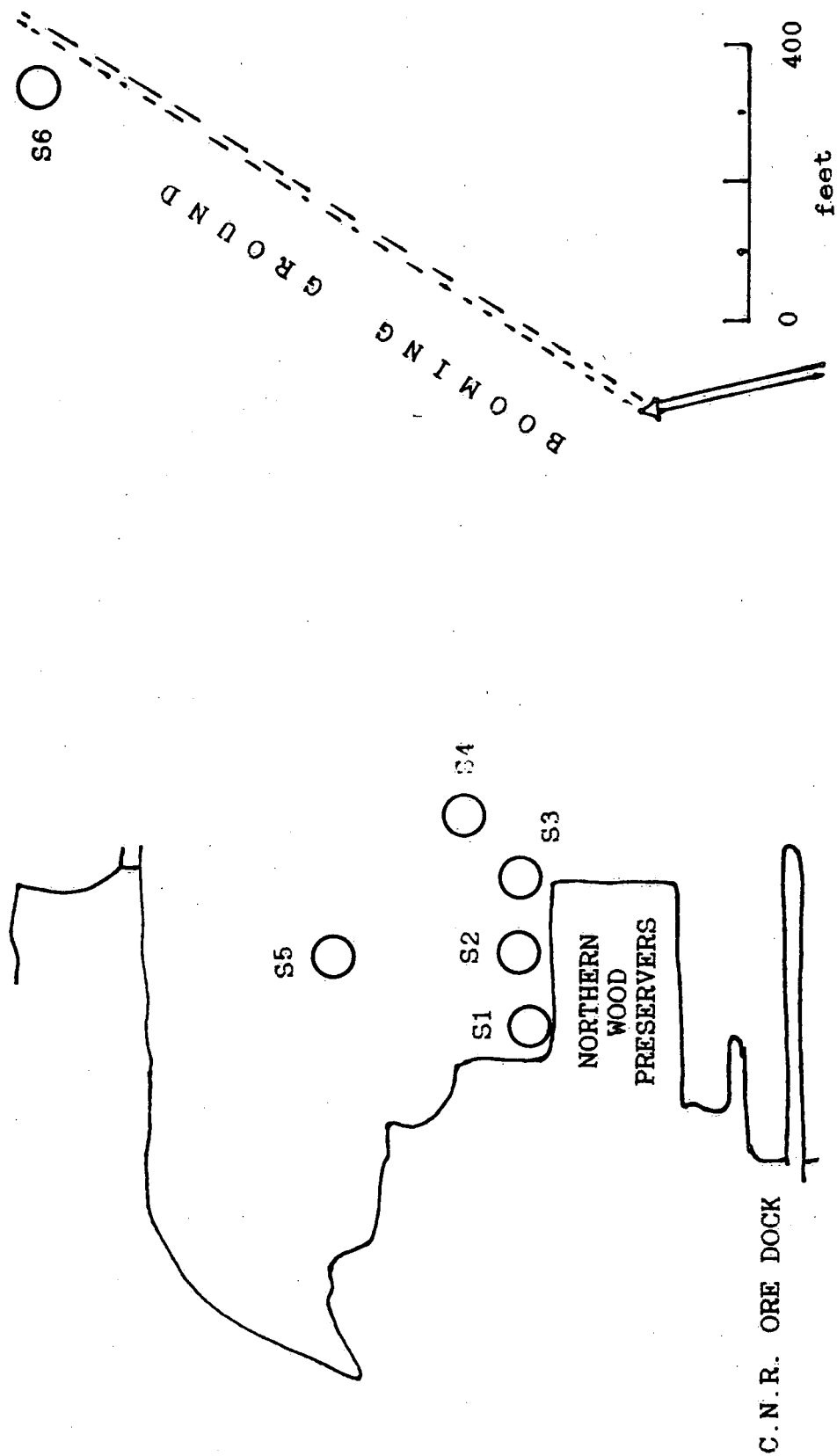


Figure 1
Sampling sites in Thunder Bay Harbour

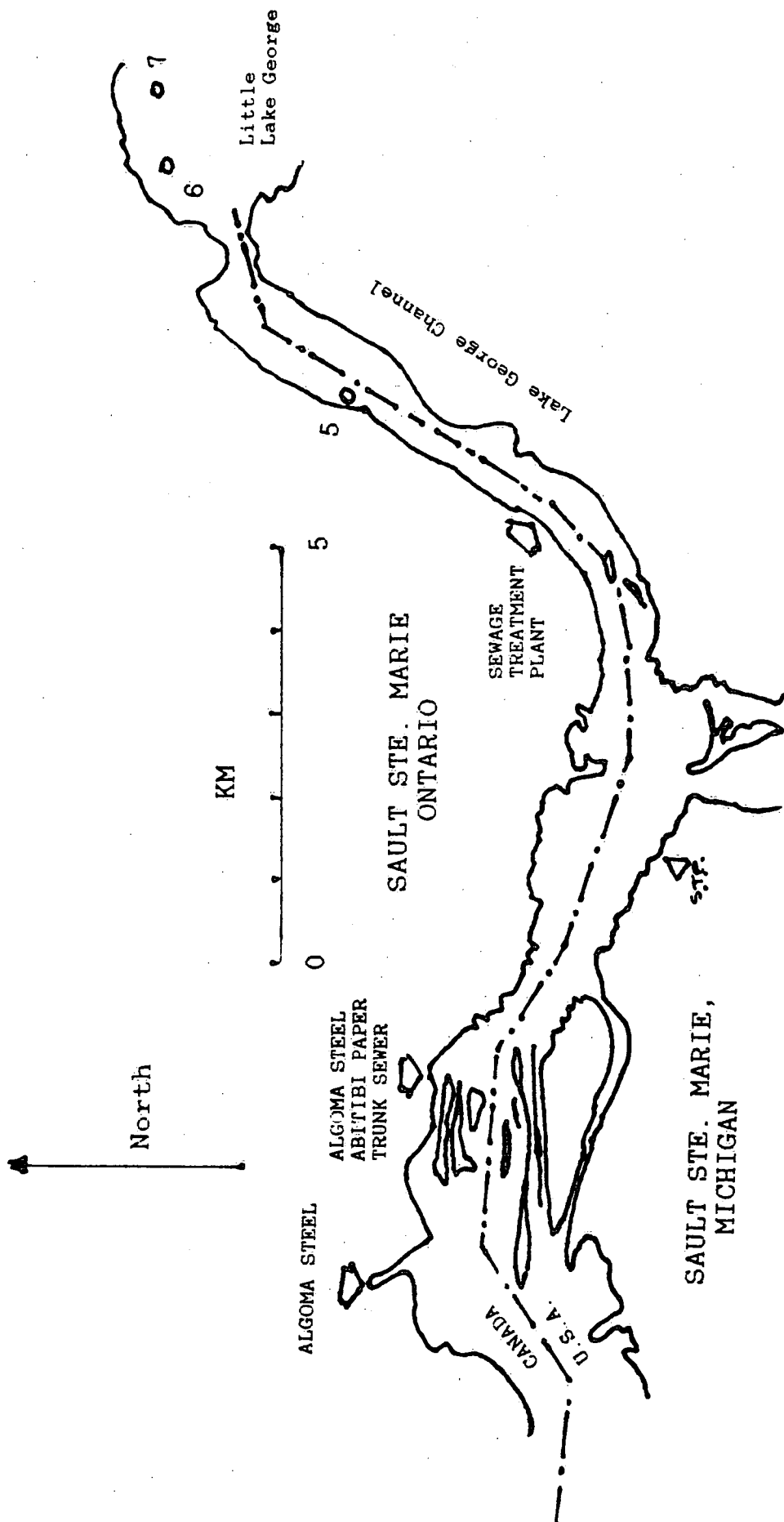


Figure 2

St. Mary's River sampling sites, 1986

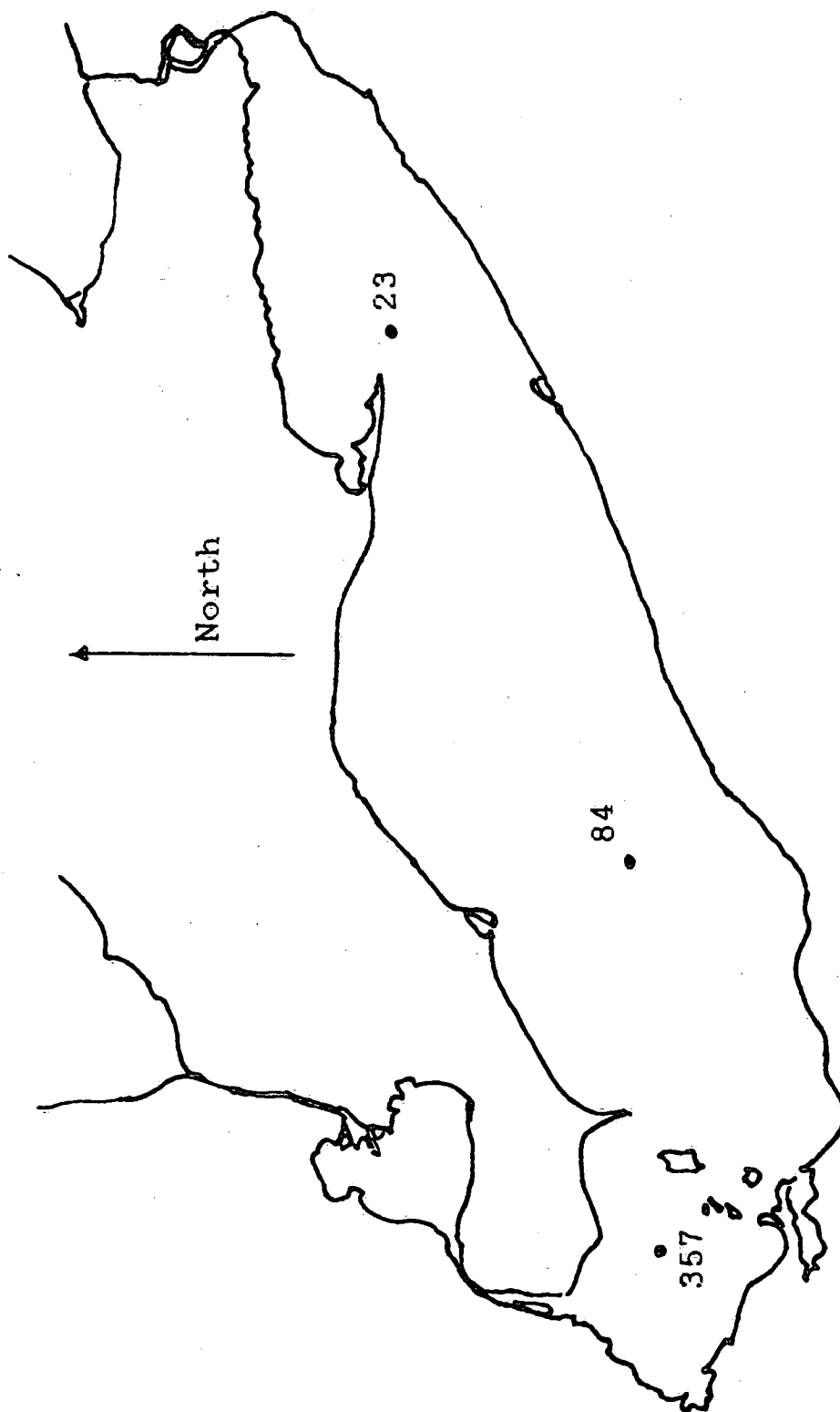


Figure 3

Lake Erie sampling sites, 1986

