POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENTS OF LAKE ERIE, GREAT LAKES: SPATIAL DISTRIBUTION, SOURCES AND PATHWAYS

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by

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A thesis submitted to the

School of Graduate Studies

in partial fulfillment of the

requirements for the degree of

Master of Science

Department of Earth Sciences
Memorial University of Newfoundland

March, 1997

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous organic contaminants often found in terrestrial and marine environments. Because of their hydrophobic character, they tend to be associated with fine particulates and transported to receiving basins by surface runoff and through the atmosphere. Studies of these pollutants in lacustrine sediments are important since many of them have carcinogenic and mutagenic properties, and can be harmful for higher organisms, including people. Such studies are especially important in highly urbanized and industrialized areas where tremendous anthropogenic pressure exerted upon the environment is combined with a high intensity of exploitation. Here I present a study on spatial distribution, sources and pathways of PAH in one of such settings, Lake Erie, lower Great Lakes.

Obliteration of PAH molecular assemblages due to different decomposition processes results in difficulties in identifying their primary sources and pathways. Compound specific isotope analysis (CSIA) has recently been shown a technique that may provide independent constraints for identification of PAH origin in sediments. Therefore, analyses of both molecular and isotopic compositions of compounds have been simultaneously employed in the study in an attempt to obtain a better insight into the regional distribution pattern and original sources of these contaminants in Lake Erie.

A cluster analysis utilizing three first principal components extracted from both molecular and isotopic data sets was performed in the first part of the study. This analysis identified three prominent areas characterized by similar molecular and isotopic composition. Portions of the lake that are immediately adjacent to the major cities comprise one such cluster. The two other clusters partitioned the lake into a southern sector and a northern sector. PAH fluvially introduced at three major cities are probably further transported and redistributed by surface and bottom circulation. This pattern of contamination superimposed on a natural background seems to be responsible for the three-cluster structure observed in the lake. In the second part of the study, the molecular and isotopic signatures of PAH were compared with those previously reported for prominent primary and secondary sources. A subtle interplay between various sources and different degree of degradation appears to account for variations in molecular and isotopic data within the previously identified zones. The research again clearly demonstrated that the isotopic signature is less subjected to weathering processes than the molecular composition and thus can greatly supplement conventional studies on PAH chemistry when source apportionment is the task. The results of both parts of the study were finally summarized in a descriptive model of sources, pathways, transport and deposition of polycyclic aromatic hydrocarbons in the sediments of Lake Erie.

ACKNOWLEDGEMENTS

I would like to thank Dr. Jun Abrajano who introduced me to the field of isotope geochemistry and whose time, dedication and support during the data analysis and writing procedure I appreciate very much. I am also very grateful to Mr. Allen Stark who collected the samples for this study and Ms. Linda Winsor who guided me through the sample preparation and instrumental procedures. Finally I would like to express my gratitude to my husband who helped me with statistical analyses and my daughter, Mary, for her help with computer graphics. I will be forever thankful for the love and support I have received from my family over this time.

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LIST OF ABBREVIATIONS

A = Anthracene

Ae = Acenaphthene

BA = Benz(a)anthracene and its isomers

BaP = Benzo(a)pyrene

BbF = Benzo(b)fluoranthene

BeP = Benzo(e)pyrene

BFl = Benzofluorenthes

BkF = Benzo(k)fluoranthene

BP = Benzo(gpi)perylene

CA = Cluster Analysis

CB = Central Basin

Chy = Crysene

CSIA = Compound specific isotope analysis

DBA = Dibenz(a,h)anthracene

EB = Eastern Basin

Fa = Fluoranthene

Fl = Fluorene

GC-MS = Gas chromatography - mass spectrometry

GC-MS-MS = Gas chromatography tandem mass spectrometry

GC/C/IRMS = Gas chromatography/combustion/isotope ratio mass spectrometry

Ip = Ideno(1,2,3 cd)pyrene

NIST = National Institute of Standards and Technology

Pa = Phenanthrene

PAH = Polycyclic aromatic hydrocarbons

PC1 = First principal component

PC2 = Second principal component

PC3 = Third principal component

PCA = Principal components analysis

PCs = Principal components

Per = Perylene

Py = Pyrene

R/V = Research vessel

UCM = Unresolved complex mixture

USEPA = United States Environmental Protection Agency

WB = Western Basin

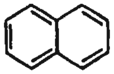
WHO = World Health Organization

1. INTRODUCTION

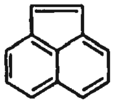
Background: Polycyclic aromatic hydrocarbons (PAH) are organic compounds that consist of two or more fused aromatic rings. Aromatic (benzene) rings are said to be fused when a pair of adjacent carbon atoms is shared. This results in a molecule in which all carbon and hydrogen atoms lie in a single plane. The PAH that consist only of unsubstituted rings are known as parental PAH (Fig. 1.1.1; Neff, 1979; Moore and Ramamoorthy, 1984).

PAH are produced from a variety of natural and anthropogenic sources. Among the natural sources of PAH formation are volcanic activity, geothermal sources, forest fires, diagenesis and natural petroleum seeps (*e.g.*, Laflamme and Hites, 1978; Youngblood and Blumer, 1975; Wakeham *et al.*, 1980). However, the natural background levels generated by the above processes are generally low. Anthropogenically produced compounds mostly derive from incomplete combustion of organic matter at high temperatures during industrial and domestic activities. The major processes that result in production of PAH include: coke production; coal gasification, gas production from petroleum; oil refinery operations; pyrolysis of wood to form charcoal, wood tars and carbon blacks; pyrolysis of kerosene to form benzene, toluene and other organic solvents; power generation from fossil fuels, domestic heating, *etc.* (*e.g.*, Andelman and Snodgrass, 1972). In addition, vehicle exhaust emissions significantly contribute to the total amount of combustion-produced polycyclic aromatic hydrocarbons. PAH can also originate from spills or disposal of various petroleum products. Finally, the wide range of human activities

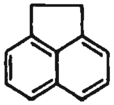
Figure 1.1.1 The 16 parental polycyclic aromatic hydrocarbons (PAH). All of them are recommended by the World Health Organization (WHO) and US Environmental Protection Agency (USEPA) to be listed as priority pollutants. The numbers in parentheses represent molecular weights of compounds. (Adapted from O'Malley, 1994.)



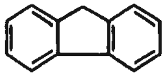
Na (128)
Naphthalene



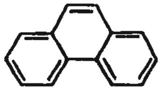
Ay (152)
Acenaphthylene



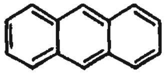
Ae (154)
Acenaphthene



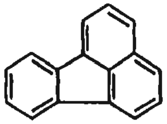
Fl (166)
Fluorene



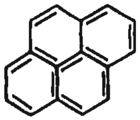
Pa (178)
Phenanthrene



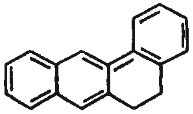
A (178)
Anthracene



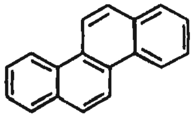
Fa (202)
Fluoranthene



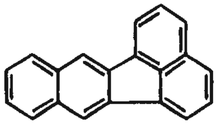
Py (202)
Pyrene



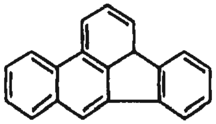
BaA (228)
Benz(a)anthracene



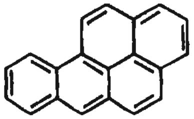
Chy (228)
Chrysene



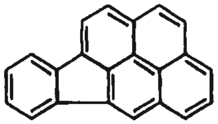
BkF (252)
Benzo(k)fluoranthere



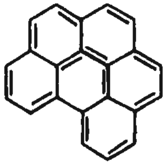
BbF (252)
Benzo(b)fluoranthere



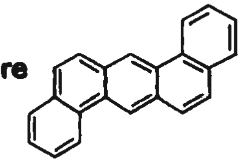
BaP (252)
Benzo(a)pyrene



Ip (276)
Ideno(1,2,3cd)pyrene



BP (276)
Benzo(gpi)perylene



DBA (278)
Dibenz(a,h)anthracene

results in production and release into the environment of a total amount of PAH that by far exceeds that produced from natural sources.

After being produced by humans through various combustion processes, polycyclic aromatic hydrocarbons usually enter the atmosphere. Initially generated in the gas phase, they are sorbed onto fine (predominantly < 5μm) particulates when the vapor cools (Van Vaeck *et al.*, 1979; Van Vaeck and Van Cauwenberghe, 1985). The smaller particles (2-3 μm) remain in suspension for longer times and may enter the upper atmosphere where they are transported over great distances (hundreds or thousands of kilometers). However, the larger particles (5-10 μm) are readily removed from the air by wet and dry deposition. In urbanized areas, the particles deposited on paved roads together with oils spilled by cars are further washed into the city sewer system or directly into rivers and streams crossing the area by rain and/or snow melt. There they are subsequently transported with suspended sediment load to enter the receiving water body. The currents existing in lakes or marine harbors can further distribute the particles across the basin before they finally settle and become incorporated into sediments. Contaminated particles can also enter the water column directly from the atmosphere through the air-water interface. In addition, petroleum-derived compounds can be introduced into the water through numerous leaks and spills originating from pleasure crafts, commercial ships, fuel tankers, harborside facilities, and offshore oil production. Seepage of crude oil from hydrocarbon reservoirs can also contribute to the PAH assemblage in sediments.

After release by the primary sources, PAH can be affected by different degradative processes which can eventually result in alteration of the assemblage. The most important among them are photooxidation, chemical and physical degradation, and microbiological transformations (Neff, 1979). The photooxidation is generally considered to be the most important mode of PAH decomposition in the atmosphere and the photic zone of water column. This process results in transformations of parental PAH through a variety of photo-induced reactions with oxygen, ozone, HO radical, and other oxidizing agents. The processes of volatilization across the air-water interface and reactions with a variety of organic and inorganic oxidants, including peroxides, nitrogen oxides, sulfur oxides, *etc*., bring about physical and chemical transformations of the PAH assemblage through removal or alteration of more mobile compounds. In addition, biological degradation which primarily occurs in the upper layer of sediments, close to the water-sediment interface, results in preferential consumption of less stable compounds by microorganisms that inhabit the substrate.

Thus PAH predominantly emanating from different anthropogenic activities are transported by rivers and streams and through the atmosphere to become eventually deposited in lacustrine and marine sediments. During the transport and after deposition, the initial PAH assemblage can be significantly altered by a variety of different processes.

Disciplinary and regional context: Studies of PAH contamination in lacustrine and marine sediments and its original sources are important. This importance is substantiated by the fact that most of the compounds have toxic properties. They tend to form carcinogenic and mutagenic dials and epoxides that react with DNA (Zedeck, 1980; Malins and Hodgins, 1981; Stein *et al*., 1990; Cerniglia, 1991). The World Health Organization (WHO) and the U.S. Environmental Protection Agency (USEPA) named sixteen parental PAH as priority pollutants (Fig. 1.1.1). After initial deposition, PAH can be resuspended and returned back to people through various food webs and with potable water. Studies of these organic pollutants are especially important in highly populated areas where levels of contamination may be extremely high while the environment is extensively exploited with recreational and commercial purposes.

Traditionally PAH studies have dealt with concentrations of individual compounds in sediments. Comparison with known molecular signatures of major primary sources was further used in the source apportionment procedure (*e.g*., Dastling and Albrecht, 1977; Lake *et al*., 1979; Simoneit, 1986; Canton and Grimalt, 1992). However, as it was discussed above, a number of processes continuously affect the PAH assemblage from the time of its release to the moment of sampling. The alteration of the initial molecular distribution results in numerous difficulties with regard to primary source identification (Wakeham *et al*., 1980). Freeman (1991) was the first to demonstrate that the determination of relative abundance of two stable isotopes of carbon (^{13}C and ^{12}C) can significantly facilitate apportionment of PAH sources and open a new prospect in studies of these organic compounds. She found that the isotopic ratios of individual compounds are characteristic of different primary sources of PAH production. Further studies showed that the isotopic composition of PAH is not significantly affected by the decomposition processes (O'Malley *et al.*, 1994). Thus, compound specific isotope analysis (CSIA) can greatly facilitate traditional PAH studies by introducing an independent constraint for elucidating their sources and pathways. This approach was further developed by O'Malley (1994), who, on the basis of both molecular and isotopic composition, apportioned sources of PAH contamination for St. John's Harbor and Conception Bay, eastern Newfoundland. Stark *et al.* (1995) studied PAH distribution in sediments at a few sites along the St. Lawrence River. A combined application of both analyses in this study allowed a deeper insight into the regional and local sources of PAH contamination in fluvial sediments. However, no studies have so far employed both methods to analyze distribution and potential sources of PAH in the lacustrine environment.

Lake Erie, Great Lakes, is one of the most highly urbanized and industrialized areas in the American midwest. The high levels of urbanization and industrialization result in extremely high amounts of toxic chemicals released in the air, soil, and water from a variety of sources. Polycyclic aromatic hydrocarbons are very common among these contaminants. However, very few studies were concerned with the distribution, sources and pathways of these compounds in the lake sediments. Those available to date have primarily dealt with local patterns of contamination (*e.g.*, Eadie *et al.*; 1982; Eadie, 1984; Eadie *et al.*, 1991; Howell *et al.*, 1996). None of the previous studies have employed the CSIA as an independent tool for source apportionment.

Thus a study of spatial distribution, sources and pathways of PAH on the scale of Lake Erie utilizing both molecular and isotopic composition of compounds would be novel and could significantly contribute to the discipline of environmental geochemistry. In addition, the understanding of regional pollution patterns and knowledge of primary sources of contamination could provide managers with an important piece of information for planning future policies with regard to prevention of further degradation of the environment of the Great Lakes Region.

Objective: ***The major objective of the study was to create a general descriptive model of sources, pathways, transport and deposition of polycyclic aromatic hydrocarbons in the sediments of Lake Erie.*** This goal was achieved in two steps which are considered as two parts of the study.

The objective of the first part was to understand the regional pattern of spatial distribution of PAH with similar molecular and isotopic composition and explain the mechanism which might be responsible for its origin. To achieve this objective, two sets of data, both molecular and isotopic composition of PAH, were obtained from instrumental analysis of samples collected from bottom sediments at different locations. After generalization through a series of analyses, the final distribution pattern involving both molecular and isotopic composition was generated using multivariate statistics. A comparison of this pattern with permanent and temporary circulation known to exist in the lake allowed the transport mechanisms to be suggested.

The second objective was to identify the major sources participating in the formation of the PAH assemblage recovered from lake sediments. To achieve this objective the original data on PAH concentrations were modified by normalizing to the total sum of more stable 4- and 5- ring compounds. This allowed them to be compared with characteristic signatures of prominent primary and secondary sources available from previous studies. The comparison was performed through a series of analyses which included some multivariate methods. Similar procedures were performed for selected compounds from the isotopic data set. The analyses were finalized by grouping the results in the space created by first principal components extracted from both data sets. The position of samples with respect to the major sources enabled the relative contribution of the latter to be estimated. The results were discussed with regard to the zones previously identified through the analysis of spatial distribution.

Finally, the results of both parts were brought together to create a general model describing major sources, pathways, transport and deposition of PAH in the lake sediments.

2. STUDY AREA

2.1 PHYSICAL GEOGRAPHY

Geographic location: The Great Lakes system is located in the central part of the North American continent on the border of the United States and Canada (Fig. 2.1.1). The system is subdivided into the upper and lower Great Lakes. Lakes Superior, Michigan and Huron are included into the upper part of the system while Lake Erie and Ontario belong to its lower portion. Lake Erie is the first water body in the lower Great Lakes, which is connected to the St. Lawrence River, the major outflow of the system, through the Niagara River and Lake Ontario (Fig. 2.1.2).

Physical features: Although Lake Erie is one of the smallest lakes in the Great Lakes system, its surface area is as large as 25,700 km^2. It has an elongated shape (length:width ratio approximately 4:1) and stretches from south-west to north-east over 388 kilometers. Lake Erie is also the shallowest lake in the system (average depth approximately 19 m) and thus possesses the smallest volume (Fig. 2.1.2). The depth slowly increases in the north-easterly direction reaching its maximum (64m) in the eastern part of the lake (Fig. 2.1.3).

Water balance: The drainage area of the lake is 78,000 km^2. The major influx of water (90%) is provided by the Detroit River entering the lake in the west and discharging as much as 5,800 m^3/s of water (Bedford, 1992; Carter and Hites, 1992). The mouth of the second largest contributor, the Maumee River, is located further south-west. Smaller tributaries enter the lake mostly along the southern shore. The most notable among them

Figure 2.1.1 The Great Lakes drainage basin. The unshaded areas indicate distribution of population in the region (1 dot represents 2500 people). The notations refer to inter-lake lock and river systems and are as follows: 1a. St. Marys River; 1b. Straits of Mackinac; 2. St. Clair River, Lake St. Clair, Detroit River; 3. Niagara River, Welland Canal; 4. St. Lawrence River. (After Fuller and Shear, 1995.)


CANADA
USA
THE GREAT LAKES BASIN
Lake Superior
Lake Michigan
Lake Huron
Lake Erie
Lake Ontario
1a
1b
2
3
4
SCALE
0 50 100 150 200 250 kilometres
0 25 50 75 100 125 150 175 miles

Figure 2.1.2 The Great Lakes profile. Note: 1. The profile is taken along the long axes of the lakes; 2. The vertical exaggeration is 2000 times; 3. Lake surface elevations are given above sea level and maximum depths are below lake surface; 4. Inter-lake lock and river systems are numbered to correspond to map in Figure 2.1.1. (After Fuller and Shear, 1995.)

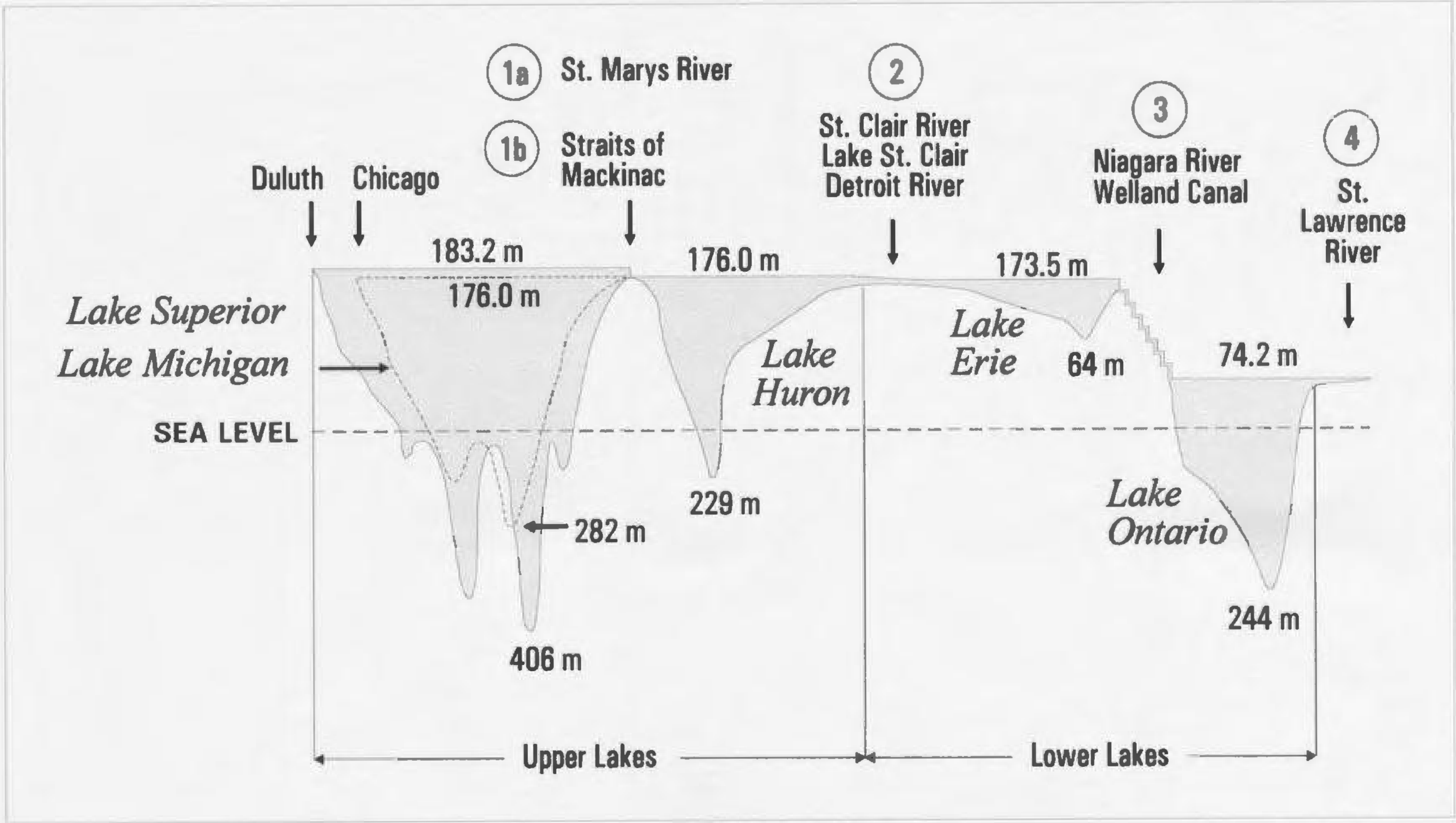
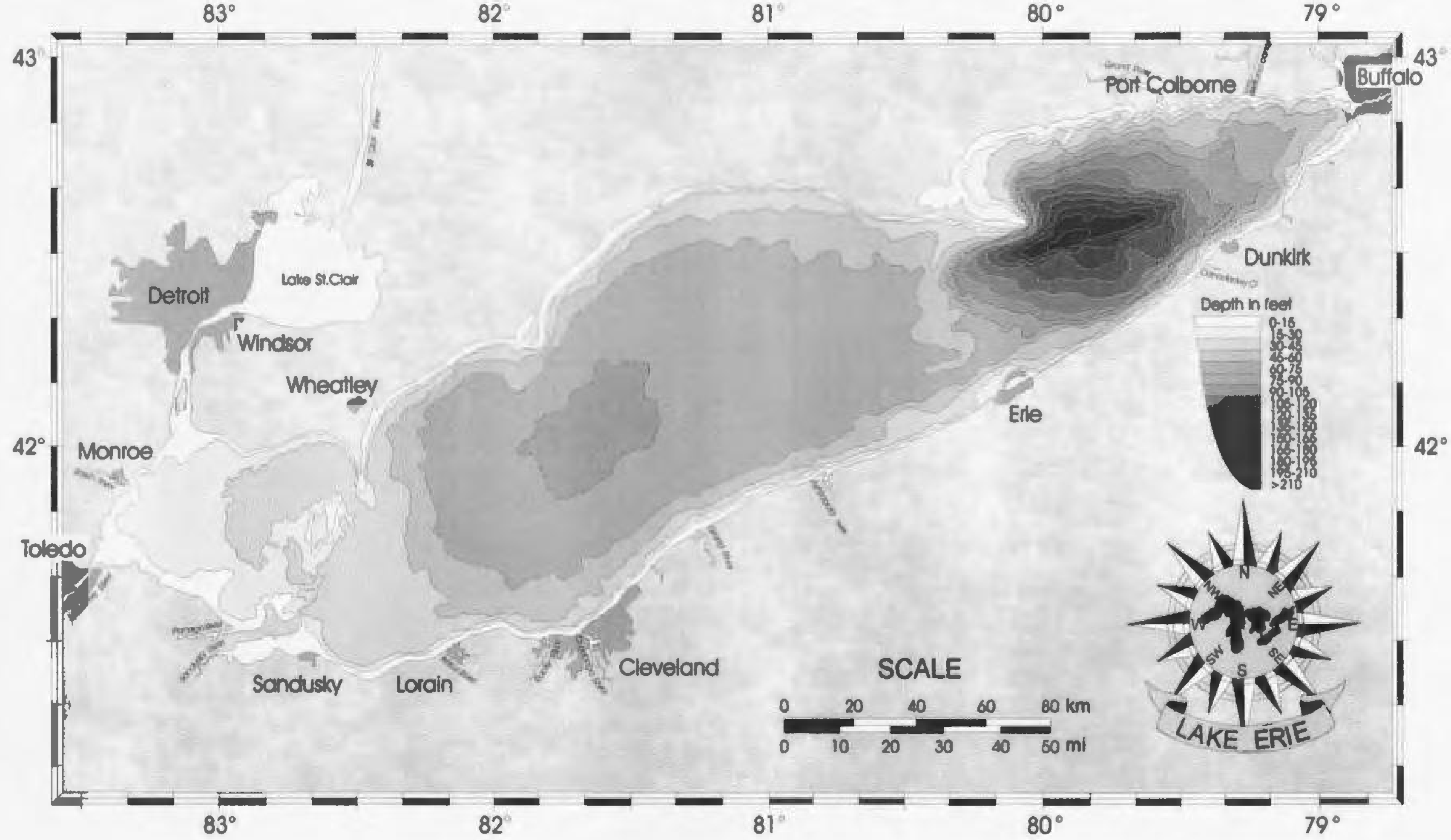

1a St. Marys River
1b Straits of Mackinac
2 St. Clair River Lake St. Clair Detroit River
3 Niagara River Welland Canal
4 St. Lawrence River
Duluth
Chicago
183.2 m
176.0 m
176.0 m
173.5 m
74.2 m
Lake Superior
Lake Michigan
Lake Huron
Lake Erie
Lake Ontario
SEA LEVEL
64 m
229 m
282 m
406 m
244 m
Upper Lakes
Lower Lakes

Figure 2.1.3 A bathymetric chart of Lake Erie. (Adapted from Ristic and Ristic, 1985.)


83°
82°
81°
80°
79°
43°
42°
Port Colborne
Buffalo
Dunkirk
Detroit
Lake St.Clair
Windsor
Wheatley
Monroe
Toledo
Erie
Sandusky
Lorain
Cleveland
Depth in feet
0-15
15-30
30-45
45-60
60-75
75-90
90-105
105-120
120-135
135-150
150-165
165-180
180-195
195-210
>210
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

are the Black River, the Cuyahoga River and the Ashtabula River. The only significant fluvial input along the northern shore is provided by the Grand River, which enters the lake in its eastern part. The Niagara River in the east is the major outlet through which water exits the lake.

Current pattern: The above pattern of influx and outflow combined with bottom topography, predominant wind direction and shore line configuration is responsible for the specific pattern of surface circulation observed in the lake. The powerful flow of the Detroit River is injected into the western part of the lake where it veers in different directions (Fig. 2.1.4). However, due to the specific bottom topography and the shore line configuration, the major flow is diverted in the easterly direction. The eastward flow in the central part is mostly restricted to the southern shore where it entrains the whole water column (Thomas *et al.*, 1976). Further in the east, the rapidly increasing hydraulic gradient rushes water out of the lake through the Niagara River outlet. In addition, the predominant winds of southerly and southwesterly directions induce Ekman circulation in the central regions. The latter results in a built up of water along the southern shore. North-westerly directed compensatory bottom currents balance out the hydraulic gradient (Hamblin, 1971; Fig. 2.1.5). Among other circulation patterns, clockwise and counterclockwise gyres found in the Central and Eastern Basins are the most prominent (Fig. 2.1.6; Saylor and Miller, 1987).

Sedimentation regime: The location of tributaries, bank stability and bottom morphology determine the general sedimentation pattern within the lake. Three distinct

Figure 2.1.4 The pattern of permanent surface circulation in Lake Erie. The arrows represent direction of surface flow and longshore drift. (Modified from Hamblin, 1971 and Ristic and Ristic, 1985.)

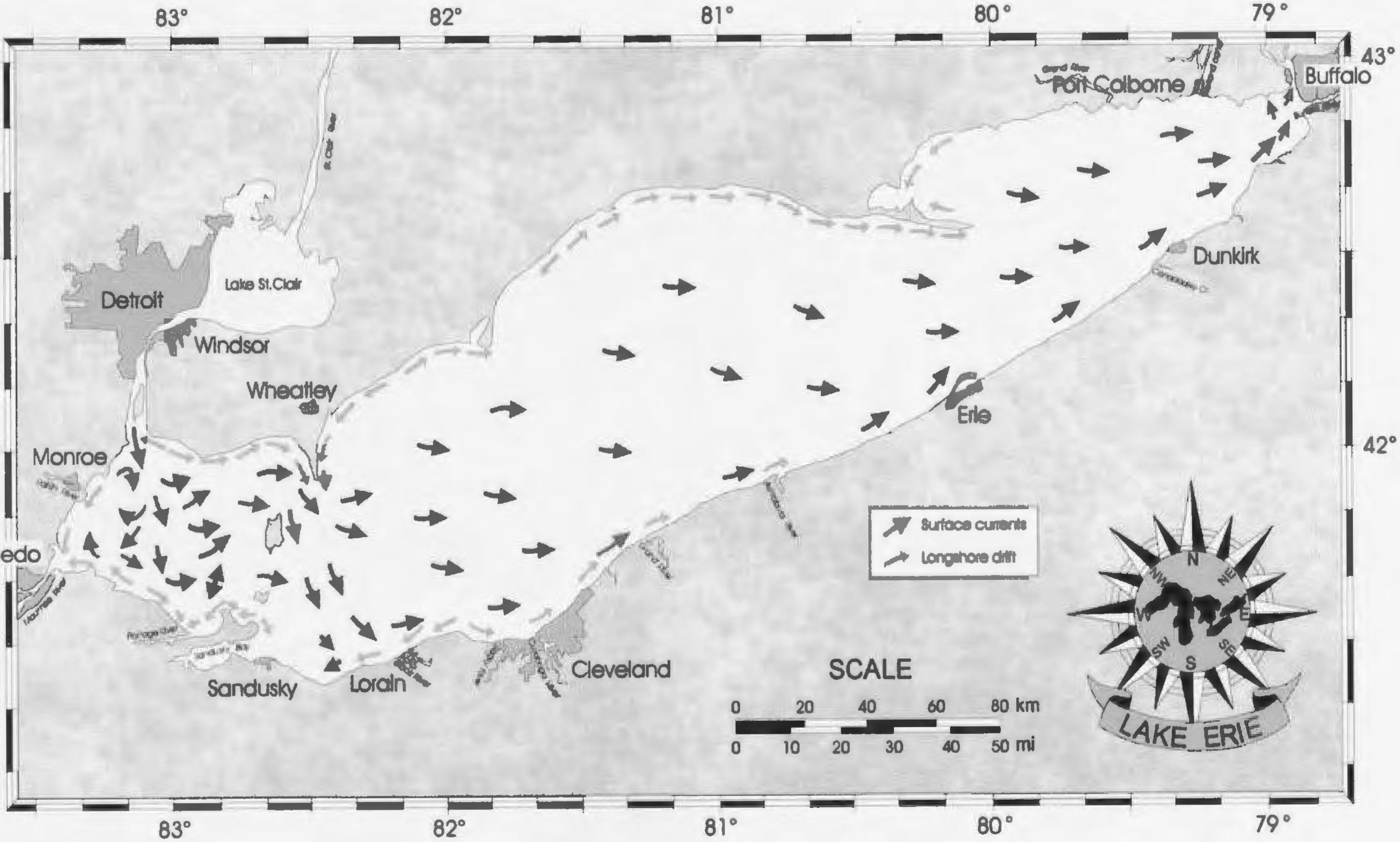

83°
82°
81°
80°
79°
43°
42°
St. Clair River
Lake St.Clair
Detroit
Windsor
Wheatley
Monroe
Toledo
Maumee River
Portage River
Sandusky Bay
Sandusky
Lorain
Cleveland
Grand River
Port Colborne
Buffalo
Dunkirk
Erie
Surface currents
Longshore drift
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Figure 2.1.5 The pattern of permanent bottom circulation in the central part of Lake Erie (Modified from Hamblin, 1971.)

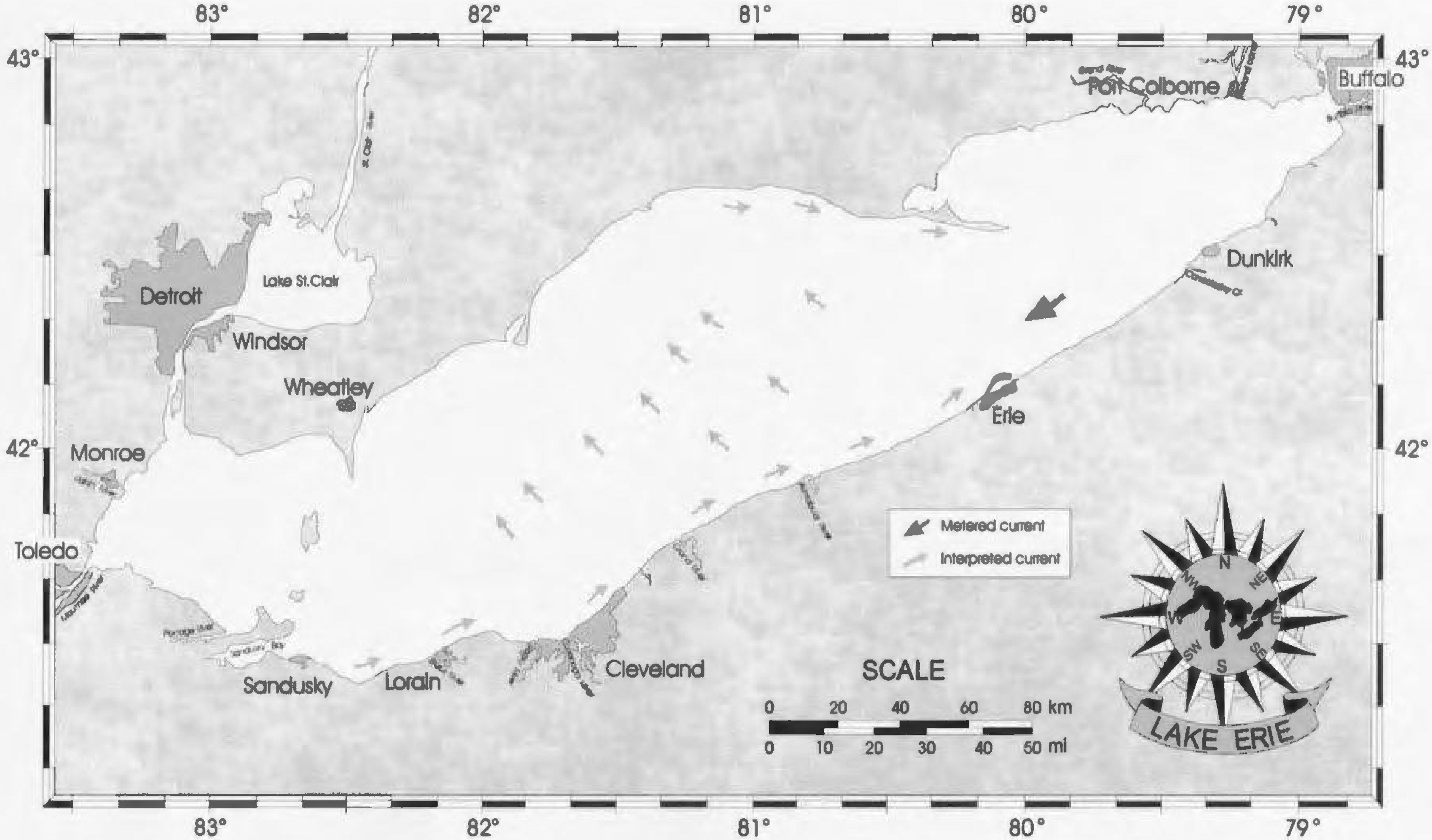
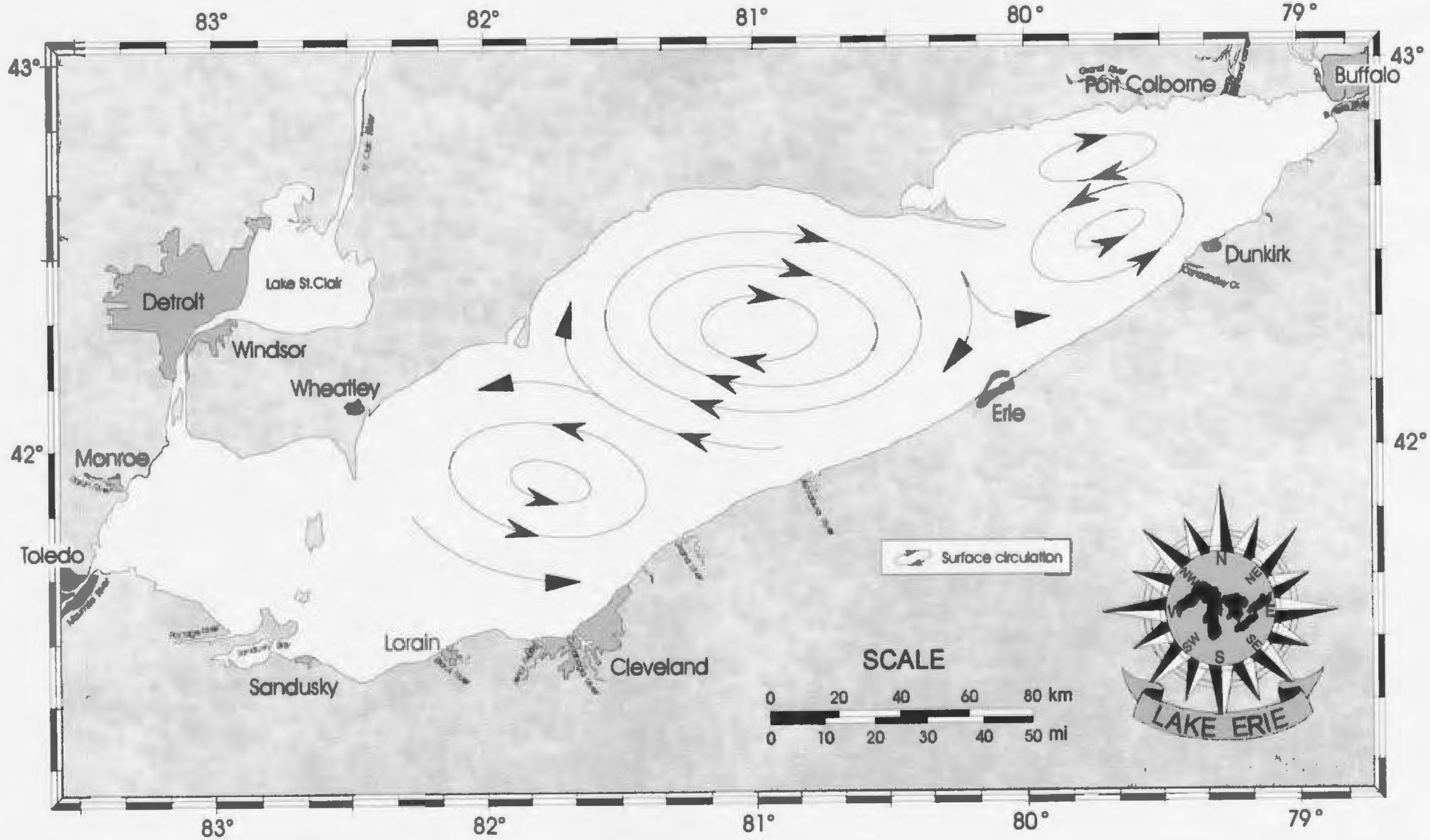

83°
82°
81°
80°
79°
43°
42°
Buffalo
Port Colborne
Grand River
Dunkirk
Lake St.Clair
Detroit
Windsor
Wheatley
Monroe
Toledo
Maumee River
Portage River
Sandusky Bay
Sandusky
Lorain
Cleveland
Erie
Metered current
Interpreted current
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Figure 2.1.6 A temporary pattern of surface circulation known to exist in the central and eastern parts of Lake Erie. (Adapted from Saylor and Miller, 1987.)


83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
Surface circulation
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

sedimentary basins, Western, Central, and Eastern are characterized by different rates of sedimentation. The highest average rates (2,160 g m^{-2} yr^{-1}) are observed in the Western Basin and attributed to the rapid deposition of suspended sediment load of the Detroit River, which contributes as much as 1.4 x 10^6 metric tons/yr of sediment (Kemp *et al.*, 1976; Kemp *et al.*, 1977). The Central Basin is characterized by significantly lower rate (580 g m^{-2} yr^{-1}) and is generally dominated by hemipelagic sedimentation. However, increased sedimentation rates are observed close to the southern shore where a few smaller tributaries enter the lake. These areas may also be affected by fluvially introduced material (Fig. 2.1.7). The high sedimentation rates (1,340, g m^{-2} yr^{-1}) in the Eastern Basin are of somewhat different nature and result from coastal cliff failure and subsequent sliding of sediment along the steep bottom slopes (Kemp *et al.*, 1977).