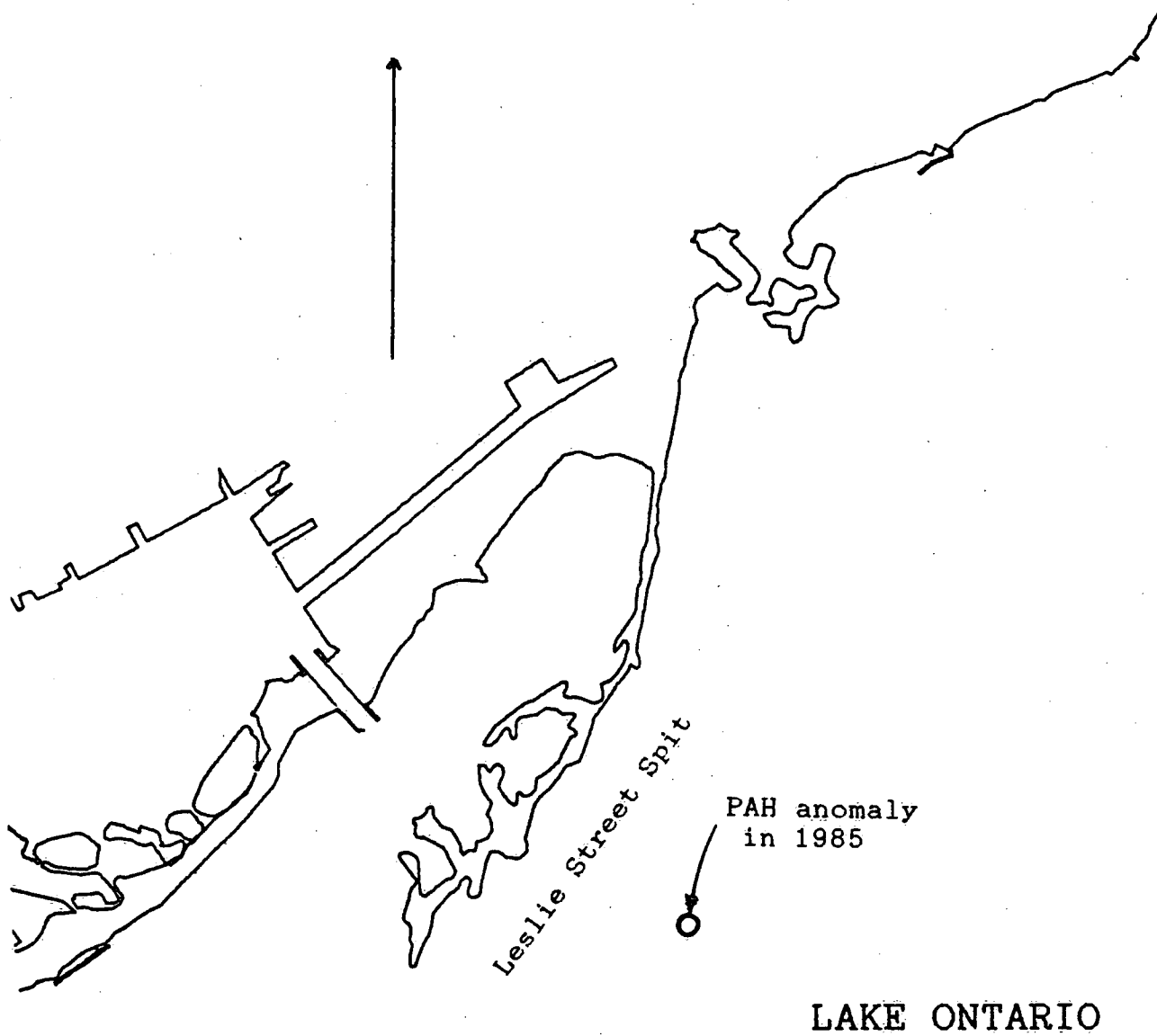


Figure 4

Toronto Harbour sampling site, 1985/86

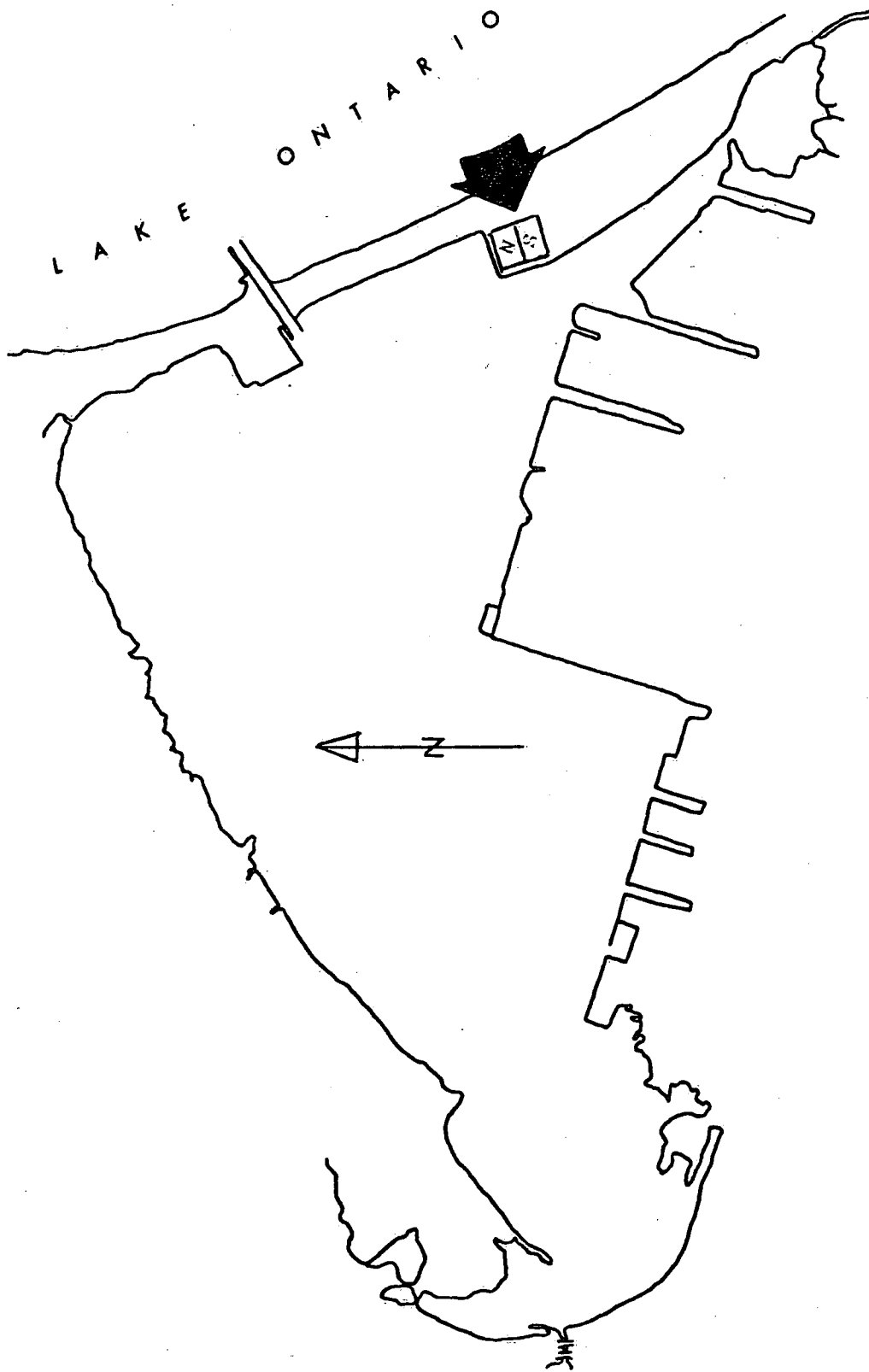


Figure 5

Hamilton Harbour sampling sites, 1986

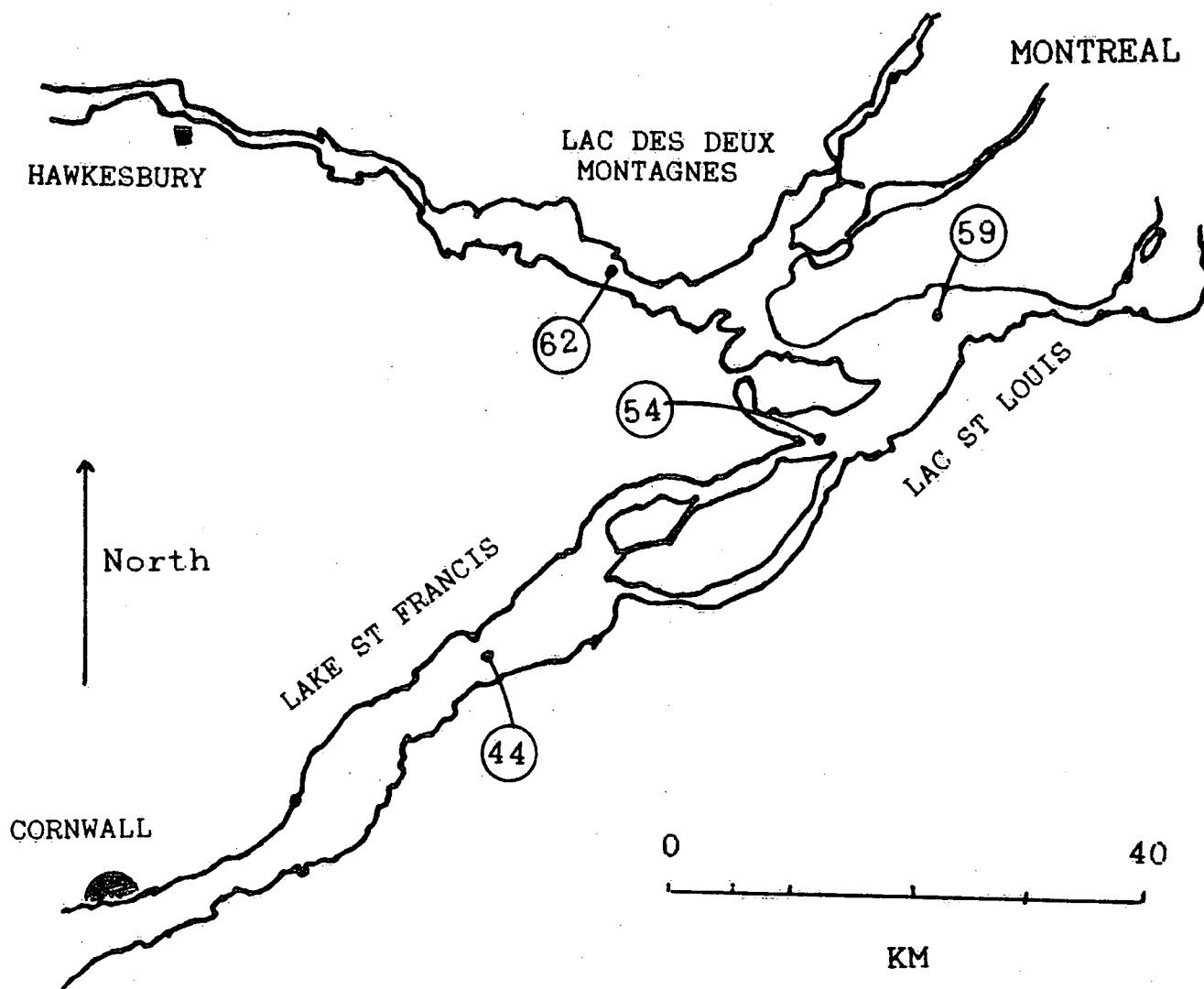
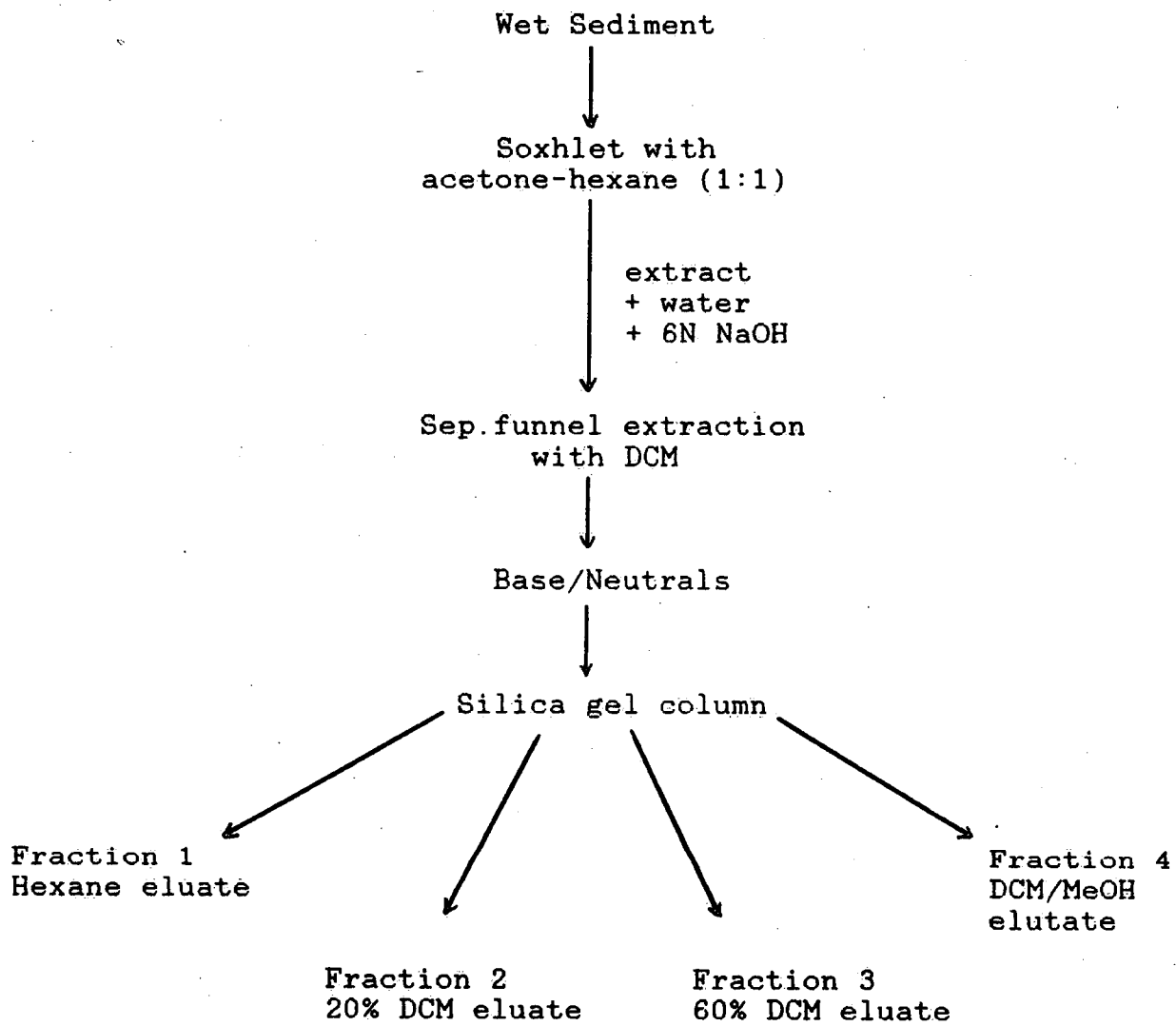