Climate: Two different types of air masses affect the lake and its watershed. The southeastern part of the lake is controlled by the maritime tropical air which originates from the Gulf of Mexico. The advection of this humid air results in moderate temperatures in summer (20^0C; Fig. 2.1.8) and an increased amount of precipitation (over 1000 mm y^{-1}; Fig. 2.1.9) throughout the year. On the contrary, the northwestern areas are influenced by the continental air from the Canadian northwest. The latter is responsible for somewhat higher summer temperatures (> 22.5^0C) and substantially drier conditions (< 800 mm y^{-1}; Fuller and Shear, 1995). The increased air temperatures in summer in turn result in somewhat elevated (>22^0C) water temperatures in this part of the lake.

Figure 2.1.7 Distribution of present-day sedimentation rates determined at 50 offshore locations and representative of the three depositional basins (After Kemp *et al*., 1977.)

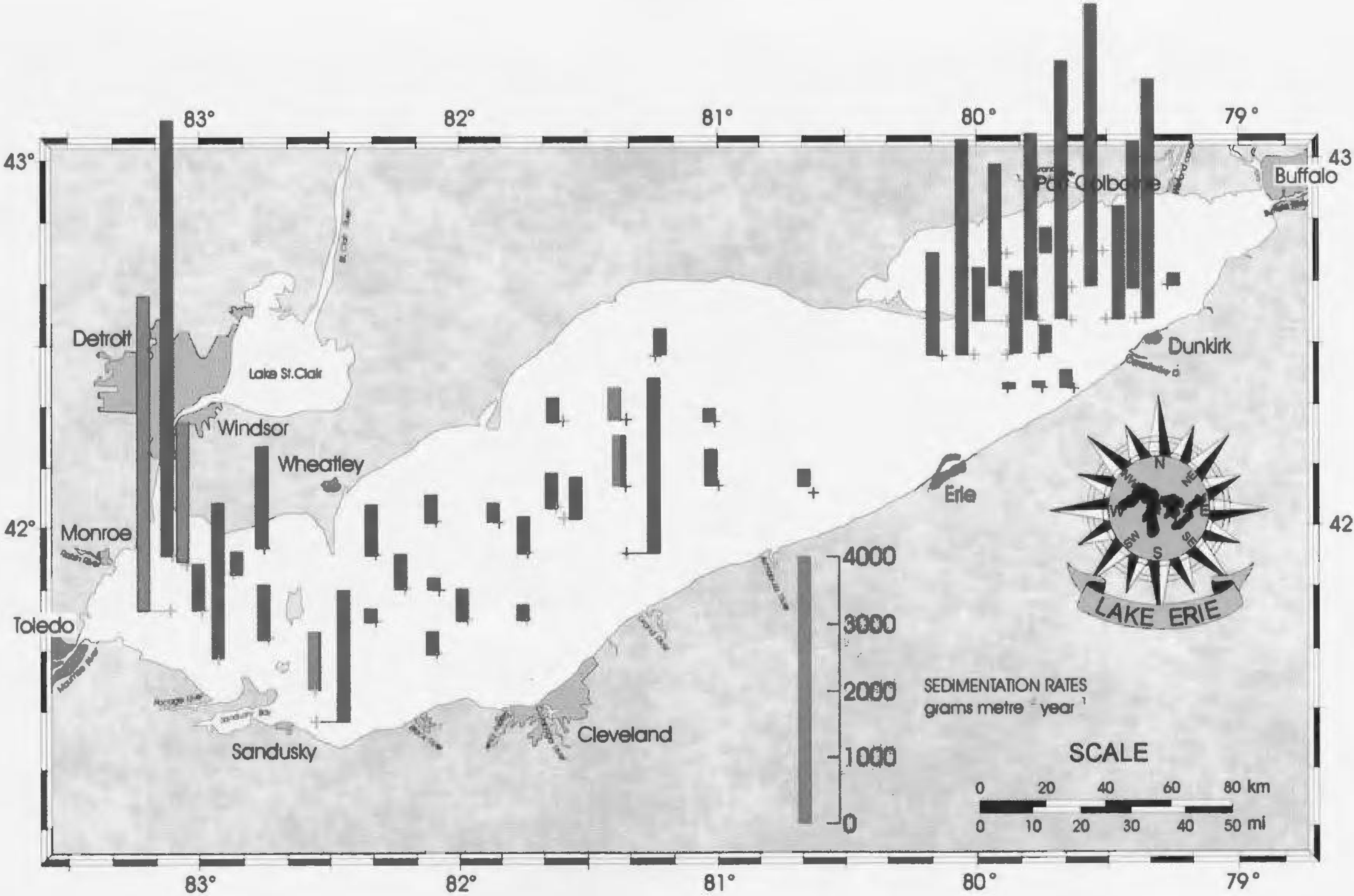

83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Monroe
Toledo
Sandusky
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
4000
3000
2000
1000
0
SEDIMENTATION RATES
grams metre⁻² year⁻¹
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Figure 2.1.8 Summer (July) air and water temperatures in the Great Lakes basin. (After Fuller and Shear, 1995.)

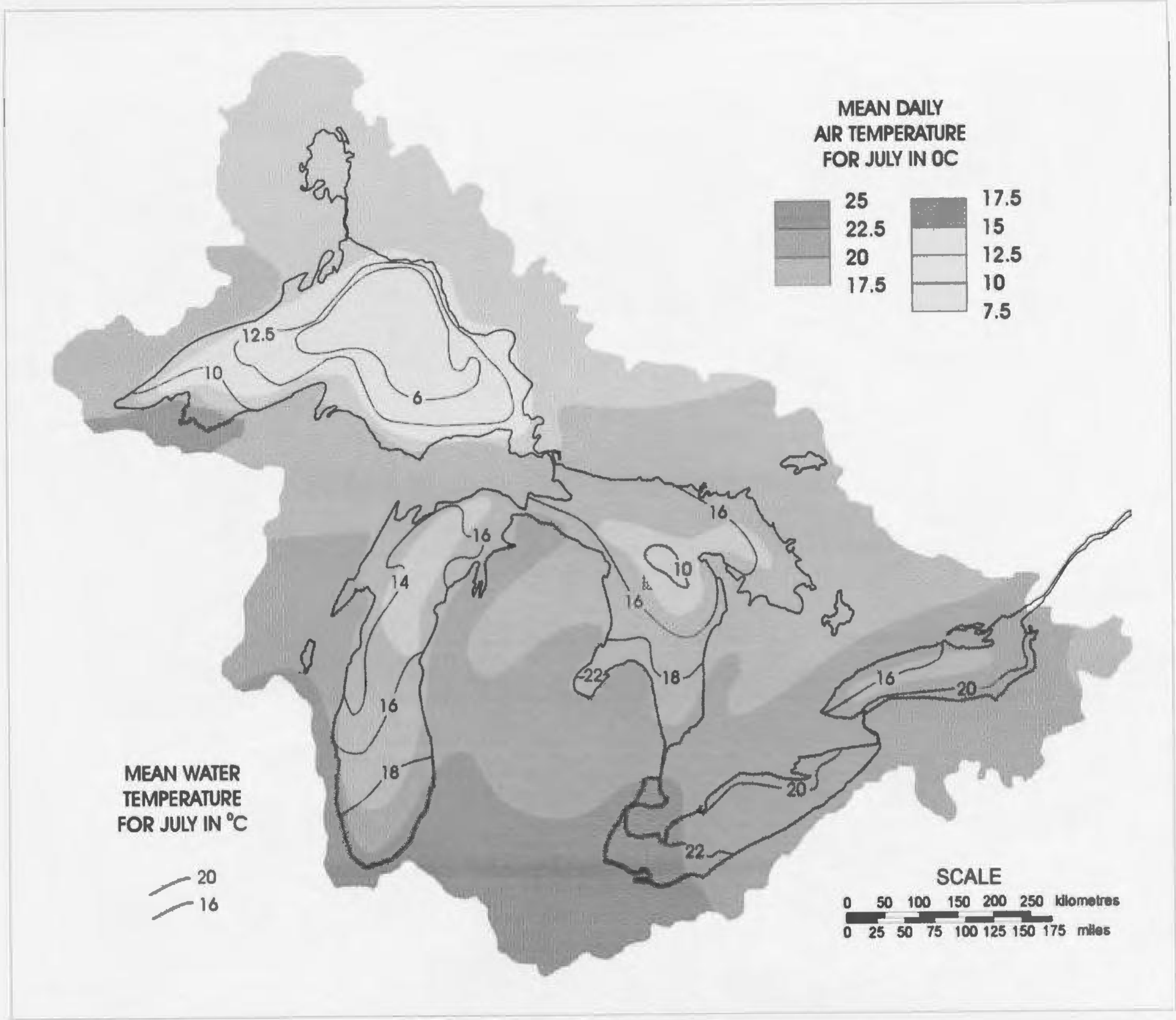
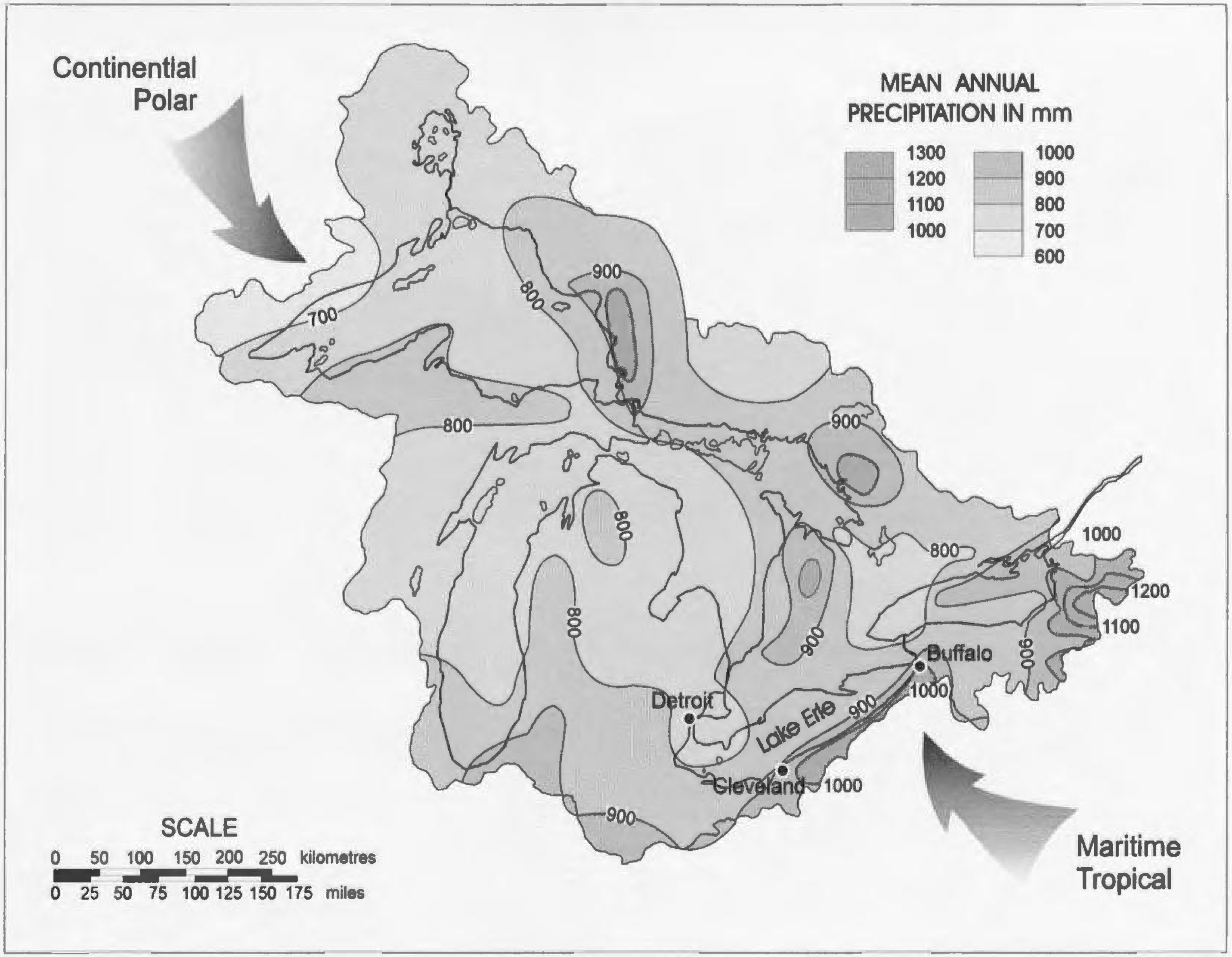

MEAN DAILY
AIR TEMPERATURE
FOR JULY IN 0C
25
22.5
20
17.5
17.5
15
12.5
10
7.5
12.5
10
6
16
16
14
10
16
16
22
18
16
20
16
18
20
22
MEAN WATER
TEMPERATURE
FOR JULY IN °C
20
16
SCALE
0 50 100 150 200 250 kilometres
0 25 50 75 100 125 150 175 miles

Figure 2.1.9 Precipitation areas within the Great Lakes basin. The precipitation regime is controlled by alternating flows of warm, humid air from the Gulf of Mexico and cold, dry air from the Arctic. (Modified from Fuller and Shear, 1995.)


Continental Polar
MEAN ANNUAL PRECIPITATION IN mm
1300
1200
1100
1000
1000
900
800
700
600
700
800
900
800
800
900
800
800
800
900
1000
1200
1100
900
Buffalo
1000
Detroit
Lake Erie
900
Cleveland
1000
900
SCALE
0 50 100 150 200 250 kilometres
0 25 50 75 100 125 150 175 miles
Maritime Tropical

Natural Resources: The lower Great Lakes region is enriched in natural resources many of which actually underlay Lake Erie (Fig. 2.1.10). The northern and eastern parts of the lake are underlain by extensive gas pools derived from Lower Silurian sandstones, Maitland Pool and a Silurian Carbonate Unit, Morpeth Pool (Carter, 1992). Besides, the Marcellus Formation, Middle Devonian, which forms the bedrock in restricted areas of the northern part of the Central Basin, is considered as a potential oil shale (Johnson *et al.*, 1989; Obermajer *et al.*, 1995). In southwestern Ontario, shallow reservoirs of Devonian age are found along the St. Clair and Detroit Rivers and northern margin of the Western Basin. In addition, Silurian oil pools exist along the Michigan shore in the western part of the lake (Fig. 2.1.10).

Thus Lake Erie spans an extensive area in the central part of the North American continent and is characterized by specific physical features, water balance, and the patterns of water circulation and sedimentation. Different regions of this vast area vary in their climatic conditions. Finally, this area is associated with extensive resources of hydrocarbons located primarily in the northern and eastern parts of the lake.

2.2 ECONOMIC GEOGRAPHY

The border between the United States and Canada splits the lake into two almost equal parts. (Fig. 2.2.1). Differences in management policies of the two countries result in a different approach to the exploitation of natural resources and industry distribution. An example of the different approach is the management of the extensive hydrocarbon reservoirs underlying the region. Exploitation of the natural resources is not allowed in

Figure 2.1.10 Distribution of natural resources (oil and gas) under and around Lake Erie. (Modified from Fuller and Shear, 1995.)

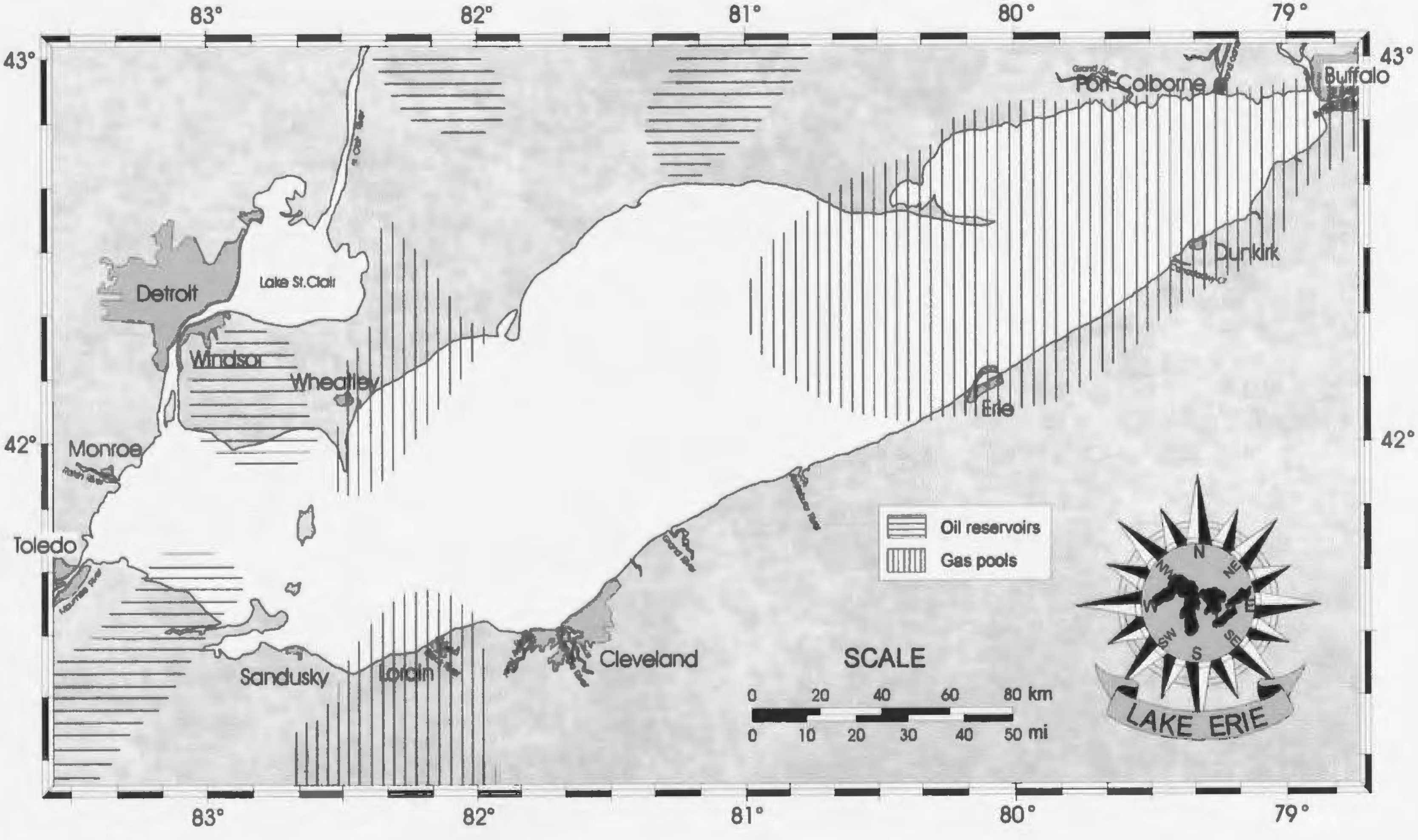
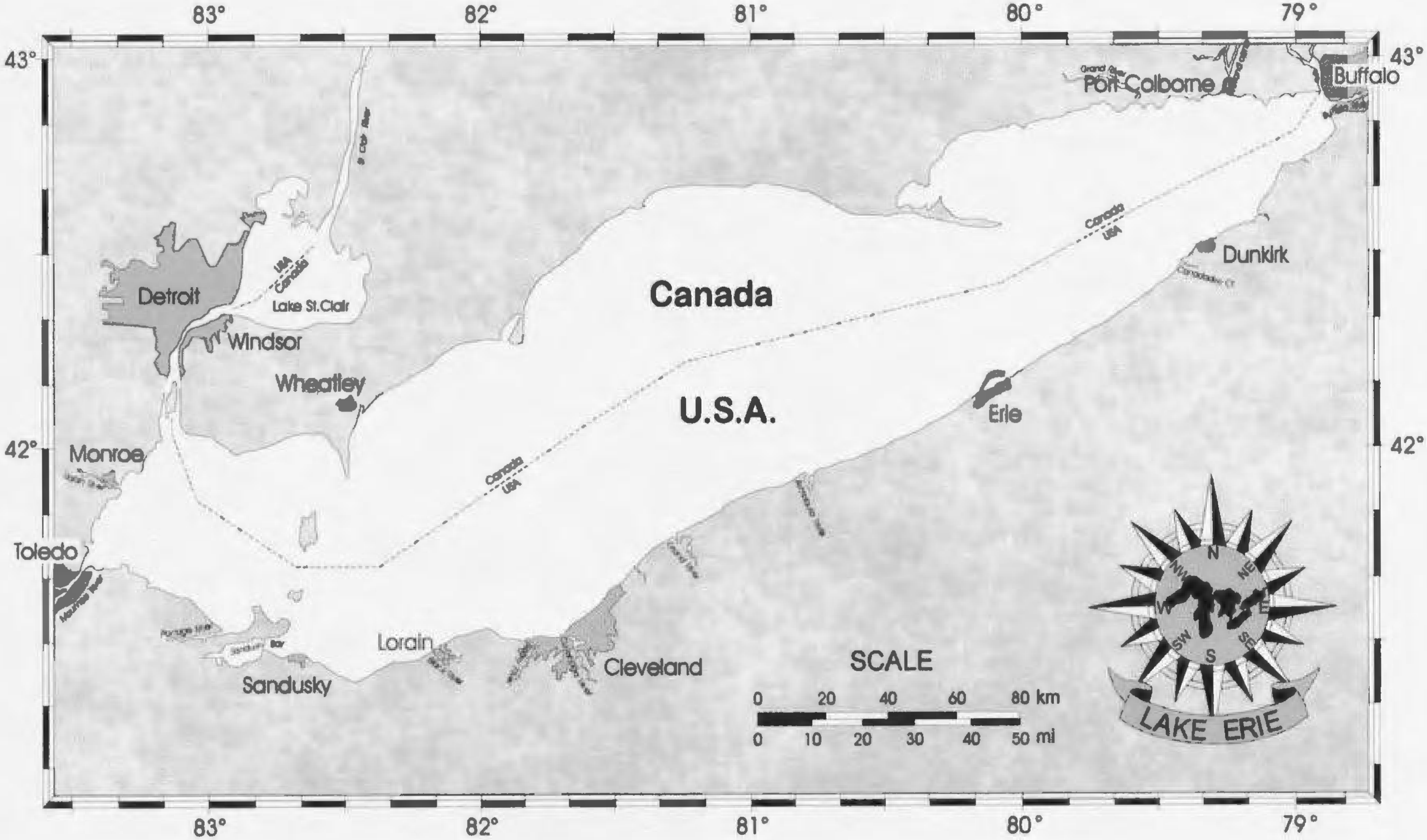

83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
Oil reservoirs
Gas pools
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Figure 2.2.1 The border between the United States and Canada. Note that this border splits Lake Erie into two almost equal parts. (After Ristic and Ristic, 1985.)

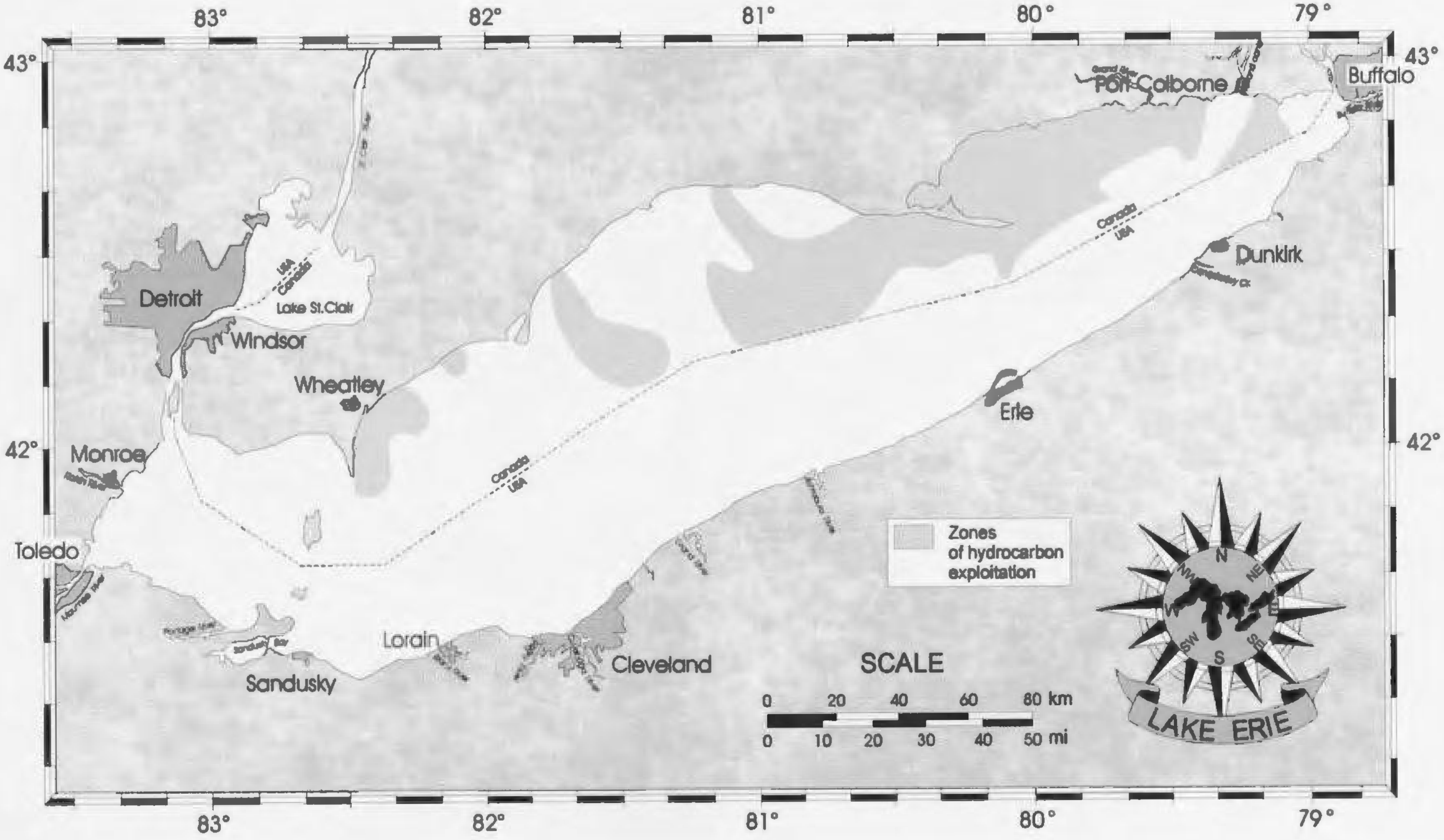

83°
82°
81°
80°
79°
43°
42°
Port Colborne
Buffalo
Detroit
Lake St.Clair
USA
Canada
Windsor
Wheatley
Canada
U.S.A.
Dunkirk
Erie
Monroe
Toledo
Lorain
Sandusky
Cleveland
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

American waters under the current US legislation. However, the hydrocarbons are being actively produced offshore in the Canadian part of the lake (Figure 2.2.2; Meyers, 1984; Canadian Hydrographic Service, 1993). In addition, a different pattern is observed in the distribution of onshore industries. The Canadian side is represented by rural areas with farming as the major industry. On the contrary, the American shore is highly urbanized and industrialized. Eight metropolitan areas are located here with the largest industrial centers Detroit, Cleveland and Buffalo (Fig. 2.2.1).

Detroit, Michigan is located on the right bank of the Detroit River 30 km upstream of the point where the river enters the lake (Fig. 2.2.1). The population of the metropolitan area is over 4.6 million. The major industry is automobile manufacturing owing to which the city is considered the "Automobile Capital of the World". The other primary industries include machine tool accessories, internal combustion engines, iron and still forging, metal cutting tools *etc*. The city either leads the nation or ranks among top three manufacturing centers in these industries. Many of the industries are coal and oil fired. Detroit's waterborne commerce includes, among others, coal and petroleum products.

Cleveland, Ohio is America's tenth largest city and situated on the southern shore of the lake on both banks of the Cuyahoga River. According to the census of 1990, the city population is 2.7 million people. The manufacturing industry dominates over many others. The high concentration of industries results in a serious environmental impact. Until recently, untreated or poorly treated industrial wastes have been released into the waters of the Cuyahoga River. In addition, direct releases of raw sewage from the

Figure 2.2.2 Areas of intensive hydrocarbon exploitation (numerous production wells) in Lake Erie. Note that exploitation is strictly confined to the Canadian parts of the lake. (Adapted from Canadian Hydrographic Service, 1993)

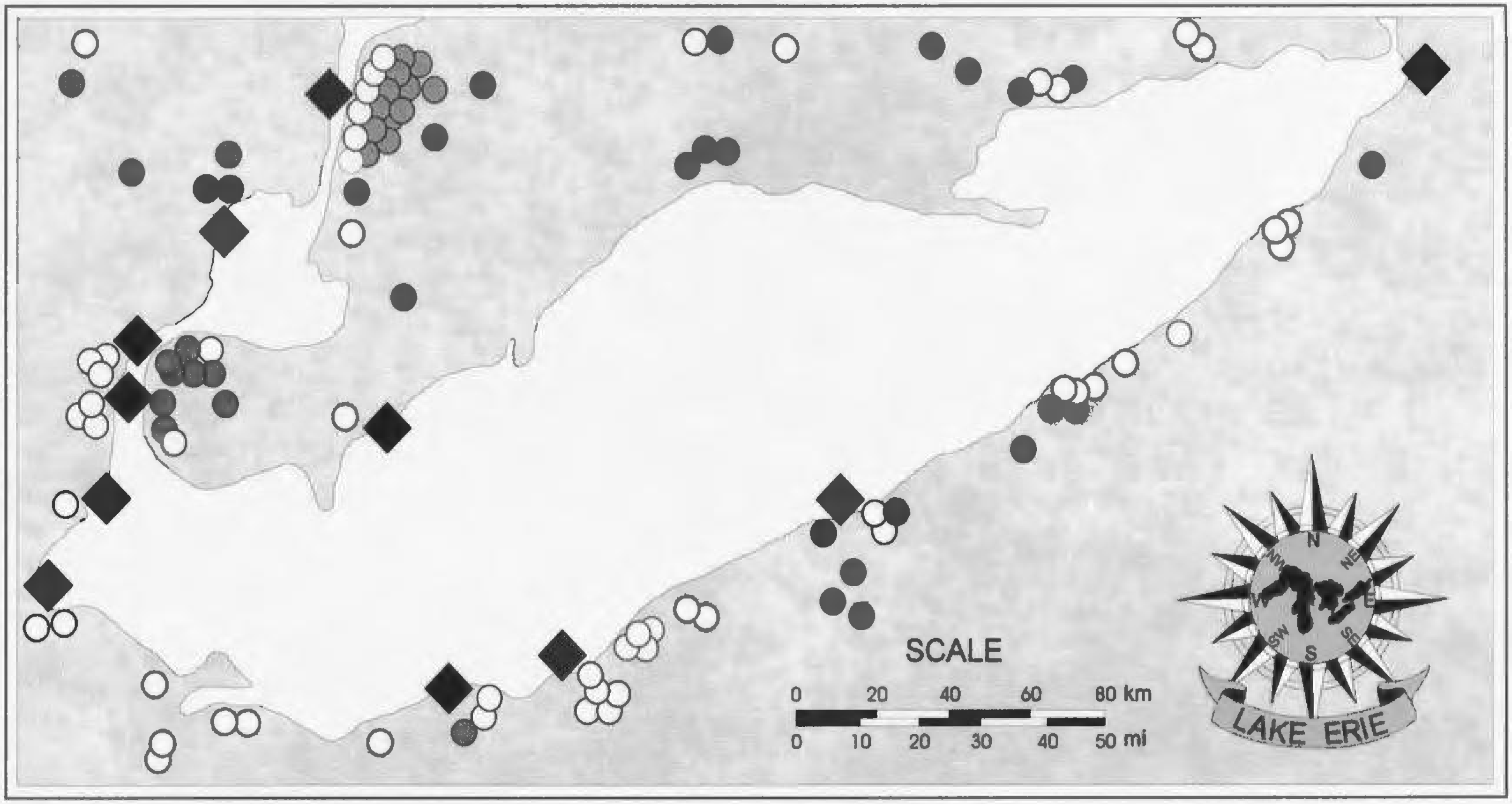

83°
82°
81°
80°
79°
43°
42°
Detroit
USA
Canada
Lake St.Clair
Windsor
Wheatley
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
Canada
USA
Zones of hydrocarbon exploitation
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

continuously overflowed combined sewer system have caused many problems in the recent past (Burns, 1985).

The city of Buffalo occupies the banks of the Buffalo River and stretches over a few kilometers along the shore of the lake in its easternmost part. Although this is the smallest of the three cities, its population exceeds 1 million people. Many industrial sites including steel and chemical plants line the banks of the Buffalo River. As a result, the river waters and sediments are highly contaminated with municipal, industrial and agricultural wastes (Gailani *et al.*, 1996).

In conclusion, there are many potential sources of contamination within and around the lake (Fig. 2.2.3). The offshore exploitation of hydrocarbons is confined to the Canadian part. However, the American side is dominated by onshore industrial centers that stretched along the southern shore of the lake. These centers are usually associated with rivers and streams which serve as conveyor belts in transporting their wastes to the lake.

Figure 2.2.3 Areas of increased waste discharges and locations of harbors and river mouths which can potentially serve as pathways of contaminants to the lacustrine environment. Note the high concentration of sites along the American shore of the lake. (After Botts and Krushelcki, 1987.)



◆ Areas of concern associated with harbours, river mouths and connecting channels.

○ Waste discharges in excess of operating permits, according to pollution probe

● Hazardous waste sites having the greatest potential impact on human health and the environment

3. METHODS

3.1 EXPERIMENTAL

3.1.1 SAMPLE COLLECTION AND PREPARATION

Sample collection: A wide sampling program was conducted by the department of Earth Sciences, Memorial University of Newfoundland in collaboration with the Department of Environment, National Water Research Institute, Burlington, Ontario. The sample collection was primarily performed by A. Stark, during the expedition of R/V LIMNOS in summer 1994 (Stark, 1994). The heterogeneous nature of sediments across the lake necessitated that two different types of samplers be used. Softer sediments were obtained with a 30 x 12 cm box corer which yielded short (< 30 cm) sediment cores. However, in most cases the substrate consisted of hard clays or glacial tills which impeded deep penetration. A Ponar Grab with a jaw volume of 8200 ml was employed at these sites.

The sampling program was designed to provide the best possible coverage of the lake, with more attention paid to the areas of high potential sediment contamination (Fig. 2.2.3). A total of 23 sites were sampled in the three major sedimentary basins of the lake (Fig. 3.1.1, Table 3.1.1). Contaminated sediment load introduced by fluvial systems is known to be an important source of sediment contamination in the receiving reservoirs. As the Western Basin is characterized by the highest, fluvial input, the density of sampling sites was increased here (9 sites). At least one site was sampled in the vicinity of major industrial centers: stations 971 and 1012 at Detroit, 962, 84 and 955 at

Figure 3.1.1 Locations of 23 sites sampled during the expedition of R/V Limnos in summer of 1994 and employed in the present study. (After Stark, 1994.)

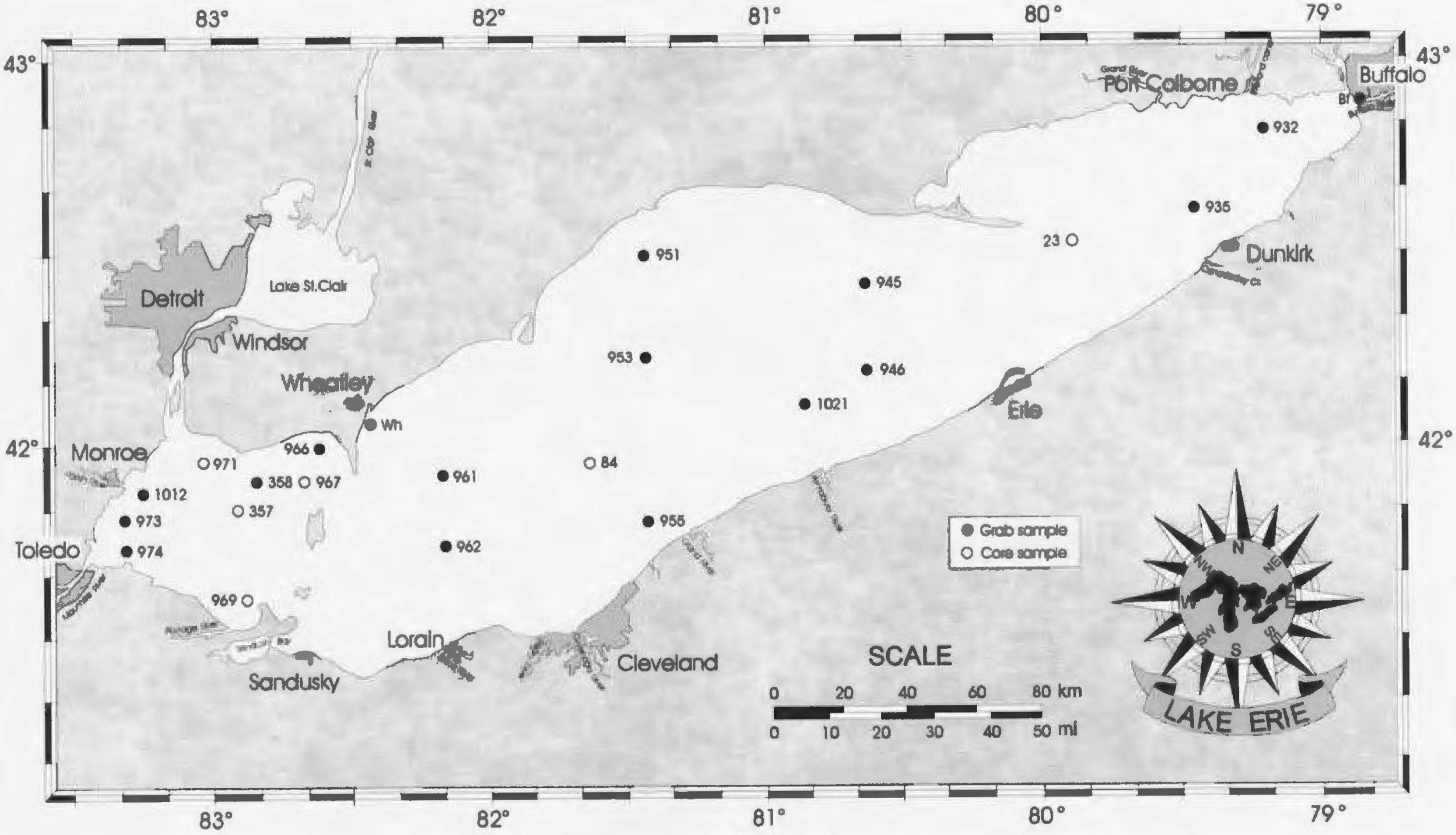

83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Wh
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
951
945
953
946
1021
84
955
961
962
966
971
358
967
357
1012
973
974
969
932
935
23
Grab sample
Core sample
SCALE
0
20
40
60
80 km
0
10
20
30
40
50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Table 3.1.1 Locations and types of samples collected during the summer of 1994 expedition of R/V Limnos and utilized in the study. Two horizons selected for further analysis from each core sample are shown in the last column.