Figure 6

St. Lawrence River sampling sites, 1986

Figure 7
Sediment Extraction Scheme



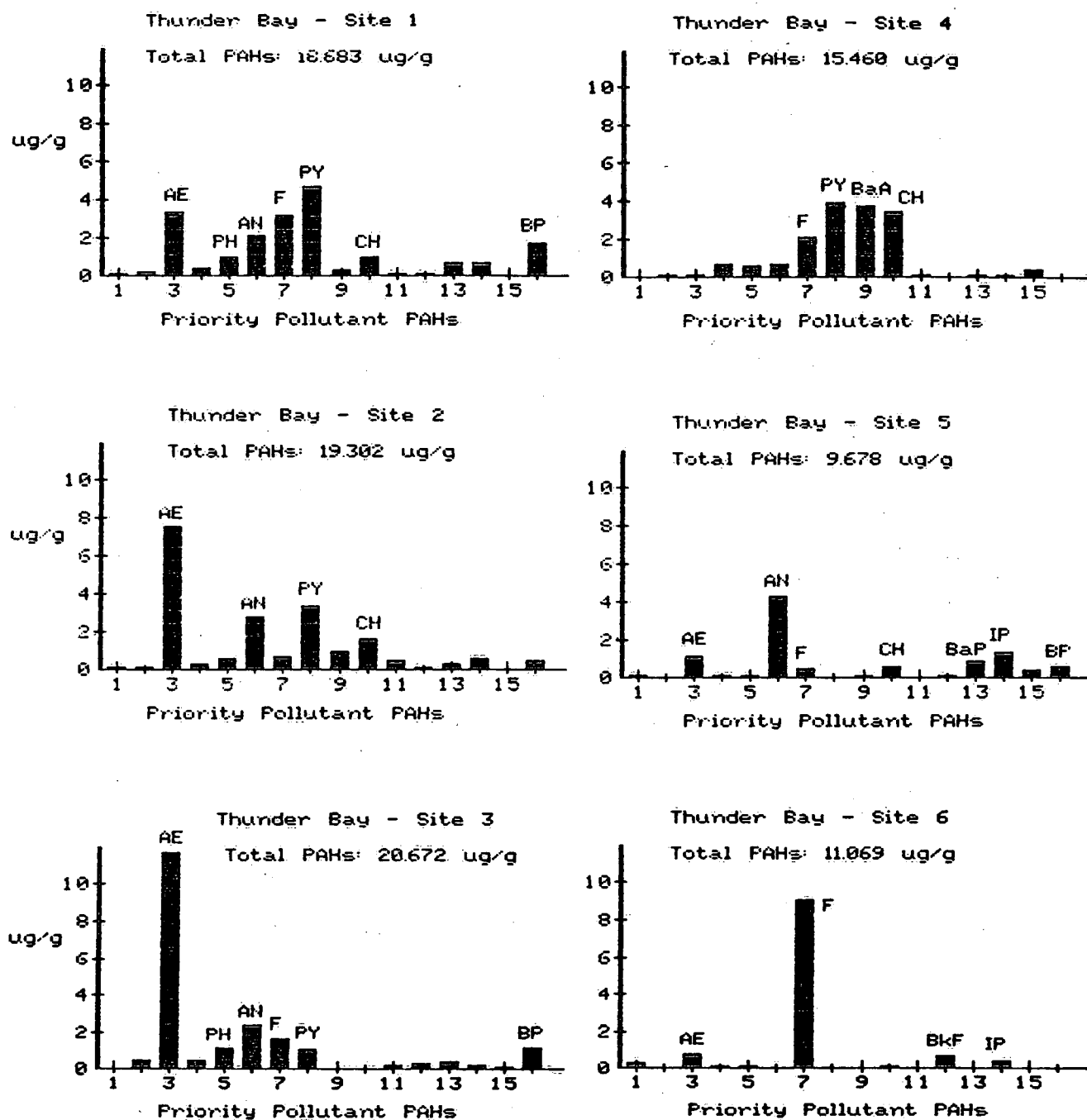


Figure 8

PAH profiles in Thunder Bay sediments

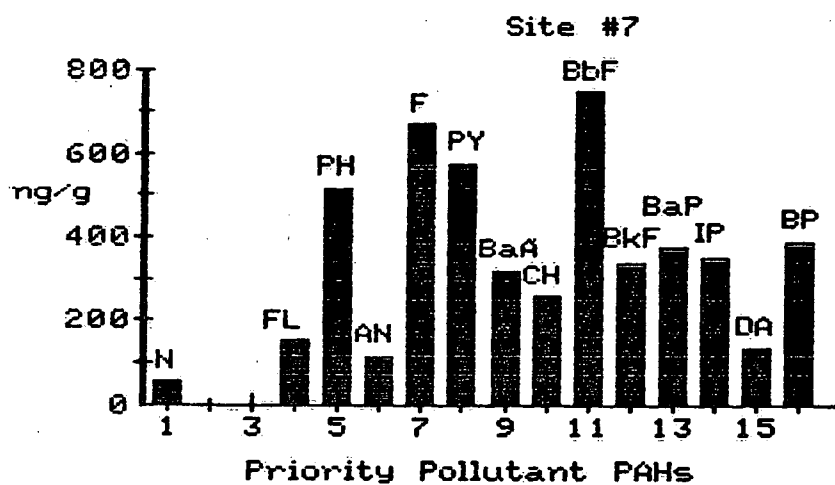
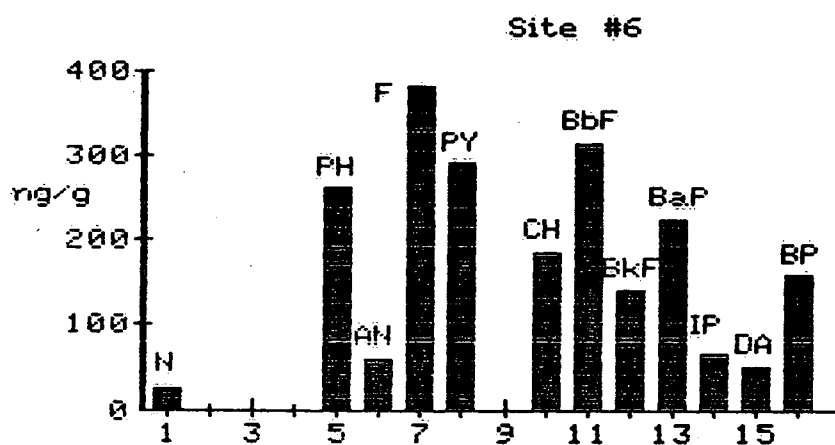
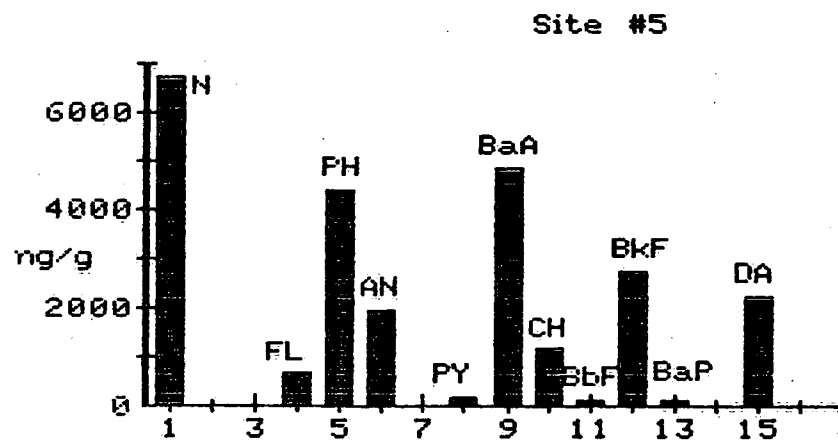