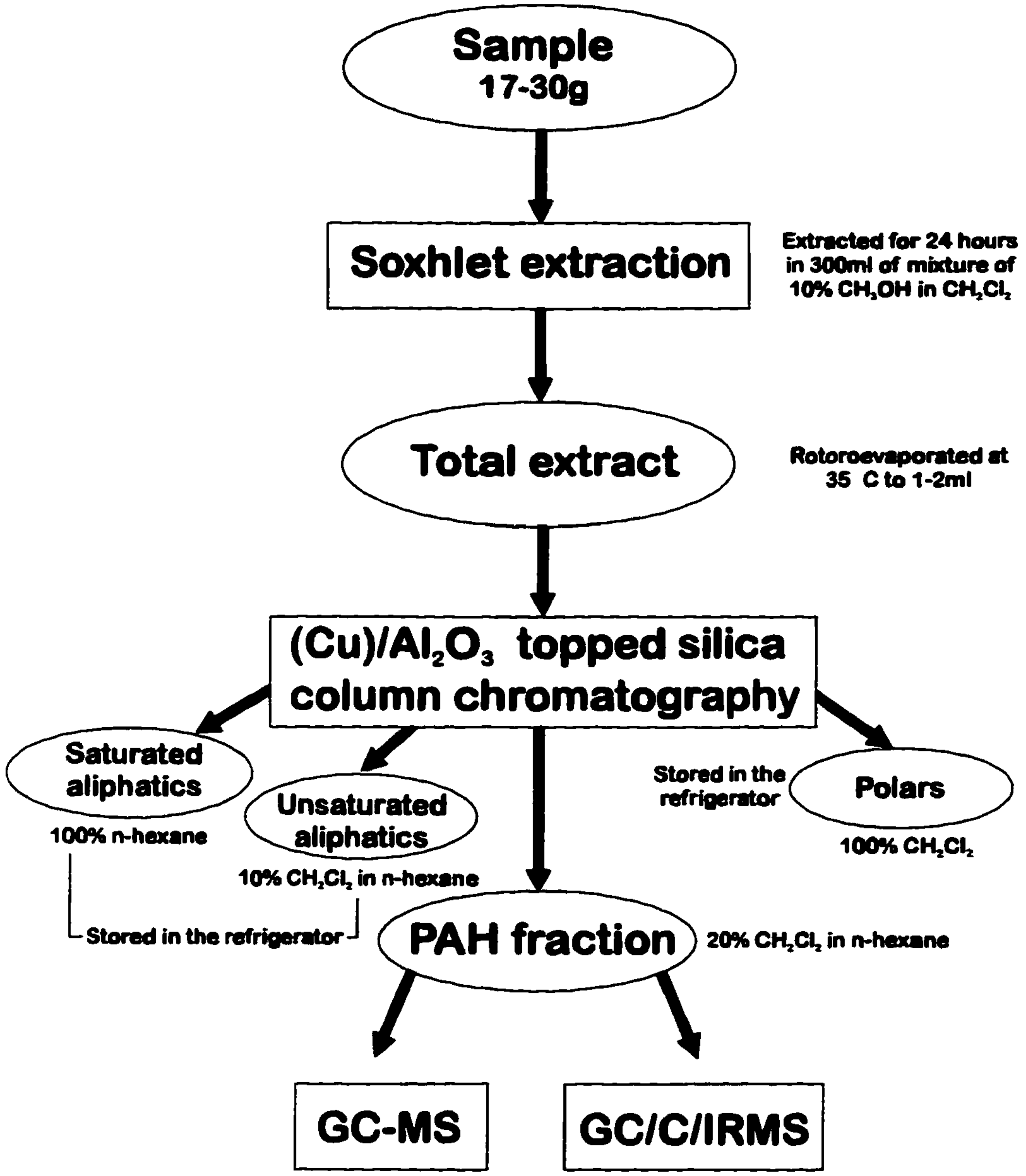
Station	Latitude, N.	Longitude, W.	Type of sample	Horizon (cm)
23	42^0 30’ 10”	79^0 53’ 14”	core	0-2; 24-26
84	41^0 56’ 06”	81^0 39’ 15”	core	0-2; 28-30
357	41^0 49’ 40”	82^0 58’ 35”	core	0-2; 28-30
967	41^0 53’ 32”	82^0 39’ 55”	core	0-2; 22-24
969	41^0 36’ 31”	82^0 55’ 30”	core	0-2; 26-28
971	41^0 56’ 58”	83^0 02’ 58”	core	0-2; 24-26
358	41^0 53’ 53”	82^0 51’ 47”	grab	-
932	42^0 47’ 32”	79^0 12’ 29”	grab	-
935	42^0 35’ 30”	79^0 28’ 01”	grab	-
945	42^0 24’ 00”	80^0 38’ 30”	grab	-
946	42^0 10’ 01”	80^0 38’ 15”	grab	-
951	42^0 28’ 32”	81^0 26’ 27”	grab	-
953	42^0 12’ 30”	81^0 26’ 30”	grab	-
955	41^0 48’ 03”	81^0 26’ 30”	grab	-
961	41^0 54’ 30”	82^0 11’ 00”	grab	-
962	41^0 43’ 04”	82^0 11’ 00”	grab	-
966	41^0 58’ 57”	82^0 37’ 31”	grab	-
973	41^0 47’ 25”	83^0 20’ 00”	grab	-
974	41^0 43’ 32”	83^0 20’ 00”	grab	-
1021	42^0 04’ 27”	80^0 51’ 58”	grab	-
1012	$41^0$52’ 48”	83^0 16’ 30”	grab	-
Wheatley (Wh)	42^0 04’ 01”	82^0 27’ 00”	grab	-
Buffalo (Bf)	-	-	grab	-

Cleveland and Bf at Buffalo. The latter station was located directly in the mouth of the Buffalo River. In addition, a few sites close to harbors and/or small river mouths considered as potential sources of PAH contamination were sampled. These are stations 1012, 974, 1021 and Wh. Immediately upon sampling, the collected material was stored on dry ice for transport to the laboratory.

In laboratory, the samples were prepared for further analytical procedures in a way that would prevent compounds from deteriorating and allow for maximum extraction of organic matter. The core samples were subsampled at 2 cm intervals. Only top and bottom samples were used for further analyses (see Table 3.1.1). To avoid potential photodegradation of PAH, the samples were dried in a darkened fumehood. The dry sediments were further homogenized using mortar and pestle to break clumps, wrapped in aluminum foil and stored at room temperature for subsequent analyses. All materials were solvent-rinsed prior to the procedures.

Extraction: The first step in the analysis of PAH in environmental samples is extraction of the lipid portion of organic matter (Fig. 3.1.2). No standard technique exists for this procedure. However, Soxhlet extraction was shown to yield sufficient recovery of PAH provided appropriate solvents, sediment:solvent ratios and sample sizes are utilized (*e.g.*, Farrington and Tripp, 1975; Lake *et al.*, 1980; Grimalt *et al.*, 1984). Therefore, this widely applied reference technique was adopted in the present study. The procedures closely followed those outlined by O'Malley (1994). However, to further increase the extraction efficiency slight modifications were introduced.

Figure 3.1.2 Extraction and purification procedure adopted in the study. (Modified from O'Malley, 1994 and Stark, 1997.)


Sample
17-30g
Soxhlet extraction
Extracted for 24 hours in 300ml of mixture of 10% CH_3OH in CH_2Cl_2
Total extract
Rotoroevaporated at 35 C to 1-2ml
(Cu)/Al_2O_3 topped silica column chromatography
Saturated aliphatics
100% n-hexane
Unsaturated aliphatics
10% CH_2Cl_2 in n-hexane
Stored in the refrigerator
Stored in the refrigerator
Polars
100% CH_2Cl_2
PAH fraction
20% CH_2Cl_2 in n-hexane
GC-MS
GC/C/IRMS

It was shown that the right choice of solvent and sediment to solvent ratio are important for favorable recovery results (Farrington and Tripp, 1975; Grimalt *et al.*, 1984; Ehrhardt *et al.*, 1991). The increased polarity of solvent usually results in more exhaustive recoveries. Therefore, the polarity of solvent was increased as compared to that used by O'Malley (1994). The latter was achieved by adding 10% of methanol to the pure dichloromethane employed in the previous study. In addition, the amount of solvent was doubled as increased sample weights (17-30g) were utilized. This allowed the appropriate sediment:solvent ratio to be maintained at a level similar to that reported by O'Malley (1994).

The previously prepared samples were placed in precleaned cellulose thimbles and Soxhlet extracted using 300 ml of solvent in a darkened fumehood. The extraction time was 24 hours with a rate of 3 cycles per hour. The extracts were further concentrated to 1-2 ml using a rotary evaporator at 35^0C then dried to constant weight under a stream of nitrogen. Samples were stored in a freezer prior to the following class separation procedure.

Class separation: This procedure involves separation of the fraction that contains PAH from the total extracts (Fig. 3.1.2). Silica column chromatography has been found to provide satisfactory separation of PAH (*e.g.*, Youngblood and Blumer, 1975; Giger and Schaffner, 1978). However, it was shown that certain modifications can further improve the results of purification (O'Malley, 1994; Stark, 1997). A higher degree of hydrocarbon isolation in this study was achieved through combining alumina and silica columns and the separation of the extracts by increased number of fractions.

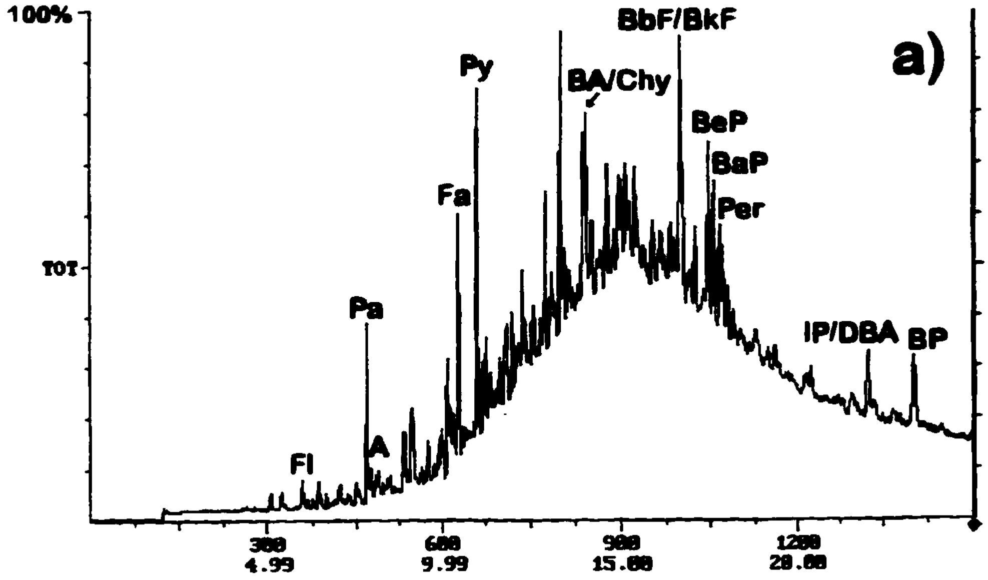
It was demonstrated by O'Malley (1994) that alumina can successfully remove the lipid-stable pigments present in sample extracts. Hence, a combination of alumina and silica columns was adopted in the study. Silica gel columns were prepared by adding 50 ml of dichloromethane to 10 grams of silica powder (Aldrich 100-200 mesh) and subsequent adding the slurry to a column (1cm diameter by 30 cm long) containing 1cm of acid washed sand as a bottom plug. The column was topped with 1cm of 7.5% deactivated alumina. To remove elemental sulfur contained in the extracts, 1cm of freshly prepared activated copper was added to the top of the column. The prepared column was purified by eluting 50 ml of dichloromethane followed by 50 ml of hexane. The extracts were dissolved in 1ml of hexane before chromatography.

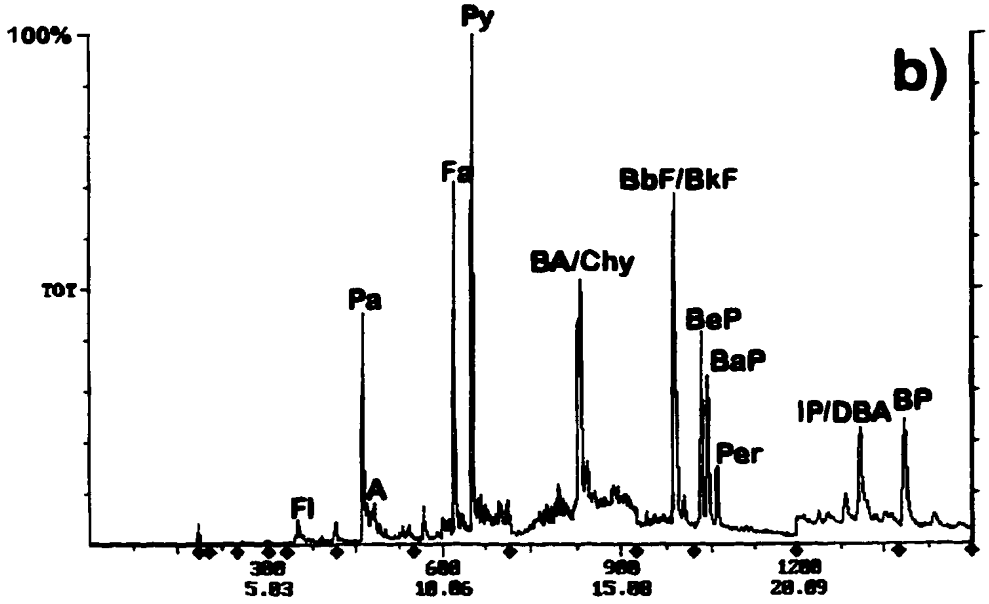
Commonly, hydrocarbons are separated into two fractions: aliphatic hydrocarbons eluted with hexane and aromatic hydrocarbons collected with 1:1 hexane:dichloromethane mixture (*e.g.*, O'Malley, 1994; Minh, 1995; Bieger, 1994). This, however, results in high abundance of unresolved complex mixture (UCM) attributed to multi-branched compounds. The mixture later creates high background noise in chromatograms and impedes peak resolution for compounds of interest. It was shown (Stark, 1997) that the purity of PAH fraction can be increased by removal of a large portion of UCM together with unsaturated aliphatic fraction. This was achieved by separation of the extract into four fractions: 1) saturated aliphatics eluted with 40 ml of hexane, 2) the unsaturated aliphatic fraction eluted with 30 ml of 1:9 dichloromethane:hexane mixture, 3) the PAH fraction collected with 30 ml of 2:8 dichloromethatne:hexane mixture, and 4) polars eluted with 30 ml of dichloromethane (Fig. 3.1.2). The obtained fractions were rotary evaporated at 35^{0}C, dried under a stream of nitrogen and stored in a freezer at -20^{0}C until further analyses.

3.1.2 INSTRUMENTAL ANALYSES

Instrumental analyses commonly start with identification of the compounds of interest present in an environmental sample. The gas chromatography-mass spectrometry (GC-MS) analysis allows different compounds to be identified on the basis of their respective retention times and mass spectra. The next task is quantification of individual PAH. The different processes of PAH degradation result in two major problems for studies of these organic compounds. The first difficulty is the high UCM appearing in chromatograms (Fig. 3.1.3a). This signal interferes with the compounds of interest and thus impedes proper quantification of individual PAH. The problem can partially be solved by applying gas chromatography-tandem mass spectrometry (GC-MS-MS), the technique that allows the background interference to be virtually eliminated (*e.g.*, Schachterle *et al.*, 1994). The second major problem caused by the decomposition processes is obliteration of the PAH assemblage. Preferential removal of certain compounds results in alteration of the assemblage and makes the identification of original sources difficult (*e.g.*, Wakeham et al., 1980). An independent set of data bearing the isotopic signature of initial sources and not subjected to such alterations could help solve

Figure 3.1.3 **(a)** The total ion chromatogram for station 971 (Detroit) with detected PAH, 100%=3 264 359. Note the high background noise created by the presence of UCM in sample. **(b)** The selected ion (MS-MS) chromatogram for the same station, 100%=2 262 144. Note the reduced noise and enhanced peak resolution resulting from this analysis.


100%
TOT
a)
BbF/BkF
Py
BA/Chy
BeP
BaP
Fa
Per
Pa
IP/DBA
BP
A
Fl
300
4.99
600
9.99
900
15.00
1200
20.00


100%
TOT
Py
b)
Fa
BbF/BkF
BA/Chy
Pa
BeP
BaP
IP/DBA
BP
Per
A
Fl
300
5.03
600
10.06
900
15.08
1200
20.09

this problem. Ratios of the two stable isotopes of carbon, ^{13}C and ^{12}C, have been repeatedly shown characteristic of primary and secondary PAH sources (Freeman, 1991; Abrajano *et al.*, 1993; O'Malley *et al.*, 1994; O'Malley *et al.*, 1996). The isotopic signatures of individual compounds are also found less affected by the decomposition processes (*e.g.*, O'Malley *et al.*, 1994; O'Malley, 1994). Therefore, to avoid the above problems and obtain reliable results for further interpretation, the identification of PAH with GC-MS was followed by their quantification with GC-MS-MS and a compound specific carbon isotope analysis (CSIA).

Identification (GC-MS): Individual compounds were identified using a Varian GC/MS Saturn-4 system. The instrument was equipped with a DB-5 capillary column (30 m x 0.25 mm I.D., 0.25 µm film thickness), with helium as the carrier gas (flow: 1mL/min). All injections were done in the splitless mode. The best chromatographic peak resolution was achieved with the injection of 0.5 µL of sample solution. Dried extracts were dissolved in hexane the volume of which varied from 50 to 3000 µL depending on concentrations of compounds in samples. The following temperature regime was chosen to perform the chromatographic separation. The oven temperature program started at 50°C for 0.1 min, and increased to 150°C at 50°C/min. It was further increased to 280°C at 10°C/min, where it remained for 29.9 min. The total run time amounted to 45.1 min. The injector temperature was held at 80°C for 0.1 min, with a subsequent increase to 280°C at 180°C/min where it remained for 43.1 min. Mass spectral data were acquired in the electron impact mode (70eV), scanning the ion range of m/z = 60 to 290 atomic mass units (a.m.u.) every second. Individual PAH were identified by comparison of retention times with the PAH calibration standards and of mass spectral fragmentation patterns with literature data (NIST-92 library).

Quantification (GC-MS-MS): Tandem mass spectrometry (MS-MS) is the most selective and sensitive technique which allows the background due to complex matrix to be significantly reduced by excluding all ions except the parent ion (Fig. 3.1.3b). The latter can further be dissociated to produce a unique product ion mass spectrum (Johnson and Yost, 1985). A detailed description of the technique can be found elsewhere (*e.g.*, Schachterle *et al.*, 1994). The MS-MS spectra for individual PAH was obtained using the same system as in previous analysis with analogous temperature program. An MS-MS software was utilized to create and insert intermediate segments between ionization and mass analysis steps. Calibration curves for the linear range from 1ng/µL to 10ng/µL (4 points on each) were plotted using external standards for 16 PAH listed as priority pollutants. Individual compounds were quantified on the basis of the calibration curves. In addition, concentrations of two other compounds Benzo(e)pyrene and Perylene, which can potentially be useful for source apportionment (*e.g.*, Yunker and MacDonald, 1995), were identified. Since standards for these PAH were not available, the concentrations were calculated relative to that of Benzo(a)pyrene. All values were initially obtained in ng/µL of solution and subsequently recalculated into ng/g of dry sediment assuming 100% recovery. The detection limits of the technique was previously tested by other researchers (*e.g.*, Schachterle *et al.*, 1994) and found to be as low as 0.5 ng/g.

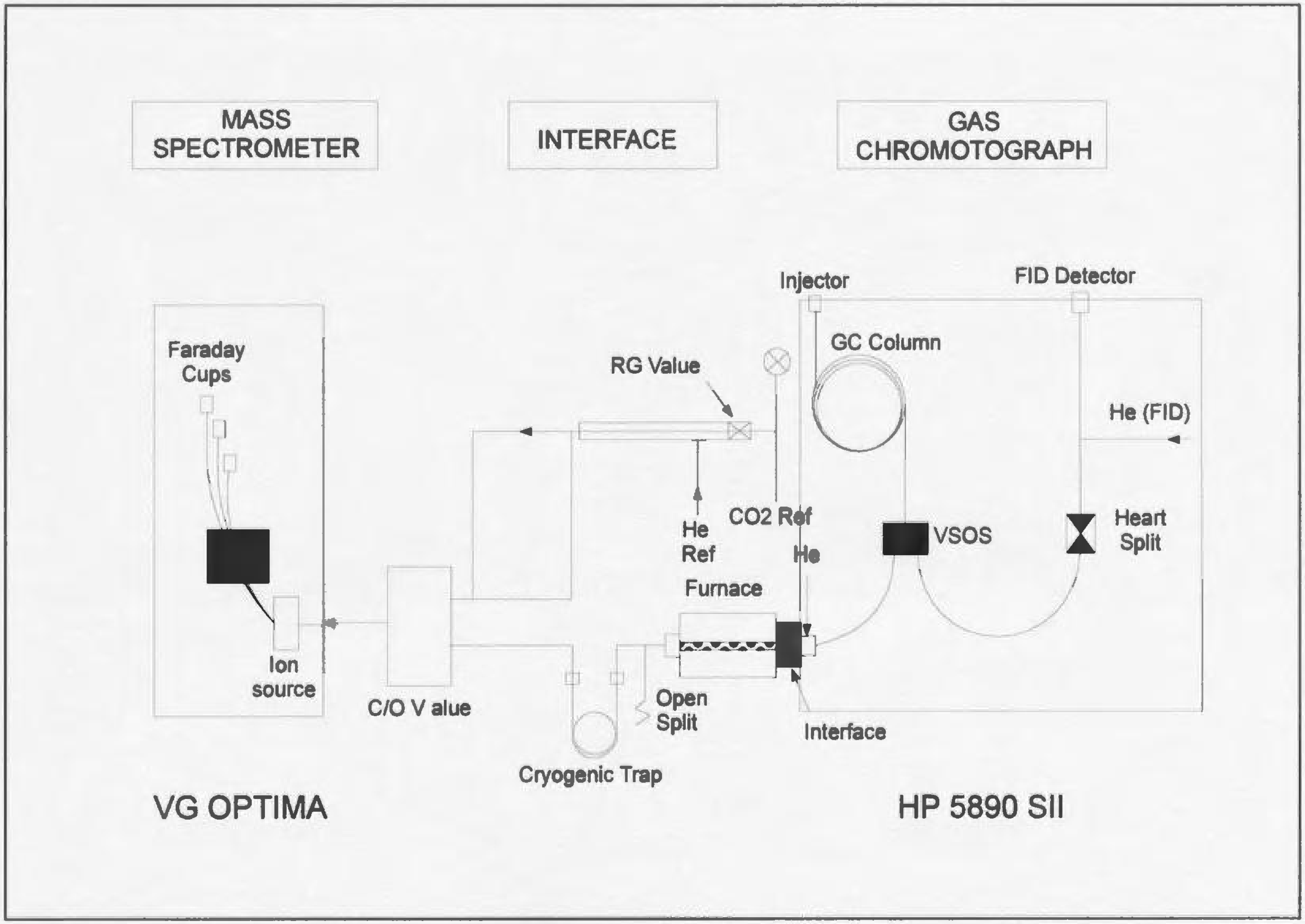
Isotopic composition (GC/C/IRMS): A CSIA was performed with a Hewlett Packard 5890 gas chromatograph coupled via a combustion interface and cryogenic trap to a VG Optima isotopic ratio mass spectrometer (GC/C/IRMS) (Figure 3.1.4). The design and specifications of the VG Isochorm Series II system and the application of the technique is discussed in detail by Freedman *et al.* (1988), O'Malley *et al.* (1994), and O'Malley (1994). The gas chromatograph was equipped with a DB-5 column (60m x 0.25mm I.D., film thickness 0.25 μm). The temperature regime used in the previous analysis was modified to improve separation of peaks for better CSIA measurements and is given in Table 3.1.2. The carbon isotopic values are reported in the conventional delta $\delta^{13}C$ notation:

$$\delta^{13}C\ (‰\ ) = 1000(R_S/R_{PDB} - 1),$$

where R represents the ratio $^{13}C/^{12}C$ in sample (S) and standard Pee Dee Belemnite (PDB). The precision of the measurements generated by the machine was previously studied by O'Malley et al. (1994) and O'Malley (1994) and was found not to exceed 0.3‰. with isotopic values accurate to within 0.6 ‰. To ensure the performance and to monitor the reliability of background corrections, all samples were spiked with three compounds of previously known isotopic composition. Acenaphthylene, not detected in samples, and two aliphatic hydrocarbon compounds (C_{25} and C_{30}) were chosen as the internal standards for CSIA.