Figure 9
PAH profiles in St. Mary's River sediments

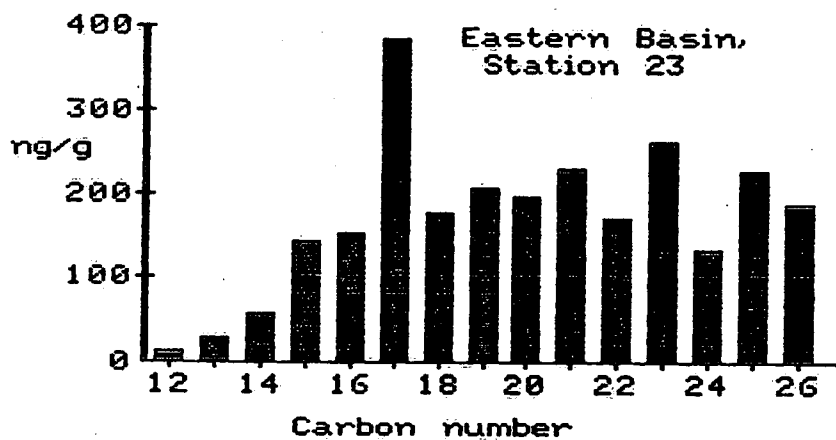
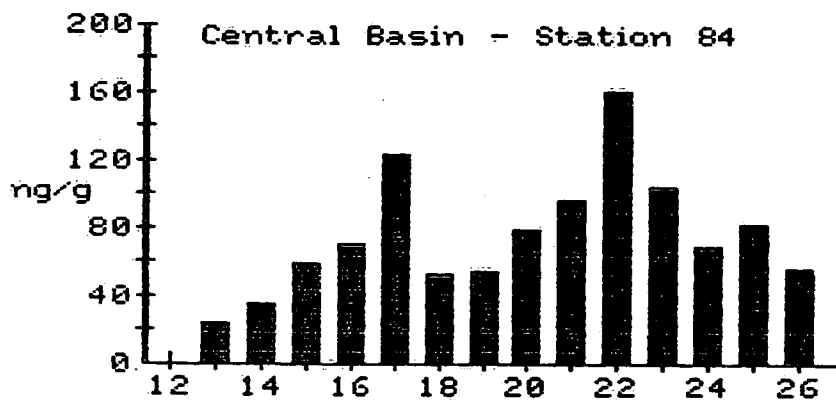
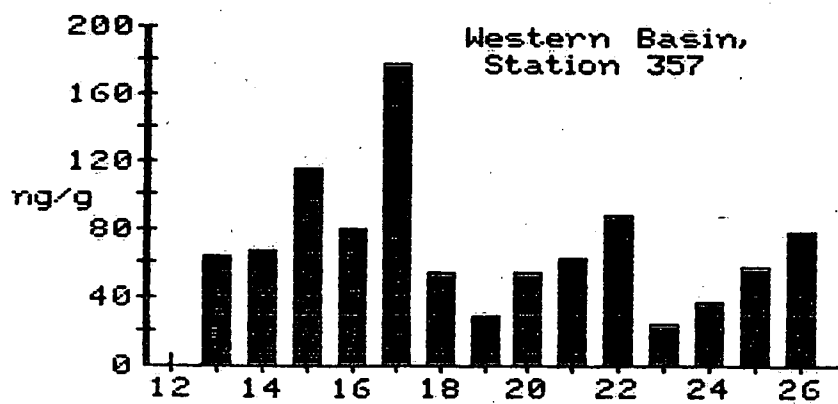


Figure 10

N-alkane profiles in Lake Erie sediments

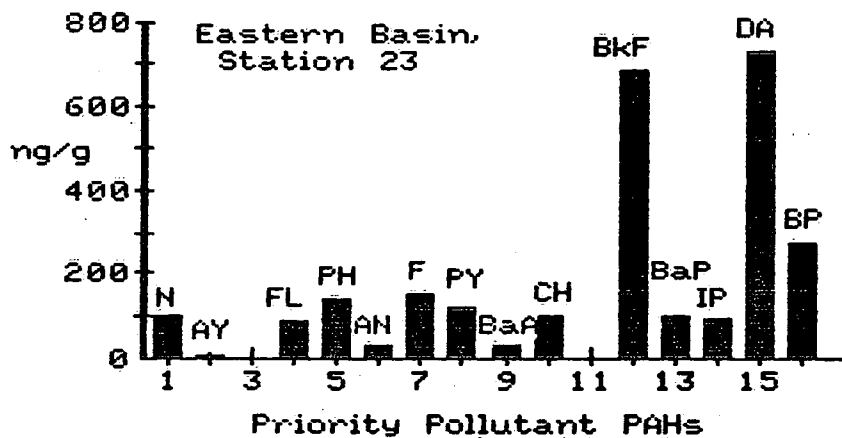
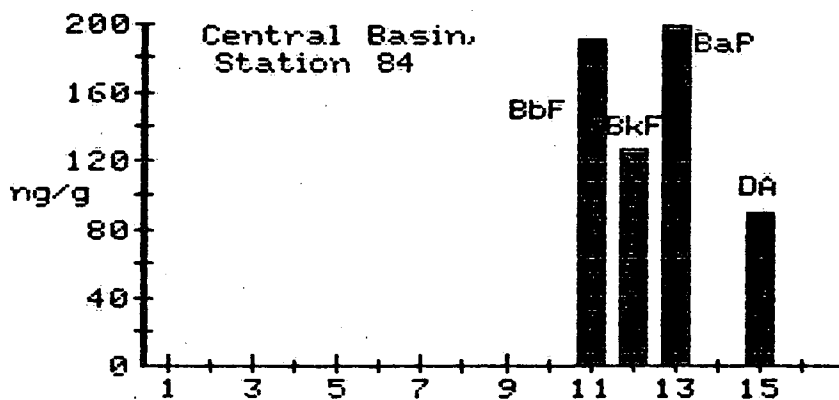
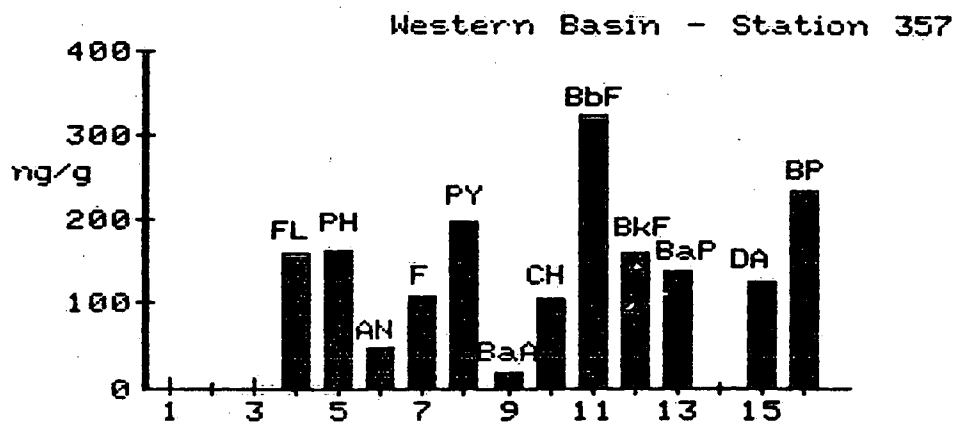


Figure 11

PAH profiles in Lake Erie sediments

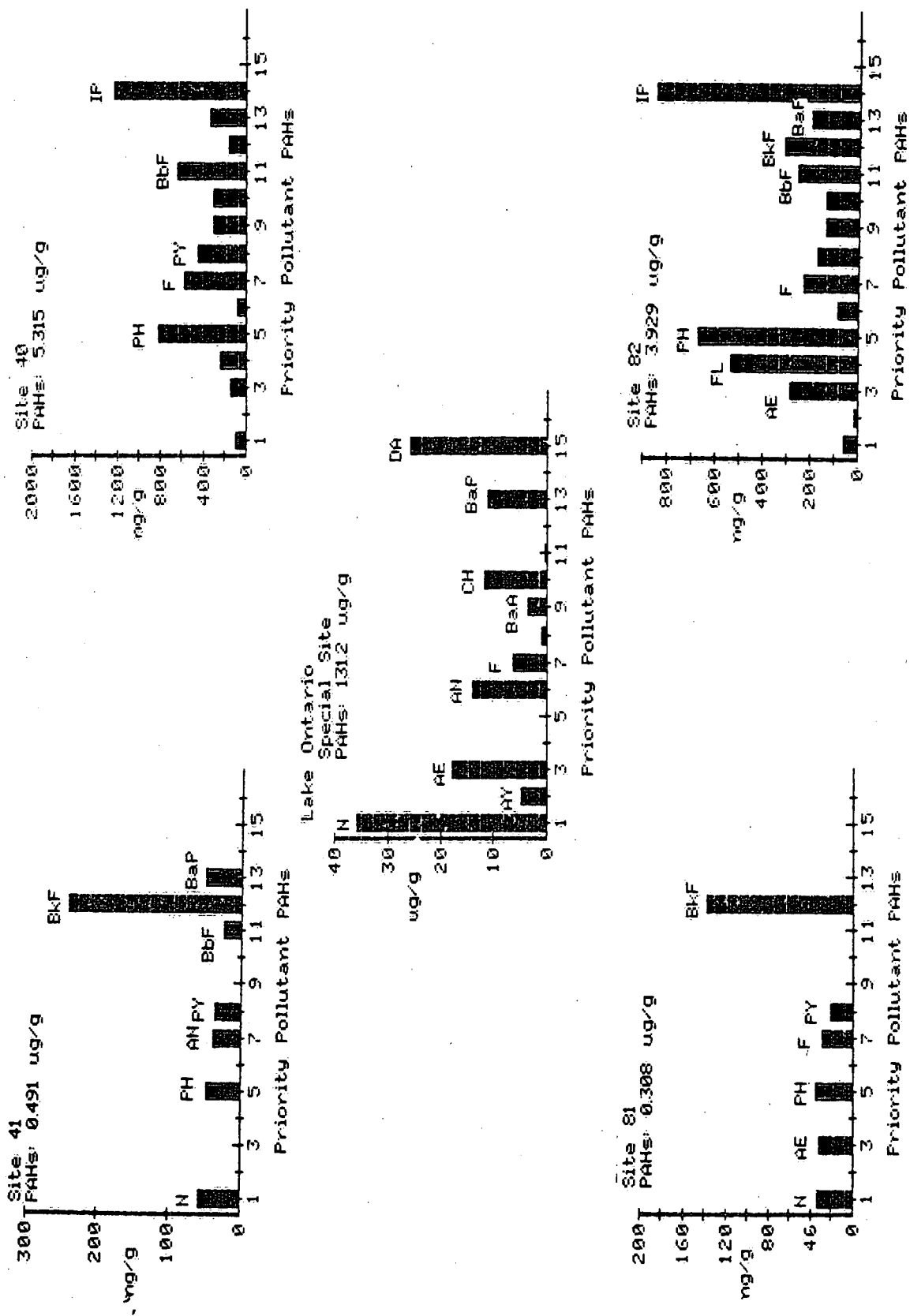
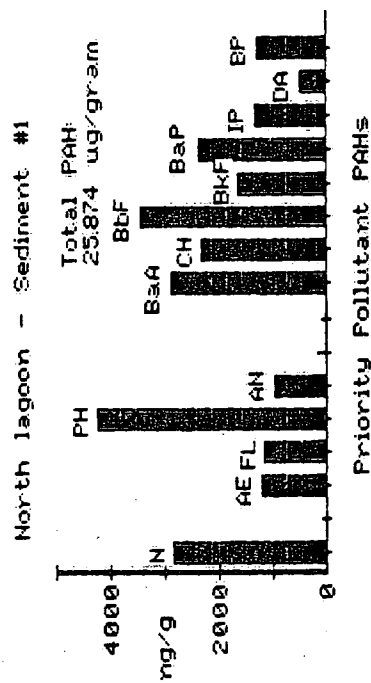


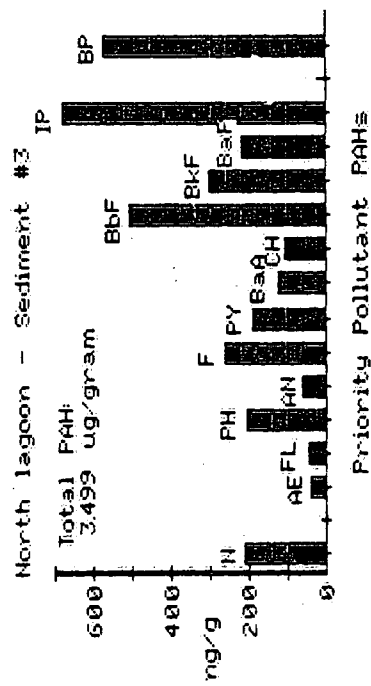
Figure 12

PAH profiles in Lake Ontario sediments

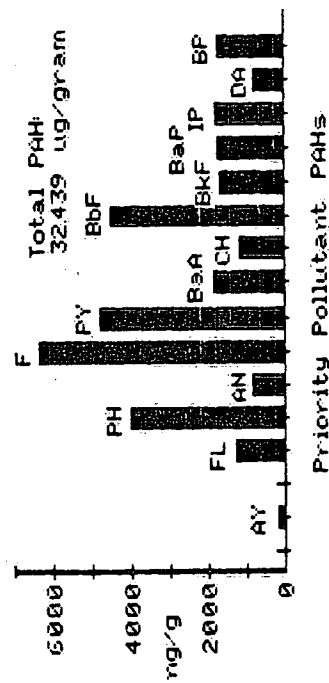
A) before liming of
South lagoon:



B) after liming of
South lagoon:



South lagoon - Sediment #2



South lagoon - Sediment #4

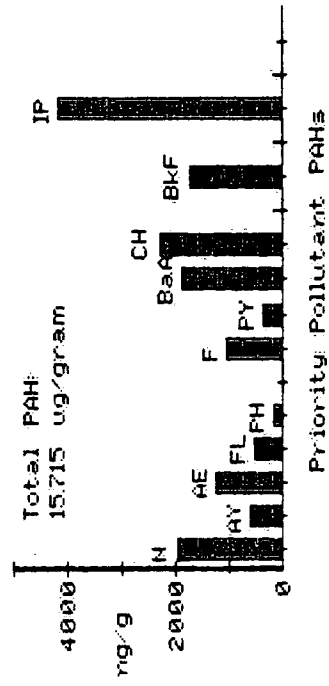
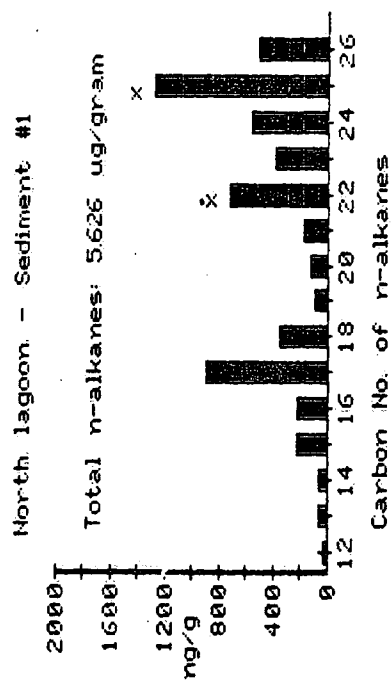


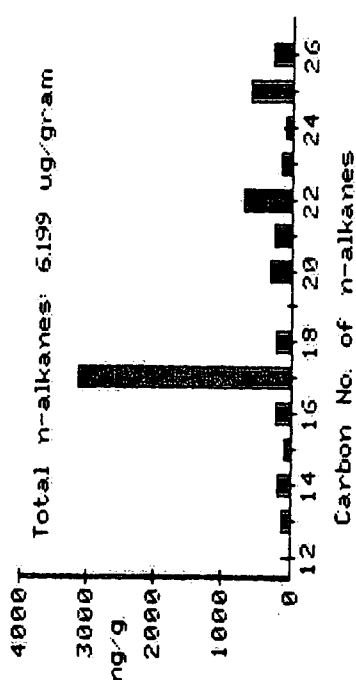
Figure 13

PAH profiles in Hamilton Harbour sediments

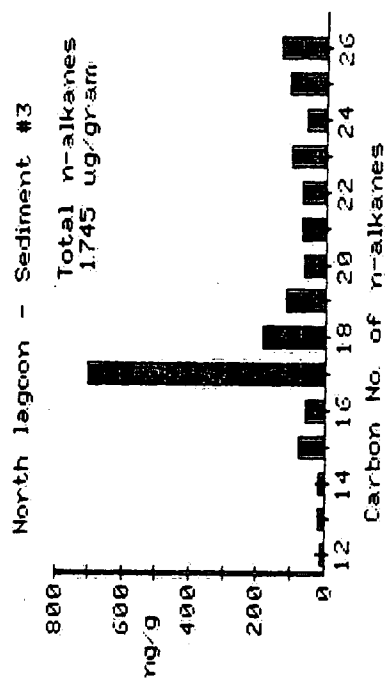
A) before liming of
South lagoon:



South lagoon - Sediment #2



B) after liming of
South lagoon:



South lagoon - Sediment #4

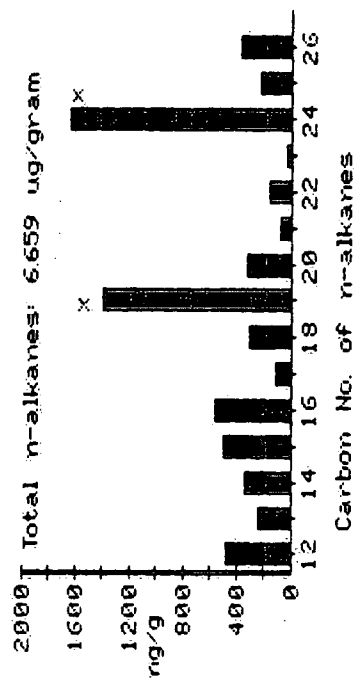


Figure 14

N-alkane profiles in Hamilton Harbour sediments

Figure 14a

N-alkane and PAH profiles in Windermere Basin sediments

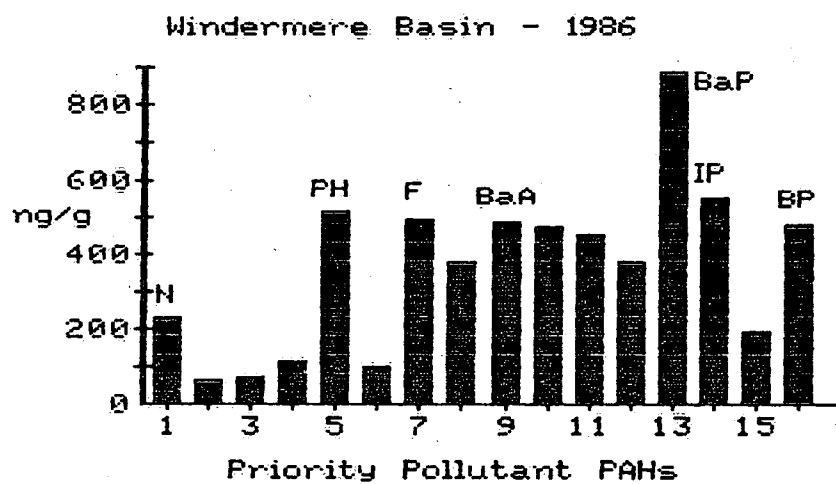
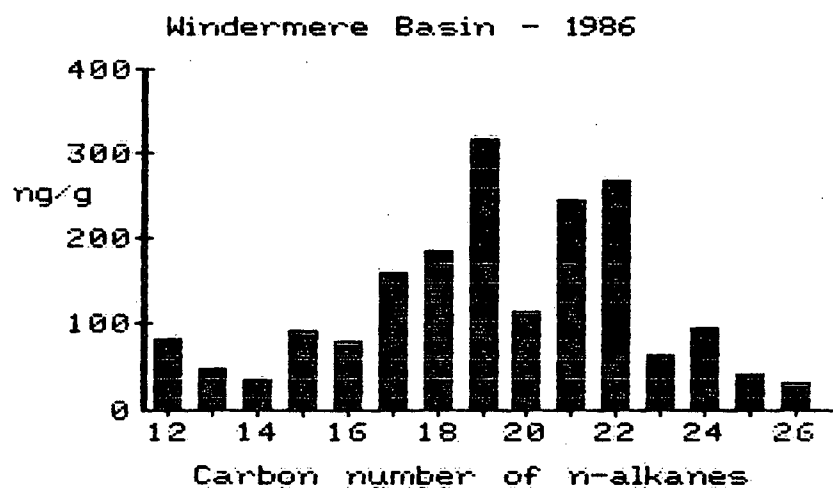
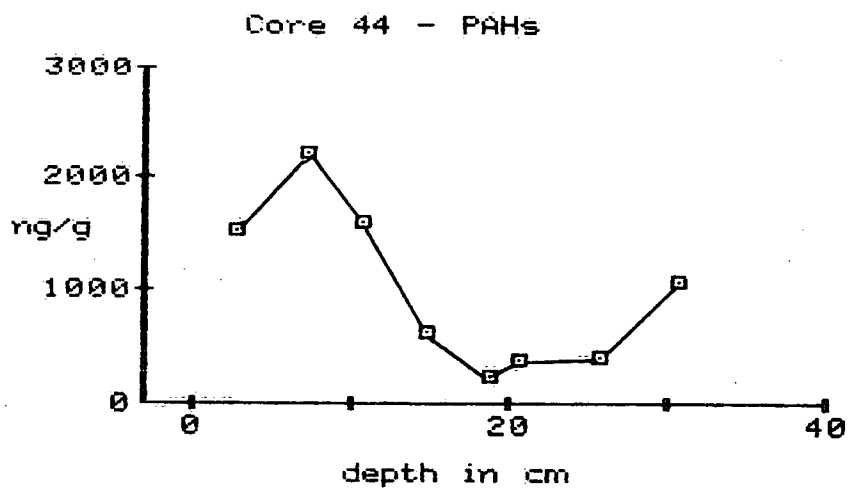
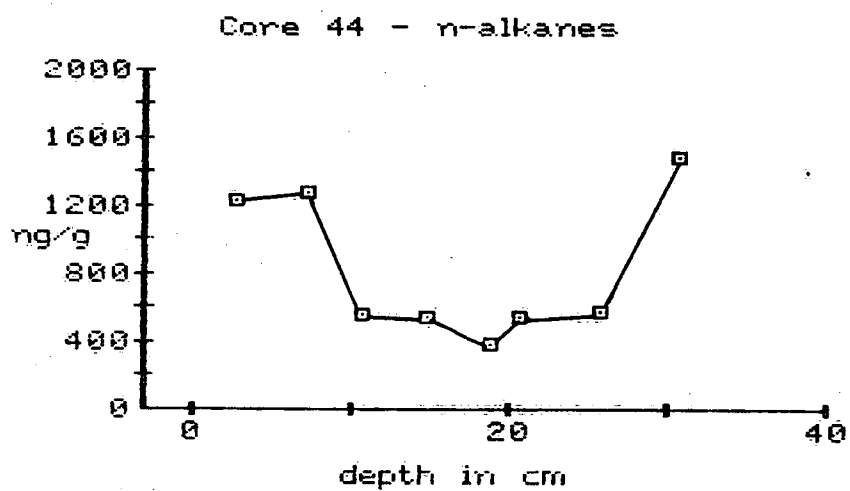