Upon completing the instrumental analyses the problem of using different types of samples arose. The grab samples in both data sets were represented by a single value

Figure 3.1.4 Configuration of Isochrom Series II (GC-C-IRMS) at Biogeochemistry Laboratory in the Department of Earth Sciences of Memorial University of Newfoundland. Abbreviations are as follows: C/O = Change over valve; RG = Reference gas valve; He = Helium gas; VSOS = Variable split open split; FID = Flame ionization detector. (After O'Malley, 1994.)



MASS SPECTROMETER
INTERFACE
GAS CHROMOTOGRAPH
Injector
FID Detector
Faraday Cups
GC Column
RG Value
He (FID)
He Ref
CO2 Ref
He
VSOS
Heart Split
Furnace
Ion source
C/O V alue
Open Split
Interface
Cryogenic Trap
VG OPTIMA
HP 5890 SII

Table 3. 1. 2 Gas chromatographic conditions applied in the GC-C-IRMS analysis.

Segment	Temperature, ^{0}C	Rate, ^{0}C/min	Time, min	Total time, min
1	35	0.0	1.00	1.00
2	150	20.0	5.75	6.75
3	150	0.0	1.00	7.75
4	280	6.0	21.70	29.45
5	280	0.0	30.00	59.45

obtained for homogeneous mixture of upper 15-20 cm of sediments. Values for top and bottom samples were available for each core. As the number of grab samples was 3 times as large and because the length of cores did not exceed 30 cm, a single value for concentrations and isotopic compositions for cores were obtained by averaging the respective top and bottom values.

3.2 DATA ANALYSIS

Two data sets, one for molecular and one for isotopic composition, were obtained from instrumental analyses. The molecular and isotopic data matrices contained 16 and 15 variables respectively measured at 23 sites (Appendices A1, A2) distributed across the lake with an area of 25,700 km^2 and multiple potential PAH sources. Further data analysis was performed in three major steps. The first step was to understand the major patterns of spatial distribution within each data set and to determine the relative contribution of different sources. These procedures employed one or two variables at a time. The second step was to generalize the information within each data set looking at a few variables simultaneously. This procedure would allow to get a better insight into the previously determined spatial trends and relative importance of various sources. The final step was to bring together the two data sets in a single analysis the results of which would further serve as the starting point for the final discussion. To solve the latter two problems, some of the methods of multivariate statistics were employed.

3.2.1 UNI- AND BIVARIATE METHODS

The first step involving uni- and bivariate methods was itself split into two parts. The first part was to identify the major patterns of spatial distribution while the second was primarily concerned with identification of potential sources forming the PAH assemblage in sediments.

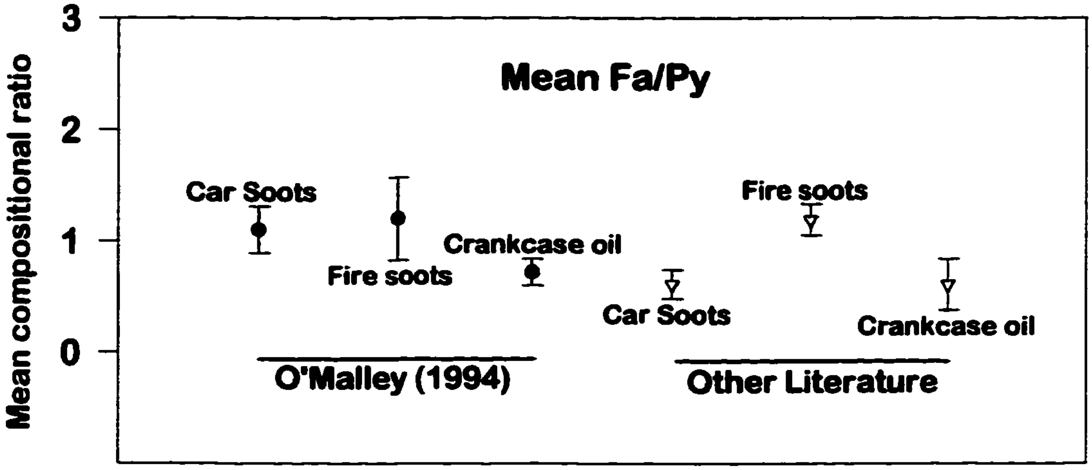
Spatial distribution: In order to understand the trends in spatial distribution of molecular and isotopic data, maximum information had to be compiled within a single graph. The shape of the lake, namely the relationships between its length and width (4:1), suggested a solution for this problem. The stations were projected on the longest lengthwise axis connecting the mouths of the Maumee River in the south-west and the Buffalo River in the north-east. The whole data set was then plotted against this axis as a single set of graphs. Analogous procedure was performed for both molecular and isotopic composition.

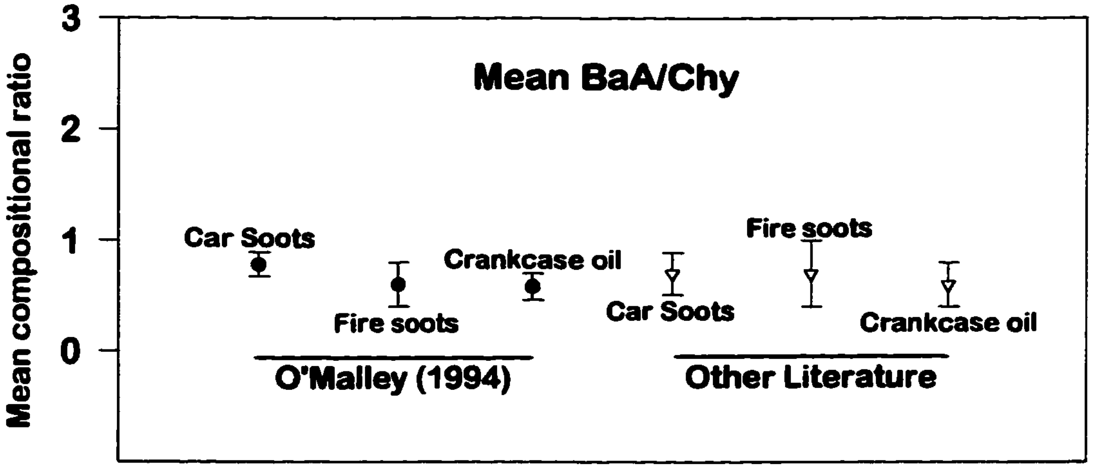
Source identification: The Isotope Biogeochemistry group at Memorial has pioneered the combined use of molecular and isotopic signatures for tracing or source apportioning PAH in sediments (*e.g.*, O'Malley *et al.*, 1996). The approach involves the definition of the molecular and isotopic "signatures" or characteristics of potential sources of PAH, and comparing these to the same signatures found in sediments. The first step in the source identification procedure was to choose appropriate data for prominent primary and secondary sources in the area of study. For the present work, molecular and isotopic compositions of potential contributors to the PAH inventory of

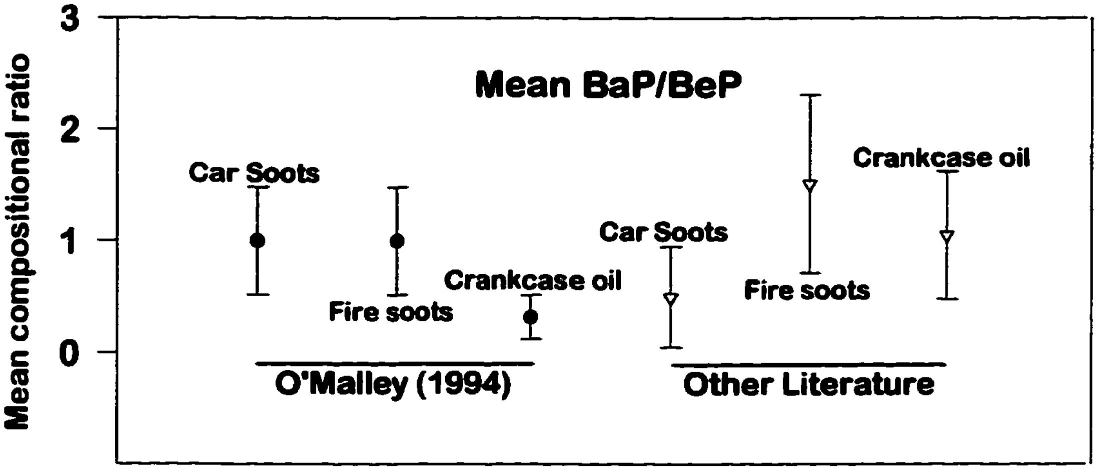
Lake Erie were derived from those previously reported by O'Malley (1994) and Stark *et al.* (1995), respectively.

A set of molecular signatures for various primary (car soots, fire soots, crankcase oil) and secondary (open road sweeps, roadside snow, city sewage) sources was analyzed by O'Malley (1994; Appendix A3). Most of the source samples were collected from eastern Canada (primarily St. John's, Newfoundland), although the resulting molecular signatures defined by O'Malley (1994) compare very favorably to those reported by other authors from other areas of North America and elsewhere (*e.g.*, DeAngelis *et al.*, 1980; Rudling *et al.*, 1982; Stenburg, 1983; Grimmer *et al.*, 1983; Alsberg *et al.*, 1985; Masclet *et al.*, 1986; Westerholm *et al.*, 1988; Broman *et al.*, 1988; Freeman and Cattell, 1990; Takada *et al.*, 1990). Ratios for normalized concentrations of prominent 4- and 5- ring compounds show that almost all samples obtained for St. John's lie within a range of one standard deviation from those compiled from other literature sources (Fig. 3.2.1). The only observed inconsistency is exhibited by the Fa/Py ratio for car soots. This disparity is not really surprising because the range and concentration of PAH that accumulates in a car muffler are known to be dependent on car age, engine operating conditions, catalytic converter efficiency and general driving conditions (Pedersen *et. al.*, 1980; Stenberg, 1983; Rogge *et. al.*, 1993). It was previously shown, for example, that old cars without a catalytic converters are likely to contribute more PAH to the environment (*e.g.*, Rogge *et al.*, 1993). The majority of cars sampled by O'Malley were old (O'Malley, 1994), and thus are probably more appropriate for the environmental study. Overall, the molecular

Figure 3.2.1 Mean and range (± standard deviation) of the compositional ratios of selected PAH in car soots, fire soots and crankcase oil identified and compared to literature data by O'Malley. (After O'Malley, 1994.)


Mean Fa/Py
Mean compositional ratio
3
2
1
0
Car Soots
Fire soots
Crankcase oil
Fire soots
Car Soots
Crankcase oil
O'Malley (1994)
Other Literature


Mean BaA/Chy
Mean compositional ratio
3
2
1
0
Car Soots
Fire soots
Crankcase oil
Fire soots
Car Soots
Crankcase oil
O'Malley (1994)
Other Literature


Mean BaP/BeP
Mean compositional ratio
3
2
1
0
Car Soots
Fire soots
Crankcase oil
Crankcase oil
Car Soots
Fire soots
O'Malley (1994)
Other Literature

signatures (expressed primarily as isomer ratios) used in the present work are consistent with what other authors have used for molecular source apportionment (*e.g.*, Wakeham *et al.*, 1980).

Stark *et al.* (1995) have determined isotopic signatures for car soots, fire soots, crankcase oil and open road sweeps at different sites of the lower Great Lakes region (around Lake Ontario and along a portion of the St. Lawrence River). Three distinct environments, large urban areas (*e.g.*, Toronto and Montreal), large industrial areas (*e.g.*, Hamilton and Cornwall), and residential municipalities or small towns (*e.g.*, Niagara and St. Leonard, Ontario), were sampled. Source samples from the different locations were found very similar in their isotopic composition with standard deviations varying from 0.1‰ (for BA/Chy in fire soots) to 0.8 ‰ (for Py in car soots; Appendix A4). The low site-to-site variability of isotopic values in a region directly adjacent to the study area may well be fortuitous, although it vastly simplified the use of the source data for source identification and apportionment.

Finally, both molecular and isotopic signatures of sources in the above studies were obtained using techniques and equipment similar to those utilized in the present work. Sample preparation procedures (extraction and class separation) adopted for this research closely followed those employed by O'Malley (1994) and Stark *et al.* (1995). Identification and quantification of individual PAH in both cases was performed using a GC/MS system with similar chromatographic conditions (O'Malley, 1994; Section 3.1). Determination of PAH isotopic composition in this study and in Stark *et al.* (1995)

utilized the same instrument (Isochrom Series II) and similar temperature programs, types of injection and internal standards (see Section 3.1).

Thus, the use of data from O'Malley (1994) and Stark *et al.* (1995) as the source end members in further analyses seems justified by their general agreement with other literature values, the proximity of sampled region to the study area and the close similarity of analytical procedures. The molecular and isotopic signatures of the crankcase oil sample (the only petroleum source with available isotopic composition) was used as the representative of petroleum-related sources throughout the study. In addition, the estimate of total (wet and dry) atmospheric deposition of PAH in the Lake Erie region (Eisenreich and Strachan, 1992) was employed as one of the secondary sources (Appendix A3).

A number of techniques were utilized to estimate the relative importance of different sources in the formation of the PAH assemblage. These included direct comparison with the source signatures as well as some more quantitative methods which allowed percentage contribution of important primary sources to be determined.

It has repeatedly been demonstrated (*e.g.*, O'Malley, 1994; Stark *et al.*, 1995; Yunker and MacDonald, 1995) that the relative abundance of kinetic and thermodynamic isomers estimated as their ratio can be indicative of the relative importance of combustion vs. petroleum sources (Appendix A5). Similarly, Py/Per ratio was shown to serve as an indicator of anthropogenic vs. natural diagenetic origin of the PAH assemblage (Wakeham *et al.*, 1980; Lipiatou and Saliot, 1992; see also Appendix A5). Four most commonly used ratios (Fa/Py, BbF/BeP, BaP/BeP, Py/Per) were computed and plotted along the longest axis of the lake in the manner previously described for the analysis of spatial distribution. The computed values were further compared to those characteristic of primary and secondary sources.

Direct comparison of sample data with the characteristic isotopic ratios for petroleum and combustion sources can also yield valuable information on the relative importance of these PAH contributors (O'Malley, 1994; Stark *et al.*, 1995). Seven compounds with available source ranges (Pa, Fa, Py, Chy, BbF, BeP, BaP) were plotted along the lake axis. Fluctuations of their isotopic values along the lake were further analyzed.

Two methods previously suggested in literature on PAH chemistry (O'Malley, 1994; O'Malley *et al.*, 1996) were used to provide quantitative apportionment of different PAH sources. Only the more stable 4- and 5- ring compounds were utilized for these analyses. The concentrations were normalized to the total sum of 4- and 5-ring PAH in order to bring them to a common scale with those reported for primary and secondary sources.

The first method allows for the apportionment of petroleum and combustion sources on the basis of the isotopic composition of a sample. It is based on a simple two-component model which allows the relative contribution percentages of the two major primary sources to be estimated. The major assumption of the model is that only two sources contribute to the formation of an individual PAH. The procedure is described in detail in Appendix A6.

Source contributions of PAH can be more accurately assessed if in addition to isotopic abundance the molecular abundance of each compound from each primary source or end-member is included in mixing equation (Vollmer, 1976; Langmuir *et al.*, 1978; O'Malley, 1994; O'Malley *et al.*, 1996). A similar procedure can be performed for the characteristic molecular ratios. The method of generating mixing curves from molecular and isotopic data is described in Appendix A7. The samples from respective data sets were plotted on mixing curves generated for various permutations of molecular and isotopic ratios. The position of sites with respect to the curves and end members allowed the relative contribution of different combustion and petroleum sources to be estimated. This analysis was also suggestive of whether any other sources different from those under consideration were responsible for the formation of the PAH assemblage in samples.

3.2.2 MULTIVARIATE METHODS

Three major problems had to be solved on the way to generalization of the two data sets. The first problem was the selection of an appropriate number of variables which would enable further statistical procedures to be meaningful. The second problem was further reduction of this number for generalization purposes. The third and final objective was bringing the two data sets together by grouping cases with similar properties. These three problems where solved twice: 1) for analysis of spatial distribution and 2) for source apportionment.

Selecting variables: It was demonstrated that to overcome the problem of dimensionality in multivariate statistics the ratio of number of cases to number of variables should not exceed three (Howarth and Sinding-Larsen, 1983). Thus, for a data set consisting of 23 cases no more than 7 variables can be utilized at a time. Therefore the first problem was selection of 7 variables for each data set which would represent the whole PAH assemblage in further analyses. Although different approaches to variable selection were used, a precaution was always taken to keep compounds with different molecular weights more or less equally represented.

One of the approaches to variable selection is analysis of the correlation matrix for the data set and excluding one of two highly correlated variables (*e.g.*, Vajnovsky and Malinin, 1992). This approach was accepted for the data on molecular composition. The significance of correlations within the molecular data set is represented by Figure 3.2.2 (see also Appendix A8). This figure shows that most of the variables are highly correlated. The seven least correlated variables (Ae, Fl, Fa, BbF, Per, DBA, BP) were chosen for further statistical analyses.

A similar analysis of the correlation matrix for isotopic composition data (Appendix A9) showed much lower significance levels (Fig. 3.2.3). This implied that in this case most variables could not be predicted from each other. However, since determination of δ^{13}C in many cases was impeded by low signal to noise ratio or low concentrations, the data set contains numerous cases with missing values (Appendix A2). Therefore, the

Figure 3.2.2 Contour plot of significance of correlations for concentrations of 16 individual PAH identified in the sediment samples from Lake Erie.

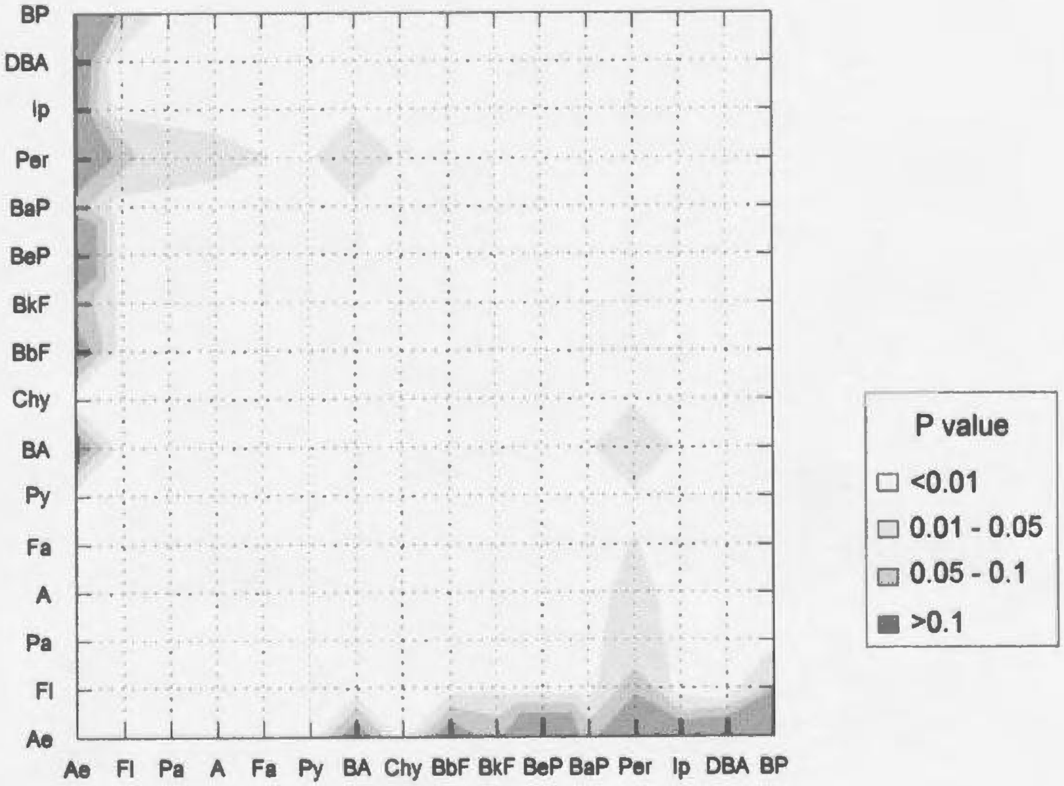
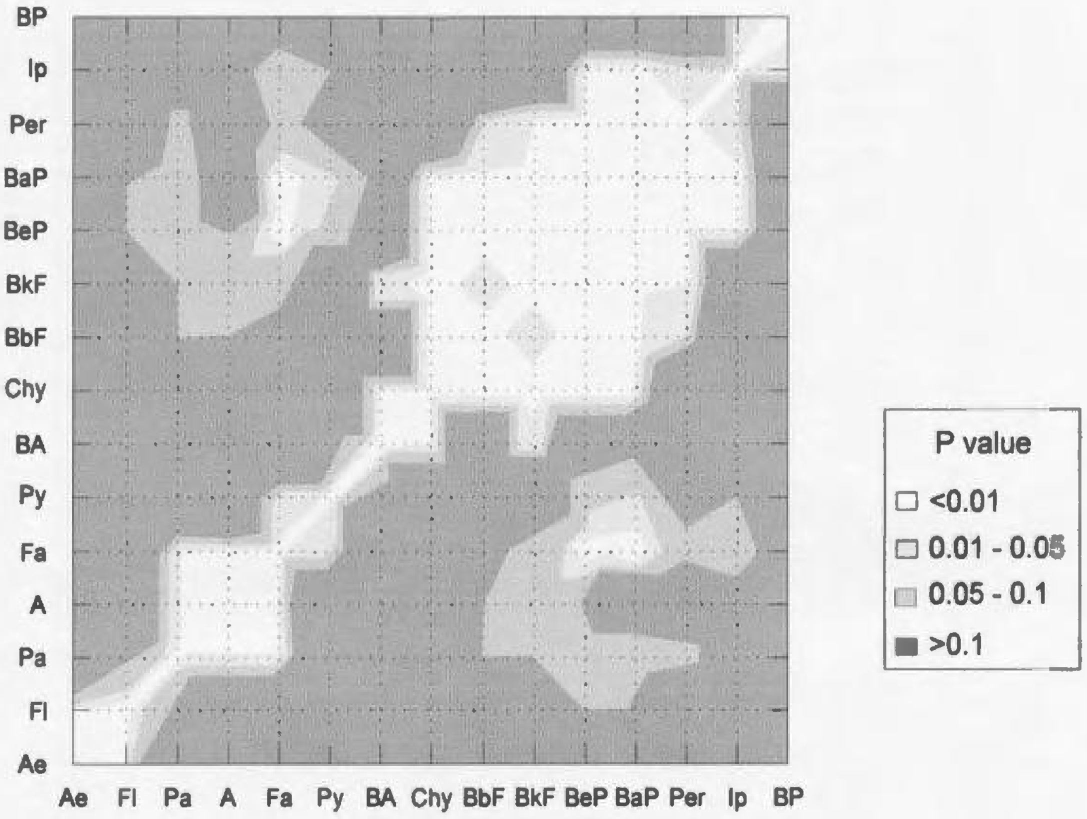

BP
DBA
Ip
Per
BaP
BeP
BkF
BbF
Chy
BA
Py
Fa
A
Pa
Fl
Ae
Ae
Fl
Pa
A
Fa
Py
BA
Chy
BbF
BkF
BeP
BaP
Per
Ip
DBA
BP
P value
☐ <0.01
☐ 0.01 - 0.05
▨ 0.05 - 0.1
■ >0.1

Figure 3.2.3 Contour plot of significance of correlations for $\delta^{13}C$ values of 15 individual PAH identified in the sediment samples from Lake Erie.


BP
Ip
Per
BaP
BeP
BkF
BbF
Chy
BA
Py
Fa
A
Pa
Fl
Ae
Ae Fl Pa A Fa Py BA Chy BbF BkF BeP BaP Per Ip BP
P value
☐ <0.01
▨ 0.01 - 0.05
▨ 0.05 - 0.1
■ >0.1

seven variables with fewer missing values were chosen for further consideration (Pa, Fa, Py, Chy, BbF, BeP, Per).

The problem of variable selection was solved differently for source identification purposes. It was shown that more stable 4- and 5-ring compounds are more suitable for this purpose than less stable 2-, 3-ring PAH (O'Malley, 1994). Among those, only compounds for which data on primary and secondary sources were available could be chosen for analyses.

Further, seven compounds with wide range of molecular weights were chosen for source identification from the molecular composition data set as indicative of relative importance of petroleum and combustion sources. In order to allow direct comparison with primary and secondary sources, concentrations of all compounds were brought to a common scale by normalizing them to their total sum (Appendix A3).

A simple solution was found for the data set for isotopic composition. Since a single source ratio was available for some isomers (*e.g.*, BA/Chy, BbF/BkF, BeP/BaP), the isotopic values of these compounds were weighted according to their relative abundance and the weighted average was used for further statistical analyses. This additional limitation brought the available number of variables down to five. All of the remaining compounds were retained for source identification procedures.

Reducing the number of variables (Principal Components Analysis): After the initial number of variables was reduced by selection, the legal statistical procedures became possible. The next major objective was further reduction of the number of variables without significant loss of information. One of the best methods designed for this purpose is the method of Principal Components Analysis (PCA). This method has repeatedly been employed in organic chemistry (*e.g.*, Brown and Maher, 1992; Korzhov *et al.*, 1995; Yunker *et al.*, 1995; Yunker and MacDonald, 1995). The procedure allows the highest percentage of variance in samples to be concentrated on two/three first principal components (PCs). These components can further be interpreted according to the weights of variables. The classic algorithm of PCA (*e.g.*, Davis, 1973; Vajnovsky and Malinin, 1992) performed in the Multivariate Statistics Module of Statgraphics 2.6 (Statistical Graphics Corp., 1987) was employed in the study. No rotation method was applied. Three first PCs were retained for further interpretation and analyses in each case. Although in some cases this somewhat exceeded the recommended Kaiser (1960) criteria, each time the number was chosen on the basis of the actual meaning of PCs and was designed to prevent possible loss of information. Although similar procedures were performed twice, for spatial distribution and source identification the results of two outputs should be viewed differently.

The first analysis was designed to yield information on relative position of stations on the components and thus to allow the similarities and differences in molecular and isotopic composition of PAH at differentially located sites to be better understood. It is clear that normalization procedure results in variations in concentration of one compound only due to change in the abundance of another. To avoid this negative influence, the actual concentration data were used in the PCA analysis for spatial distribution. This analysis also employed a greater number of variables which represented a wider range of molecular weights.

Conversely, the PCA for source identification was designed to demonstrate the position of sites with respect to the major primary and secondary sources. In this procedure, a number of available sources was statistically treated together with samples. The comparison with sources required normalization of the original concentration data and consequently, the results reflect only relative importance of different compounds in samples, with the influence of their absolute loading eliminated. Only more stable 4-, 5-ring compounds were retained for this procedure. In addition, the selection of variables was limited by data available for the sources. All the above resulted in somewhat different meaning of components in this case.

Grouping: The problem of grouping was essential for the study. This problem was substantiated by the vast spatial scale on which sampling was performed and utilization of two different data sets. Simple averaging could not suffice in this case as the stations were dispersed over an area of 25,700 km^2 with many potential PAH sources. Finally, the ultimate problem was to bring the two data sets together for discussion purposes. The method of Cluster Analysis (CA) allows different objects to be grouped on the basis of similar properties (*e.g.*, Davis, 1973; Vajnovsky and Malinin, 1992). This method has successfully been employed in organic chemistry (*e.g.*,Weiss *et al.*, 1994). Therefore, the cluster analysis was further utilized for grouping samples and sources with similar molecular and isotopic composition.

Clustering of principle components as non-correlated variables was strongly recommended (*e.g.*, Roux, 1991; Vajnovsky and Malinin, 1992). Two major classes of clustering exist: the hierahicial or linkage methods which produce a tree diagram and the non-hierarchical splitting or partitioning technique which results in separation of the sample cloud into non overlapping clusters. In an extensive comparison study performed by Willett (1987) the latter was found to yield results comparable with or superior to the former. Its application has been strongly recommended for analysis of chemical databases (Willett, 1987). The non-hierarchical methods are especially useful when heterogeneous data sets are analyzed and maximizing between-cluster relative to within-cluster variations is the task (Systat, Inc., 1992). Following these ideas, the principal components obtained from the previous analyses and weighted according to the percentage of total variance explained within each data set were further clustered using a non-hierarchical K-means procedure to maximize between-cluster variation. The STATISTICA 5.1 Cluster Analysis Module was used for the analyses (StatSoft, Inc., 1995). Euclidean distances were utilized as the distance measure to account for the weighting procedure.

Although similar procedures were performed twice for the analysis of spatial distribution and source identification, a different number of clusters was used. The first CA combined principal components from the spatial distribution analysis. Three clusters were ordered in this case. The choice was suggested by the examination of the univariate graphs from the previous step. The fewer cluster option also facilitated the final description. The second cluster analysis joined the results of PCA designed for source identification. More detailed description was required in this case to understand how the sources cluster with samples. Therefore for this procedure the number of clusters was doubled.

4. RESULTS

4.1 SPATIAL DISTRIBUTION

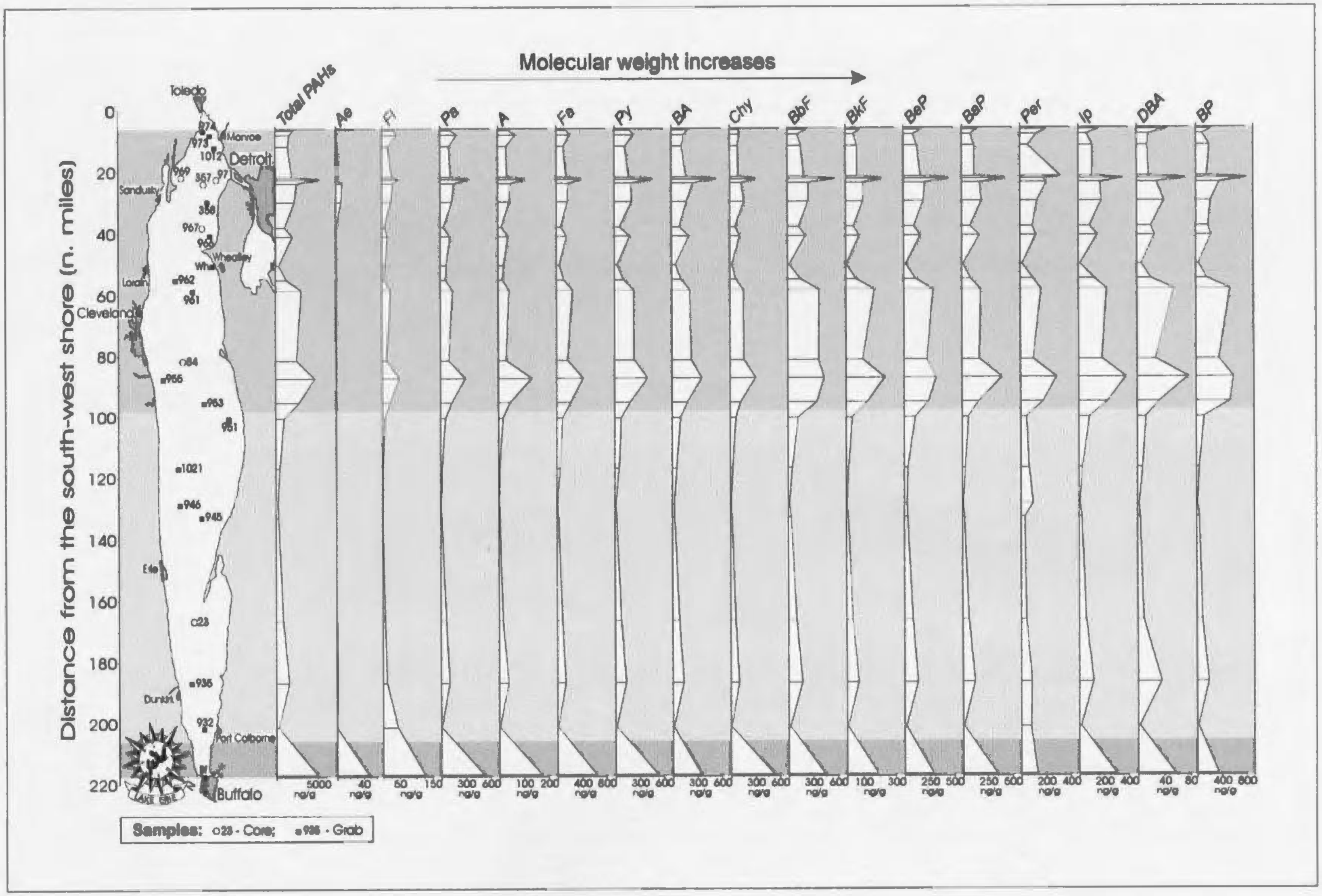
4.1.1 MOLECULAR COMPOSTION

4.1.1.1 Concentration profiles

All raw data on the molecular composition of compounds are presented in Appendix A1. A general idea of the spatial distribution of PAH in lake sediments and the relationships between different compounds can be obtained through consideration of their profiles plotted against the longest lengthwise axis of the lake (Fig. 4.1.1). The plotting procedure is explained in detail in the chapter dealing with methods (Section 3.2.1). Total concentrations of PAH (TPAH) vary substantially across the lake (224-5304 ng/g). A similar, highly variable pattern is shown by the individual compounds. The concentration profiles can be subdivided into three distinct zones on the basis of spatial distribution of different level PAH contamination: the western zone, the central-eastern zone, and the Buffalo zone.

The western zone: The western zone includes stations in the Western and western part of the Central Basin (974, 973, 1012, 969, 971, 357, 358, 967, 966, Wh, 962, 961, 84, 955, 953). Although concentrations are highly variable within this zone, it is generally characterized by high total PAH levels (avg. 2365 ng/g). The highest total concentrations are observed at stations 971(at the mouth of the Detroit River; 5304 ng/g) and 955 (off Cleveland; 4709 ng/g). Most individual compounds peak at the same

Figure 4.1.1 Concentrations of 16 parental PAH identified in sediment samples from Lake Erie. Vertical scale represents distance (nautical miles) from the south-west shore measured along the longest axis (from Toledo to Buffalo). The shading pattern is as follows: medium gray = western zone; light gray = central-eastern zone; dark gray = Buffalo zone.


Molecular weight increases
Distance from the south-west shore (n. miles)
0
20
40
60
80
100
120
140
160
180
200
220
Toledo
974
975
Monroe
1012
Detroit
969
357
971
Sandusky
358
967
960
Wheatley
Wha
Lorain
962
961
Cleveland
84
956
963
951
1021
946
945
Erie
23
935
Dunkirk
932
Port Colborne
Buffalo
Lake Erie
Total PAHs
Ae
Fl
Pa
A
Fa
Py
BA
Chy
BbF
BkF
BeP
BaP
Per
Ip
DBA
BP
5000 ng/g
40 ng/g
60 150 ng/g
300 600 ng/g
100 200 ng/g
400 800 ng/g
300 600 ng/g
300 600 ng/g
300 600 ng/g
300 600 ng/g
100 300 ng/g
250 500 ng/g
250 500 ng/g
200 400 ng/g
200 400 ng/g
40 80 ng/g
400 800 ng/g
Samples: ○23 - Core; ▪935 - Grab

stations. Higher molecular weight compounds (over 202) seem to be predominant throughout the zone.

The central-eastern zone: This zone includes stations 951, 1021, 946, 945, 23, 935, and 932 located in the Central and Eastern Basins. The zone is generally characterized by low levels of PAH pollution, average total concentration 682 ng/g. However, significant variability is observed throughout the zone with total concentrations ranging from 224 to 1583 ng/g.

The Buffalo zone: The Buffalo zone includes a single station located in the mouth of the Buffalo River. The sample is characterized by extremely high total PAH concentration (4979 ng/g). Low molecular weight compounds (Ae, Fl, Pa, and A) play an important role in the PAH assemblage demonstrating the highest concentration levels within the lake.

In summary, three major zones are seen across the lake. The western zone and the Buffalo zone have higher PAH concentrations as compared to the central-eastern zone. The stations closest to the three major cities, Detroit, Cleveland and Buffalo showed the highest concentrations. The PAH assemblage at Detroit and Cleveland seems to be dominated by 4-, 5- and 6-ring compounds while predominantly 3- and 4- ring PAH are observed at Buffalo.

4.1.1.2 PCA for molecular composition (spatial distribution)

A principal components analysis performed on compounds characterized by various molecular weights (Ae, Fl, Fa, BbF, Per, DBA, BP) can offer a deeper insight into the relationships between different sites across the lake (Appendix B1; for more information on the procedure see Section 3.2.2). The three first components accounted for 95.8% of total variance in samples and were chosen for further analyses and interpretation.

The first component explained 67.8% of total variance (Fig. 4.1.2). All variables are represented by positive and approximately equal weights. This component is deemed to represent total PAH contamination in the lake sediments. The interpretation is confirmed by high correlation ($r=0.99$; $p<0.001$) of this component with total PAH concentration (Fig. 4.1.3a). Stations at Buffalo, Cleveland, and Detroit lie within the range of extreme positive values demonstrating very high total PAH contamination (Fig 4.1.4a). At the opposite end of the spectrum, the lowest levels of contamination are observed at stations 951, 1021, 946, Wh, 945, 23 and 932, with PC 1 values < -1.5. The rest of the stations are distributed between these two end-member groups.

The second component explains 20.2% of total variance. This component represents the opposition between lower (Ae, Fl, Fa) and higher (BbF, Per, DBA, BP) molecular weight compounds (Fig. 4.1.2). The interpretation is confirmed by high correlation of this component with the difference between sums of concentrations of the higher and lower molecular weight compounds (Fig. 4.1.3b). Stations off Detroit (971) and Cleveland (955) significantly differ in their position on the second component from the Buffalo station (Fig. 4.1.4b). This difference shows that lighter compounds (Ae, Fl, Fa) are important in the PAH assemblage at Buffalo while assemblages recovered off Detroit and Cleveland are entirely dominated by heavy (over 228) compounds. All other stations

Figure 4.1.2 Weights of variables (compounds) in 3 first PCs extracted by PCA utilizing the concentrations of 7 selected PAH (Ae, Fl, Fa, BbF, Per, DBA, BP). Three first PCs explained 95.8% of total variance in samples.