Figure 15

N-alkanes and PAHs in St. Lawrence River Core #44



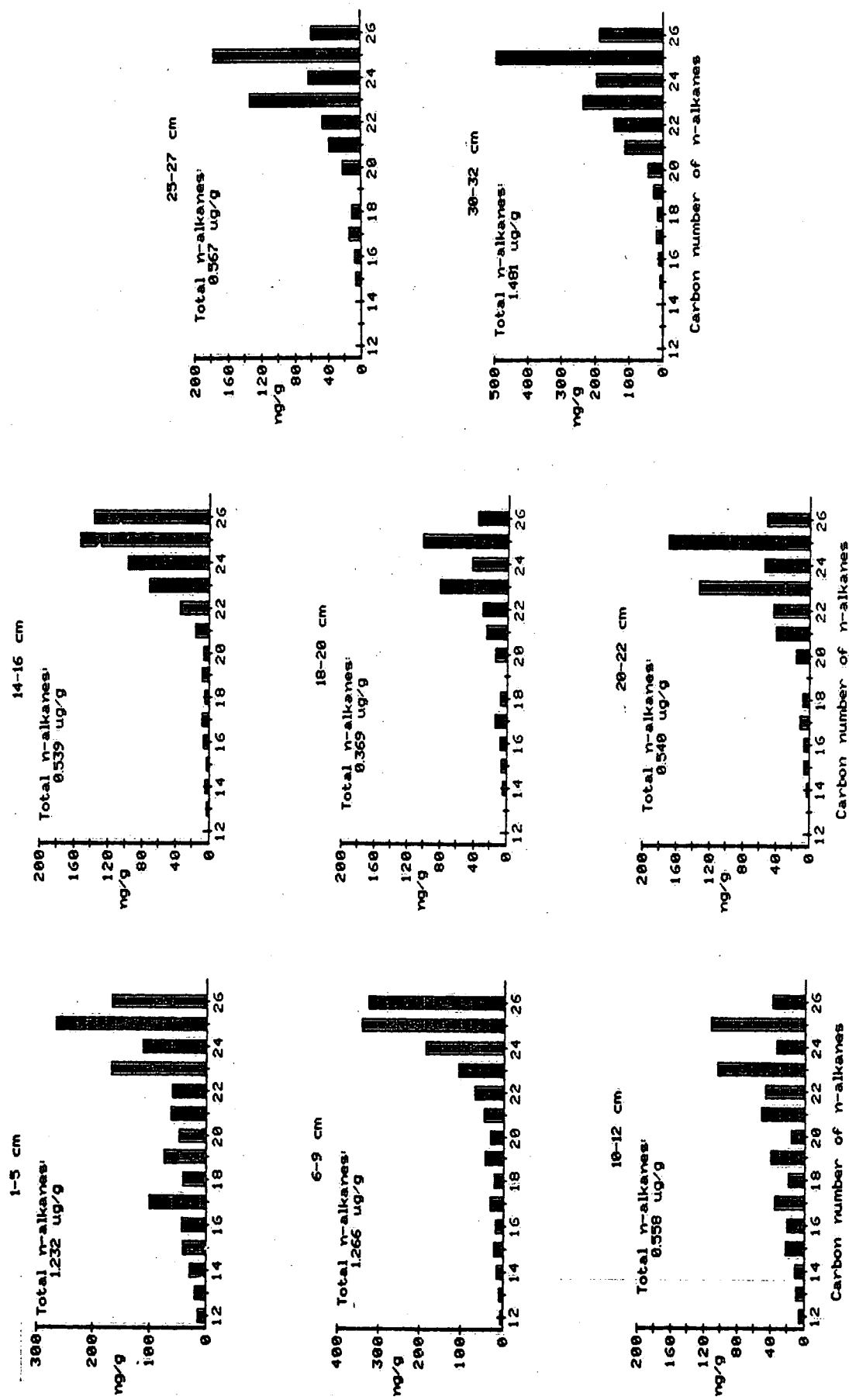


Figure 16

N-alkane profiles in St. Lawrence R. core #44

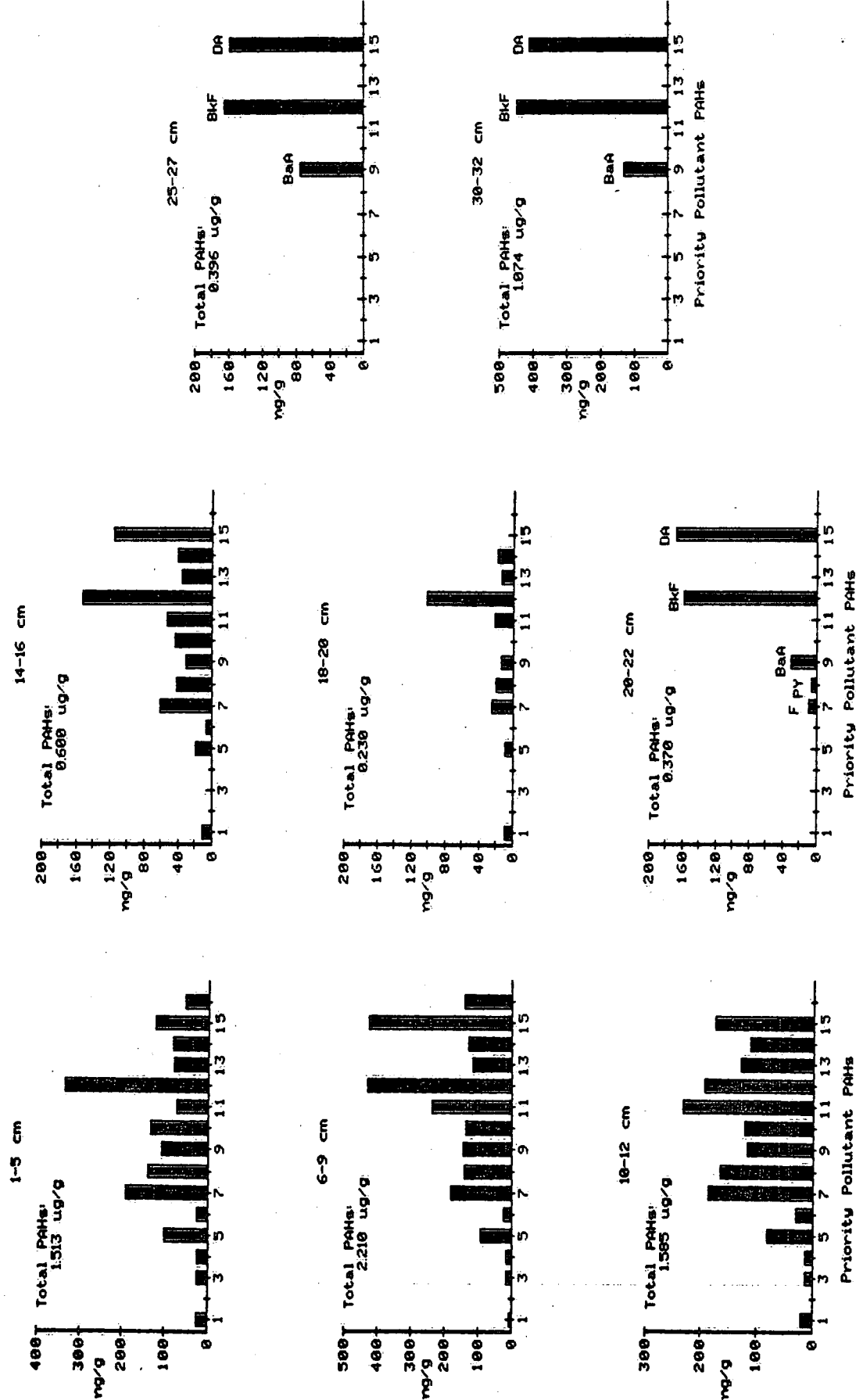
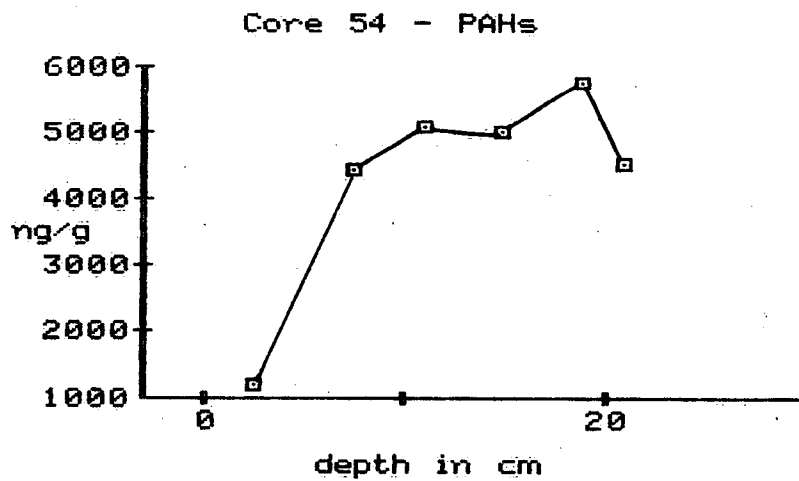
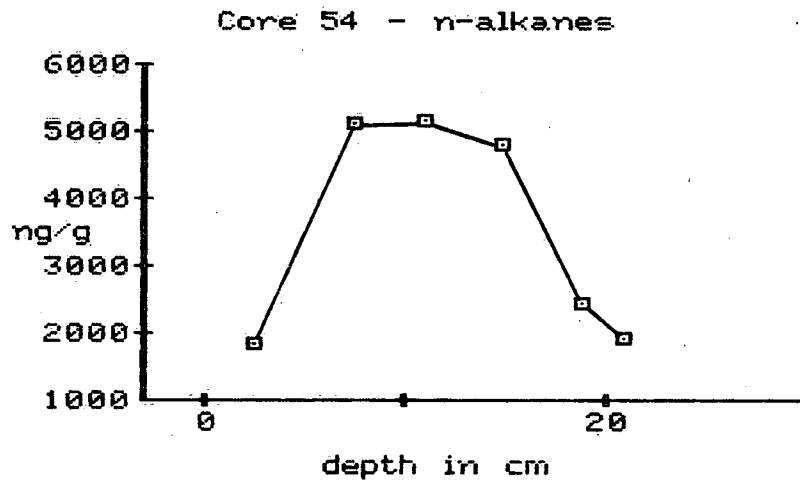


Figure 17

PAH profiles in St. Lawrence R. core #44

Figure 18

N-alkanes and PAHs in St. Lawrence River Core #54



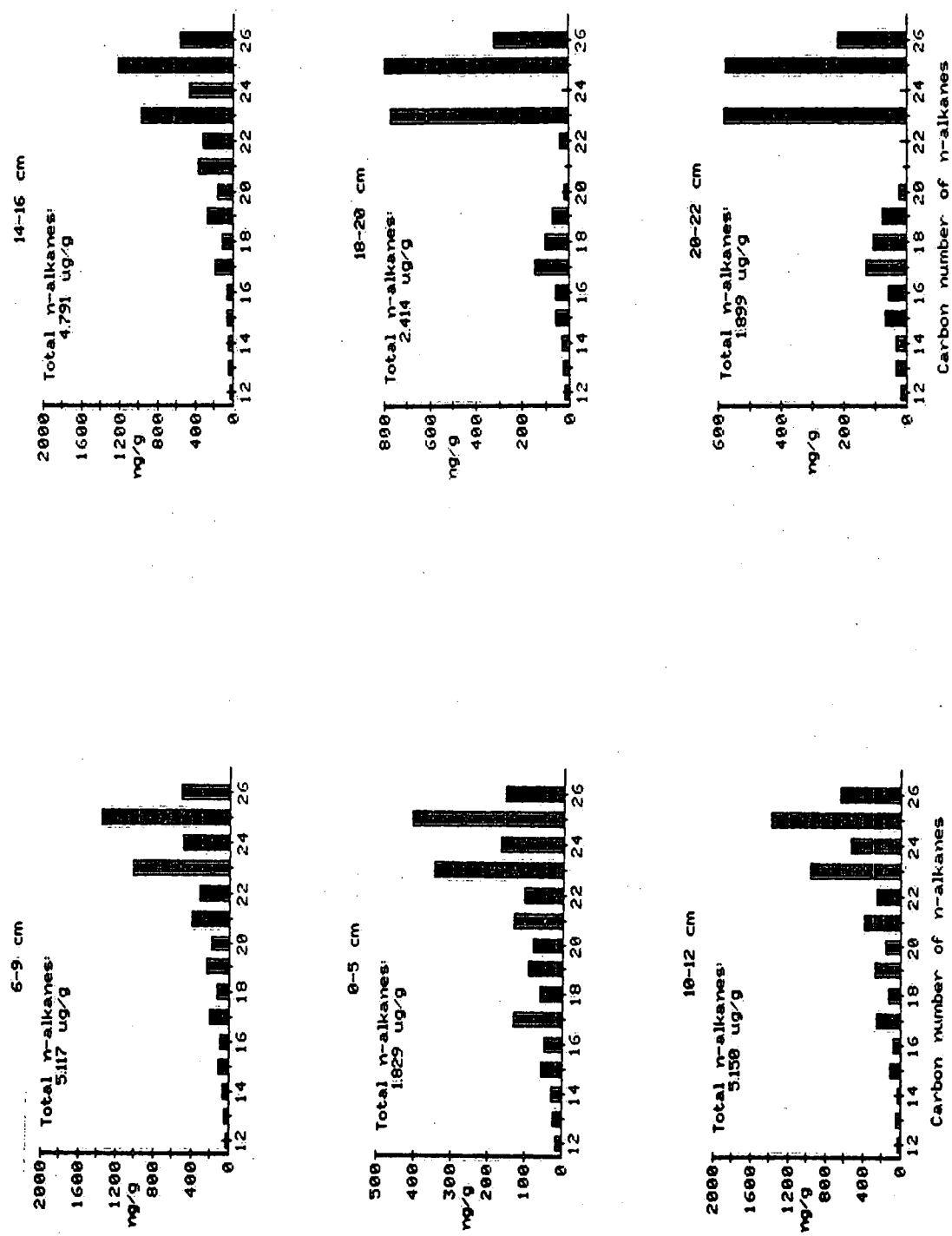


Figure 19

N-alkane profiles in St. Lawrence R. core #54

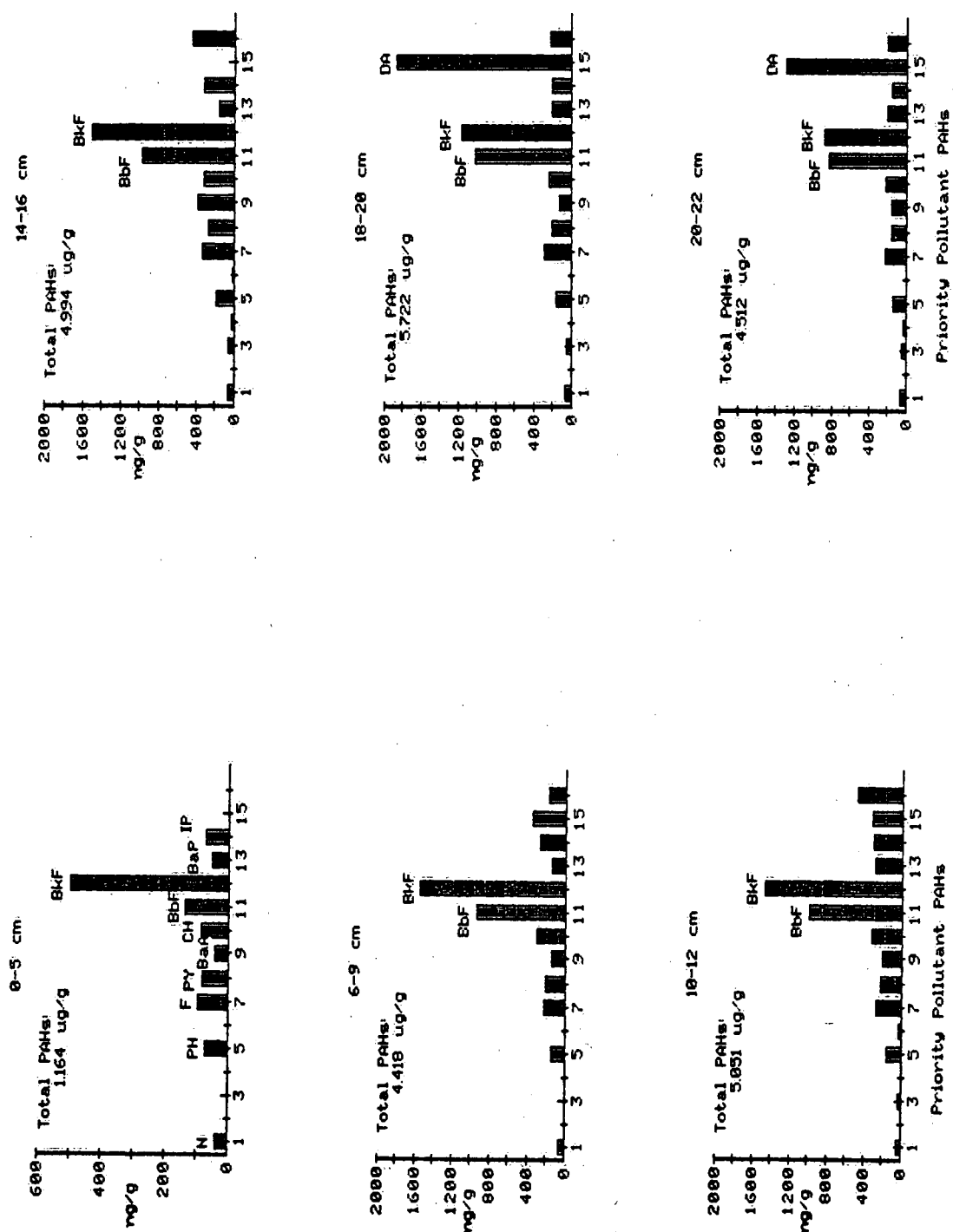
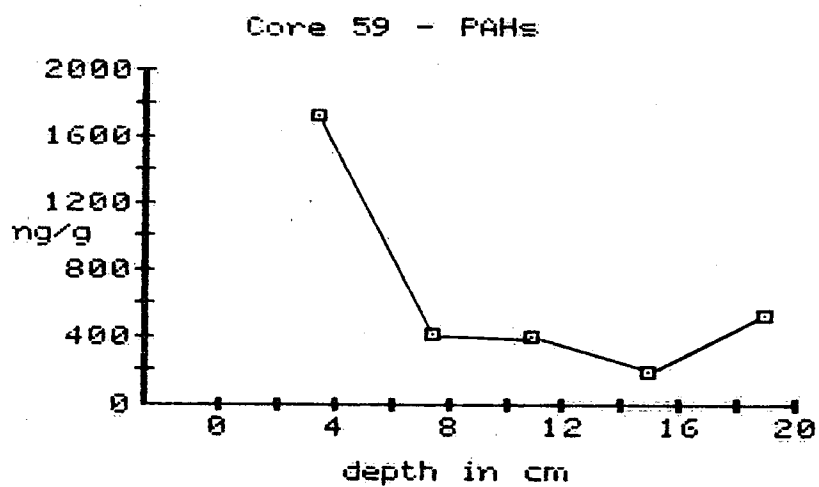
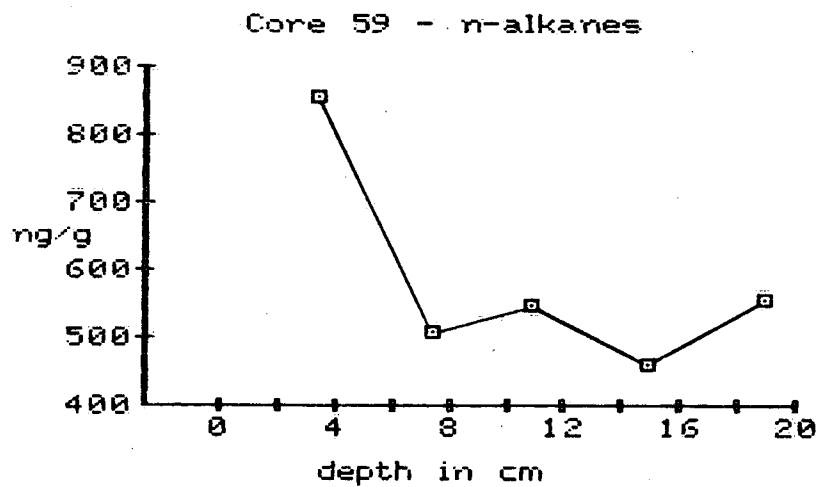


Figure 20

PAH profiles in St. Lawrence R. core #54

Figure 21

N-alkanes and PAHs in St. Lawrence River Core #59



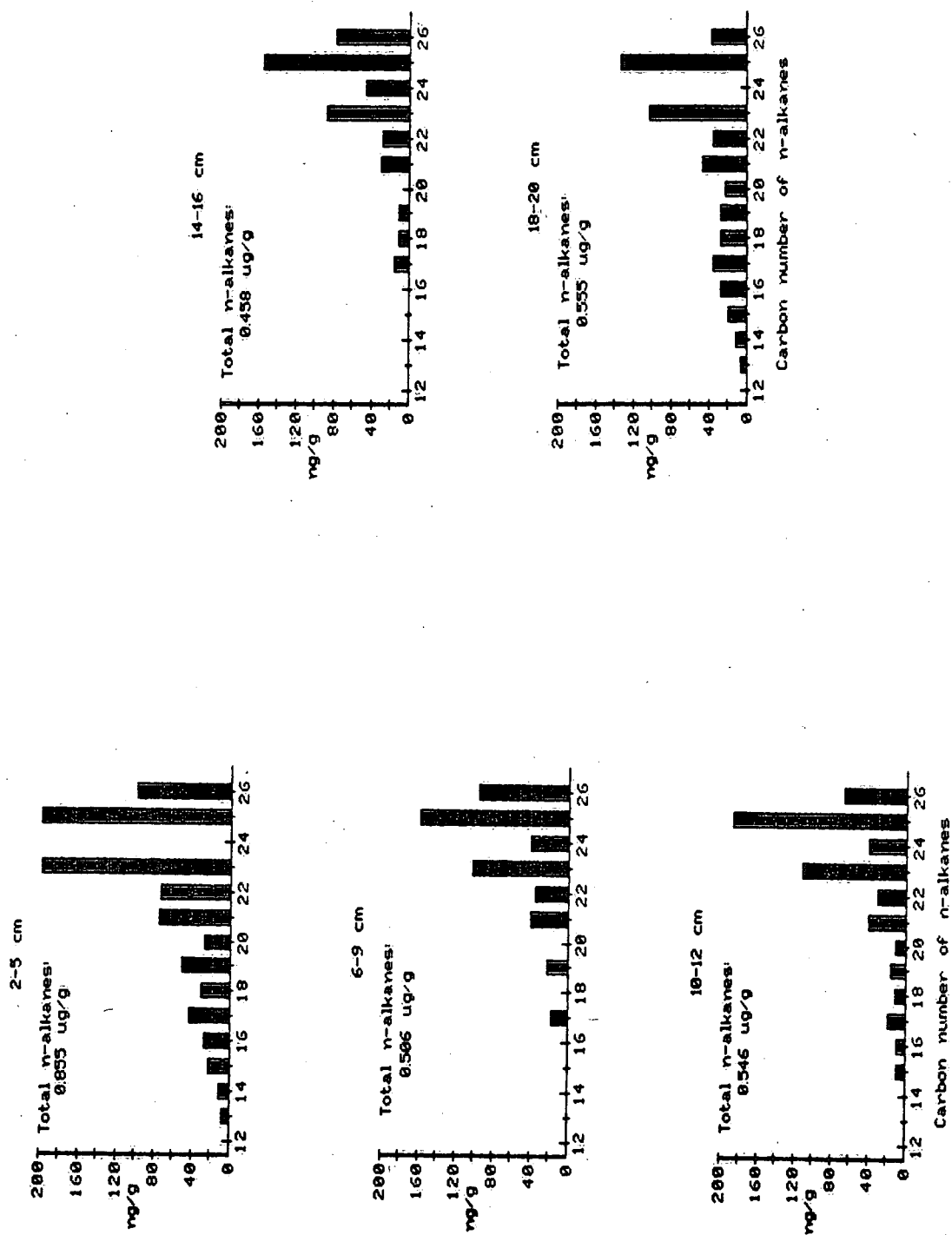


Figure 22

N-alkane profiles in St. Lawrence R. core #59

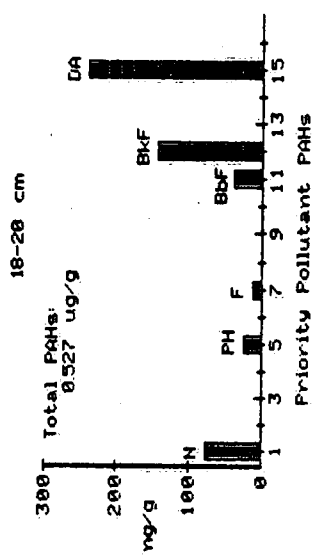
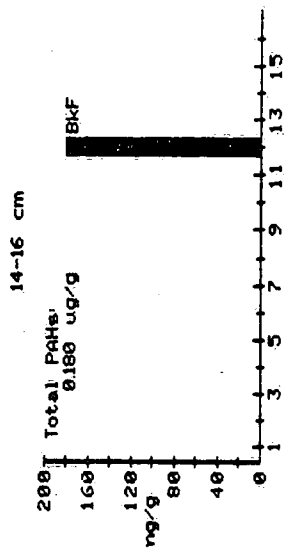
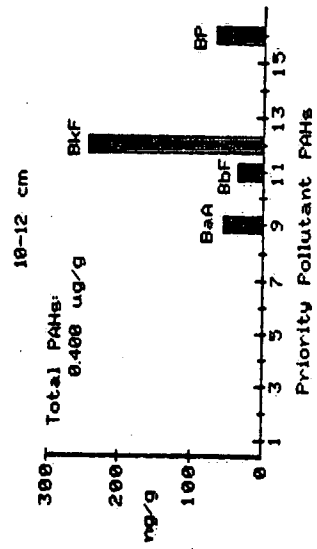
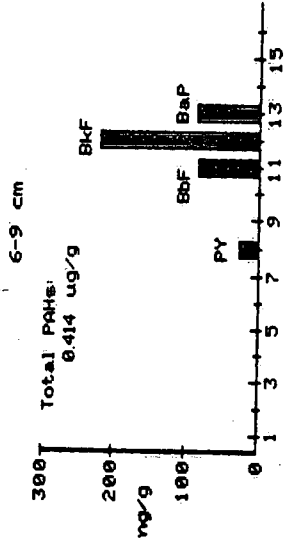
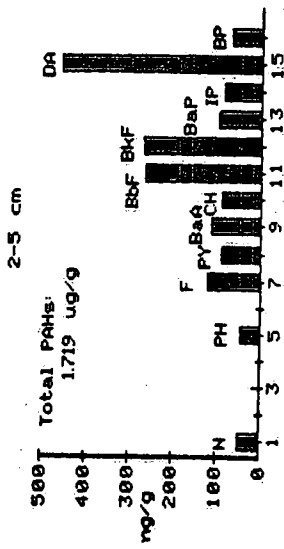
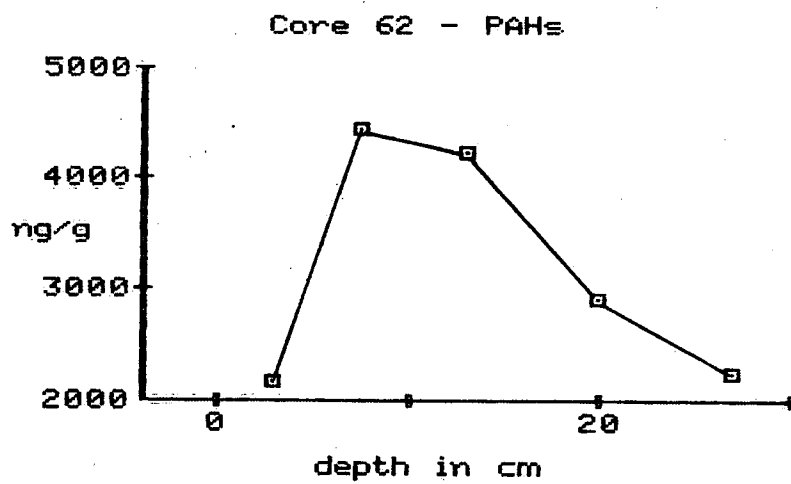
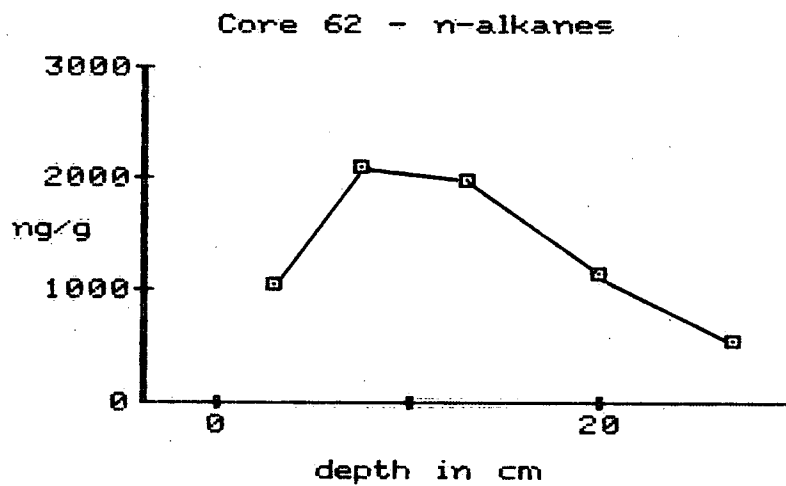


Figure 23

Figure 24

N-alkanes and PAHs in St. Lawrence River Core #62



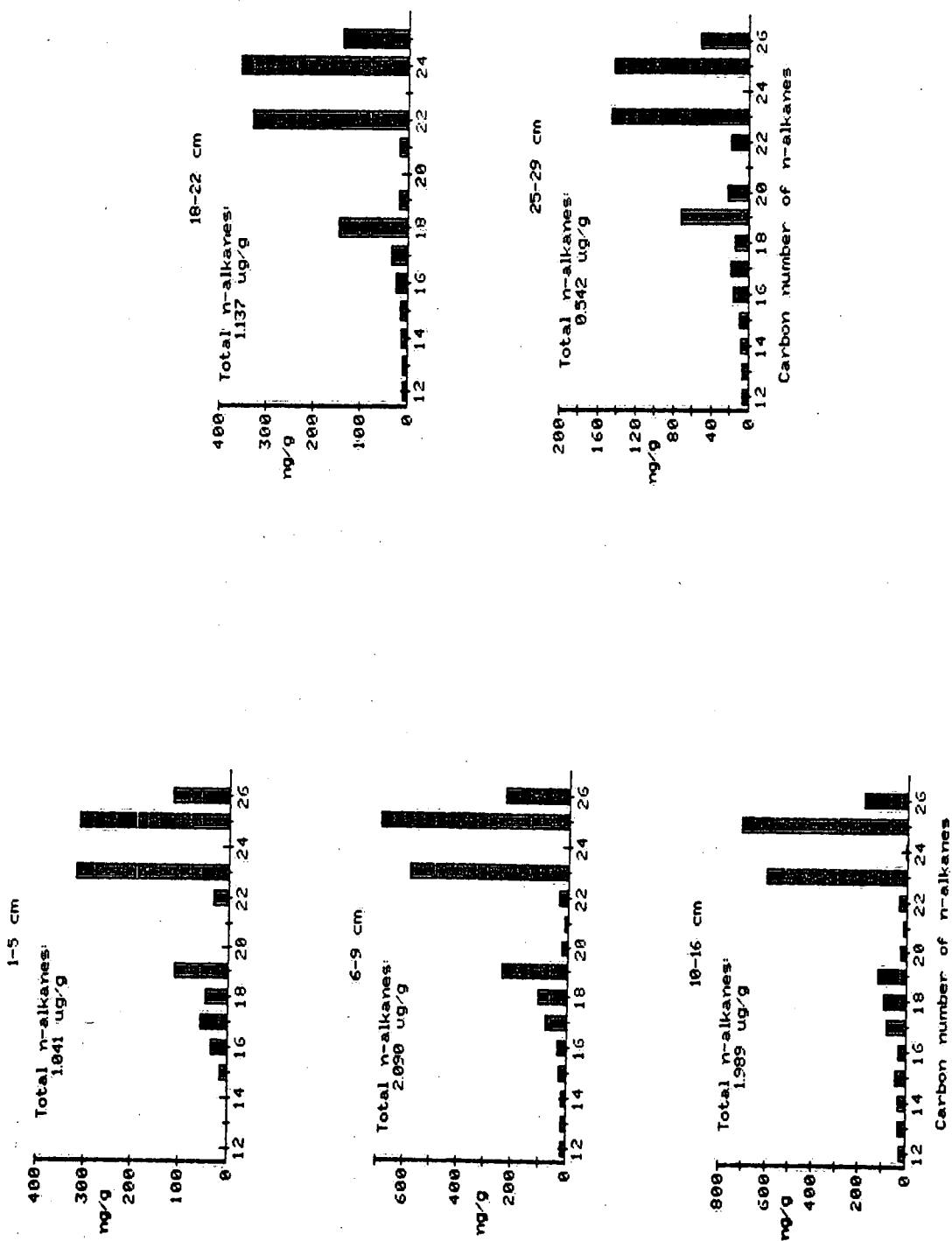


Figure 25

N-alkane profiles in St. Lawrence R. core #62

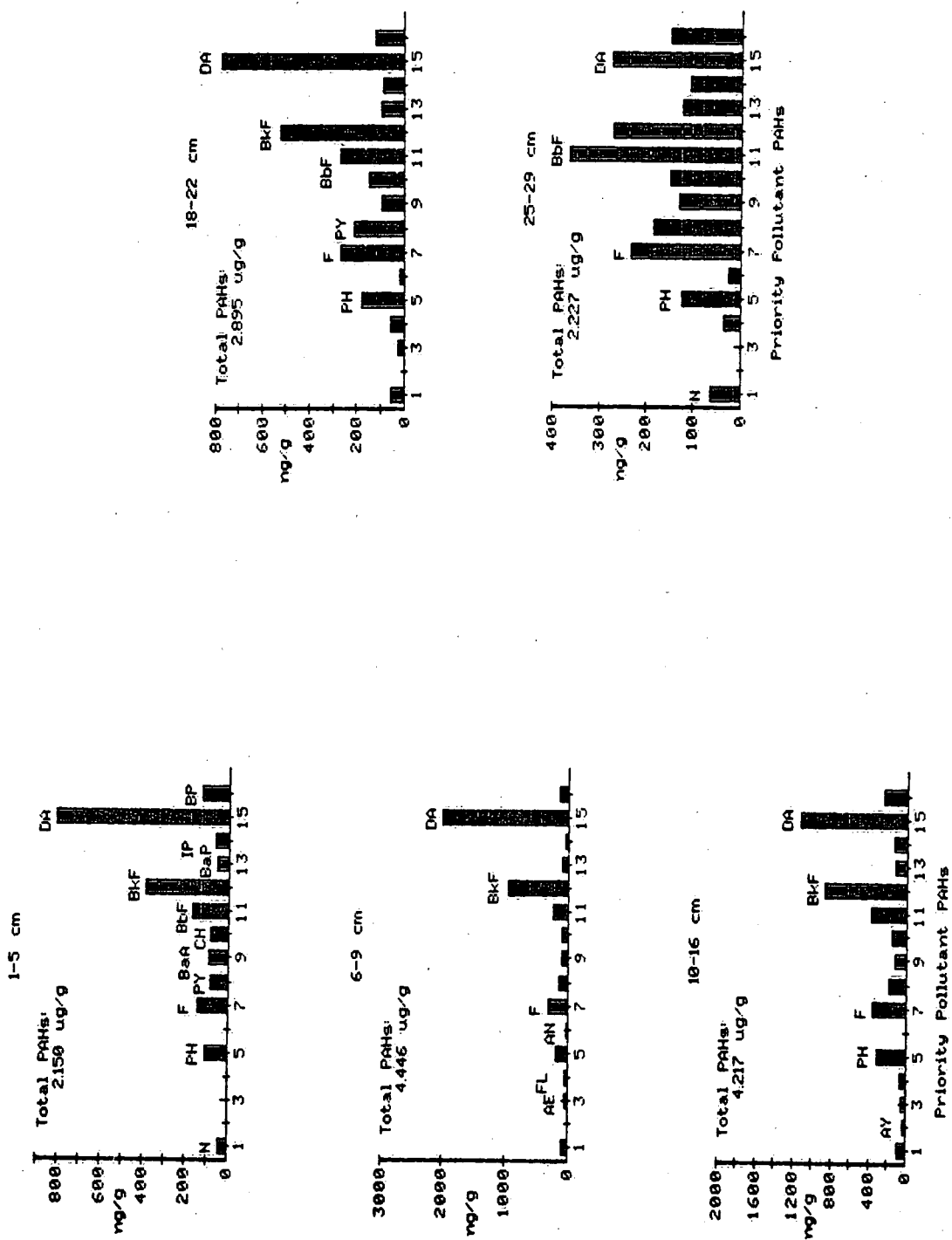


Figure 26

PAH profiles in St. Lawrence R. core #62