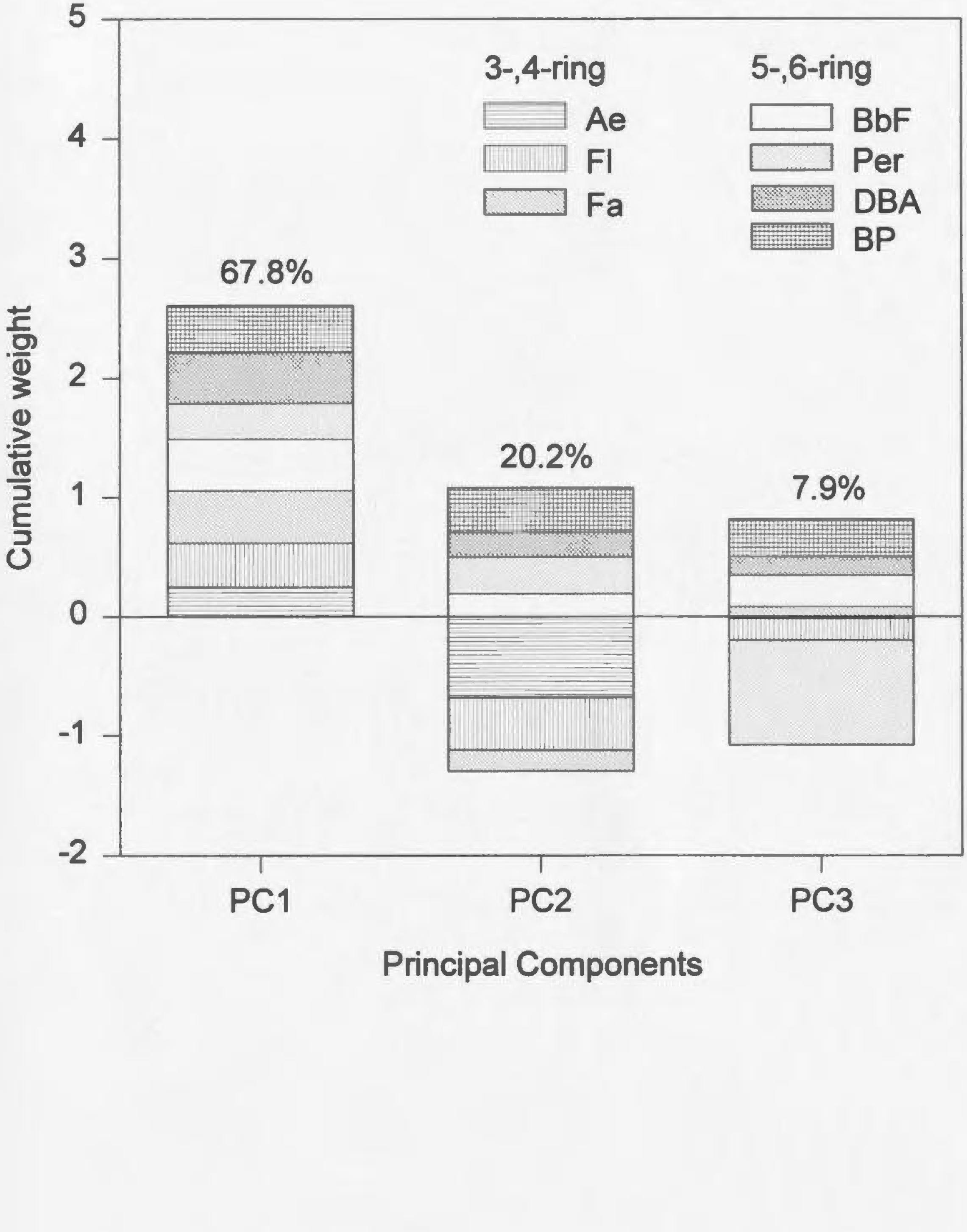

5
4
3
2
1
0
-1
-2
Cumulative weight
3-,4-ring
Ae
Fl
Fa
5-,6-ring
BbF
Per
DBA
BP
67.8%
20.2%
7.9%
PC1
PC2
PC3
Principal Components

Figure 4.1.3 Regression of three first PCs on the parameters they are deemed to represent: **(a)** 1st PC vs. total PAH concentration of 7 selected compounds (Ae, Fl, Fa, BbF, Per, DBA, BP); **(b)** 2nd PC vs. the difference between total concentrations of lower (Ae, Fl, Fa) and higher (BbF, Per, DBA, BP) molecular weight compounds; **(c)** 3rd PC vs. concentration of Per. Correlation coefficients and significance levels are also shown.

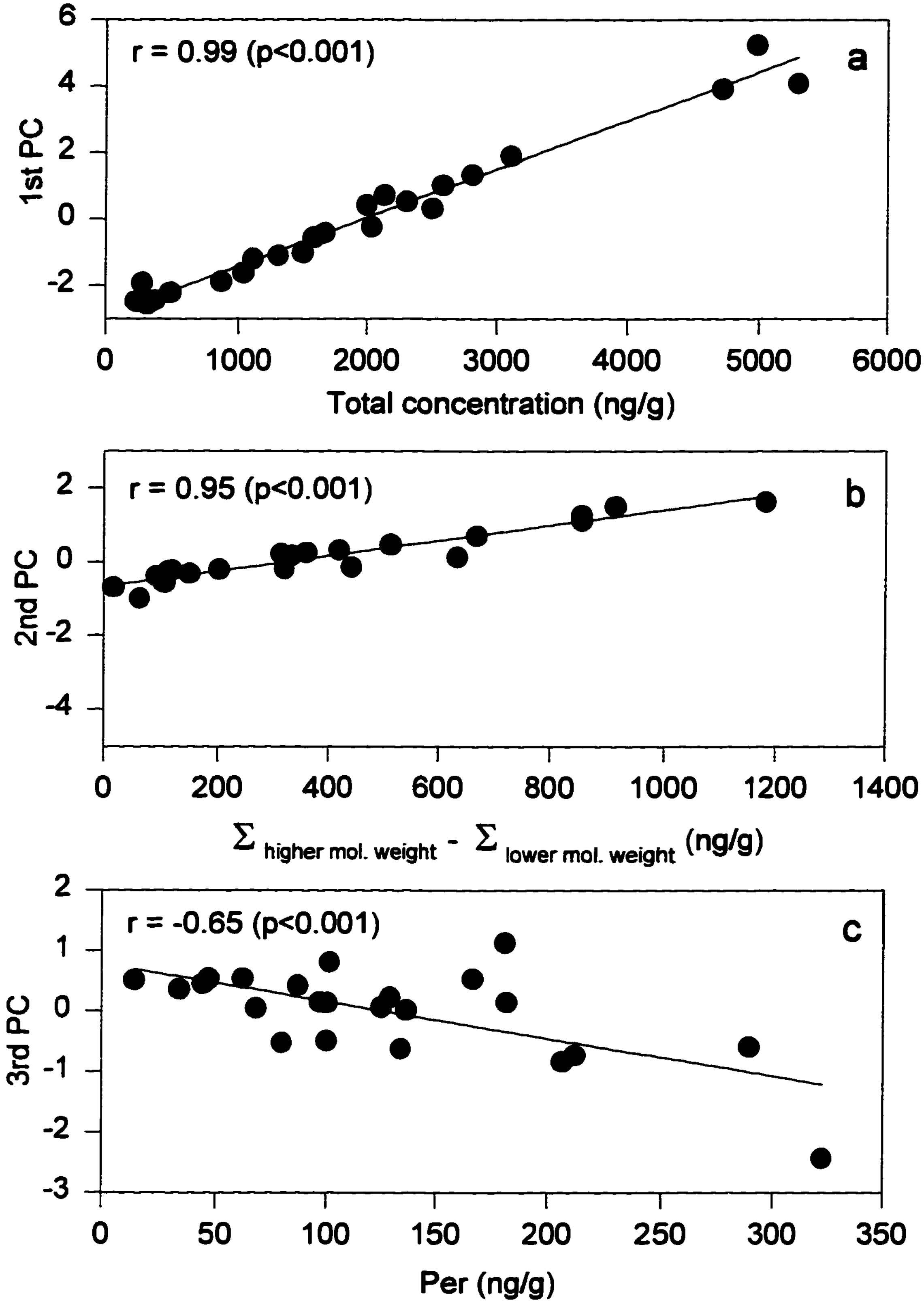
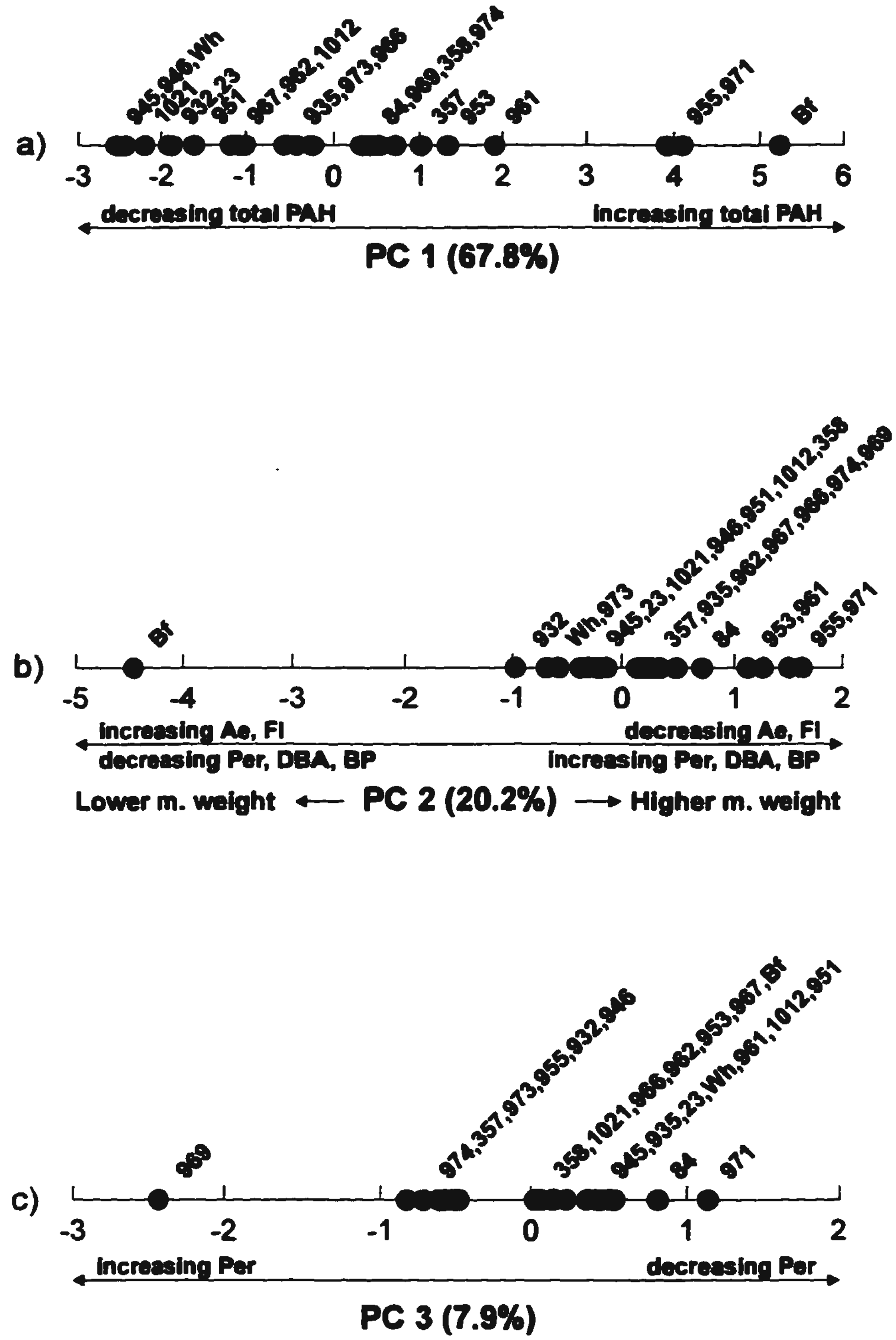

r = 0.99 (p<0.001)
a
1st PC
6
4
2
0
-2
0
1000
2000
3000
4000
5000
6000
Total concentration (ng/g)
r = 0.95 (p<0.001)
b
2nd PC
2
0
-2
-4
0
200
400
600
800
1000
1200
1400
Σ higher mol. weight - Σ lower mol. weight (ng/g)
r = -0.65 (p<0.001)
c
3rd PC
2
1
0
-1
-2
-3
0
50
100
150
200
250
300
350
Per (ng/g)

Figure 4.1.4 Distribution of samples along **(a)** 1st PC, **(b)** 2nd PC and **(c)** 3rd PC identified by PCA utilizing concentrations of 7 selected compounds (Ae, Fl, Fa, BbF, Per, DBA, BP). Three first PCs explained 95.8% of total variance in samples.


a)
945,946,Wh
1021
932,23
951
967,962,1012
935,973,986
84,969,358,974
357
953
961
955,971
Bf
-3
-2
-1
0
1
2
3
4
5
6
decreasing total PAH
increasing total PAH
PC 1 (67.8%)
b)
Bf
932
Wh,973
945,23,1021,946,951,1012,358
357,935,962,967,986,974,969
84
953,961
955,971
-5
-4
-3
-2
-1
0
1
2
increasing Ae, Fl
decreasing Ae, Fl
decreasing Per, DBA, BP
increasing Per, DBA, BP
Lower m. weight ← PC 2 (20.2%) → Higher m. weight
c)
969
974,357,973,955,932,946
358,1021,986,962,953,967,Bf
945,935,23,Wh,961,1012,951
84
971
-3
-2
-1
0
1
2
increasing Per
decreasing Per
PC 3 (7.9%)

demonstrate the relationship between lower and higher molecular weight compounds similar to that of Detroit and Cleveland, station 932 closest to Buffalo.

The third component accounts for 7.9% of total variance in samples and is characterized by a very high negative contribution (77%) of Per (Fig 4.1.2). This component is deemed to mainly represent this compound (Fig 4.1.3c). The contribution of Per is generally low across the lake. However, station 969 is shifted towards extreme negative values which indicates importance of the compound at this station.

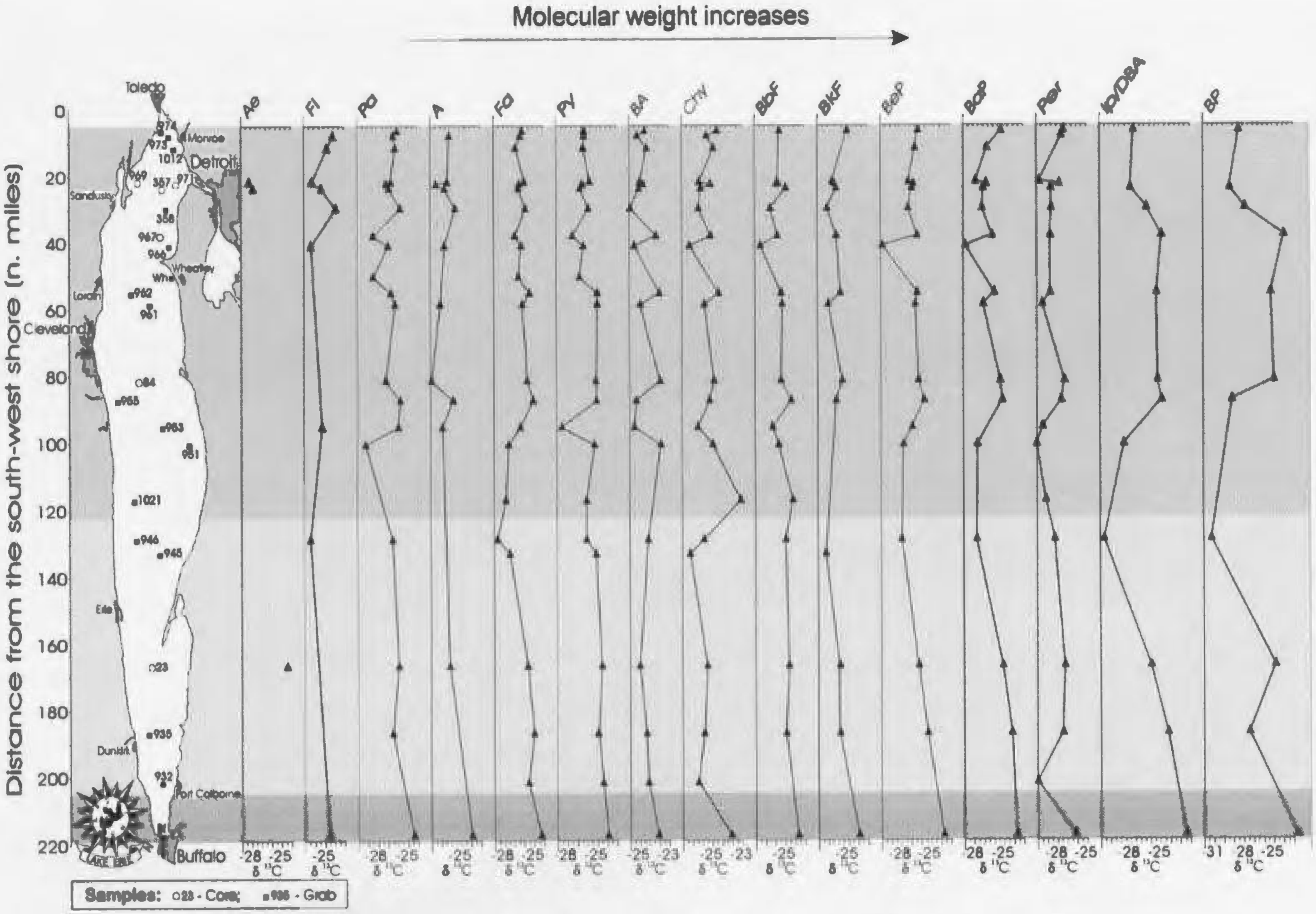
These statistical considerations can be summarized as follows. Stations 971, 955 and Buffalo are characterized by extremely high relative concentrations of PAH in sediments as indicated by the 1st PC. This is consistent with the conclusion previously made from the concentration profiles. Stations located in the northern part of the Central and Eastern Basins showed the lowest levels of contamination. The nature of PAH contamination at Buffalo is very different from that at Detroit and Cleveland, with lighter compounds being of greater importance. All stations demonstrate relationship between higher and lower molecular weight compounds similar to that of Detroit and Cleveland. Station 969 is characterized by a very high concentration of Per.

4.1.2 ISOTOPIC COMPOSITION

4.1.2.1 Isotopic profiles

The original data on isotopic composition of individual compounds can be found in Appendix A2. As in the case with molecular composition, a spatial distribution pattern can be obtained through viewing lengthwise isotopic profiles (Fig. 4.1.5). The isotopic

Figure 4.1.5 Isotopic composition ($\delta^{13}C$) of 15 parental PAH identified in sediment samples from Lake Erie. Vertical scale represents distance (nautical miles) from the south-west shore measured along the longest axis (from Toledo to Buffalo). The shading pattern is as follows: medium gray = western zone; light gray = central-eastern zone; dark gray = Buffalo zone.



Molecular weight increases
Ae
Fl
Pa
A
Fa
Py
BA
Chy
BbF
BkF
BeP
BaP
Per
Ip/DBA
BP
Distance from the south-west shore (n. miles)
0
20
40
60
80
100
120
140
160
180
200
220
Toledo
Monroe
Detroit
Sandusky
Wheatley
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
LAKE ERIE
974
973
1012
969
357
971
358
967
966
Whe
962
961
84
955
953
951
1021
946
945
23
935
932
-28 -25
δ 13C
-25
-23
-31
Samples: ○23 - Core; ■935 - Grab

ratios of different compounds have a large range (from -29.7‰ to -22.1‰). The profiles can be split into three zones that are similar to those found for molecular composition in their size and distribution along the lake (Fig. 4.1.1).

The western zone: This zone is the largest and includes stations from the Western Basin and the western part of the Central Basin (974, 973, 1012, 969, 971, 357, 358, 967, 966, Wh, 962, 961, 84, 955, 953, 951, 1021). It is characterized by a very high degree of variability between samples (from -29.7‰ to -22.1‰). Station 971 at Detroit exhibits average isotopic values for individual compounds (from -27.7‰ to -24.6‰). The other major city within this zone, Cleveland, shows slightly heavier $\delta^{13}C$ values varying from -27.5‰ (Pa) to -24.3‰ (BbF). However, this difference is within the reproducibility range.

The central-eastern zone: The central-eastern zone includes the two easternmost stations from the Central Basin (946 and 945) and almost all stations, from the Eastern Basin (23, 935, and 932). This zone shows somewhat lower variability (from -30‰ for Per to -24.4‰ for BA) and is generally marked by depleted in ^{13}C compounds.

The Buffalo zone: This zone is represented by a single station at Buffalo (Bf) and characterized by very heavy isotopic values for all compounds (from -26.2‰ for Per to -23.1‰ for BA and Chy). The extreme enrichment of all compounds makes this station unique on the lake scale.

To summarize, the three-zone pattern previously found for molecular composition, which is based on TPAH concentrations, can also be distinguished in isotopic profiles.

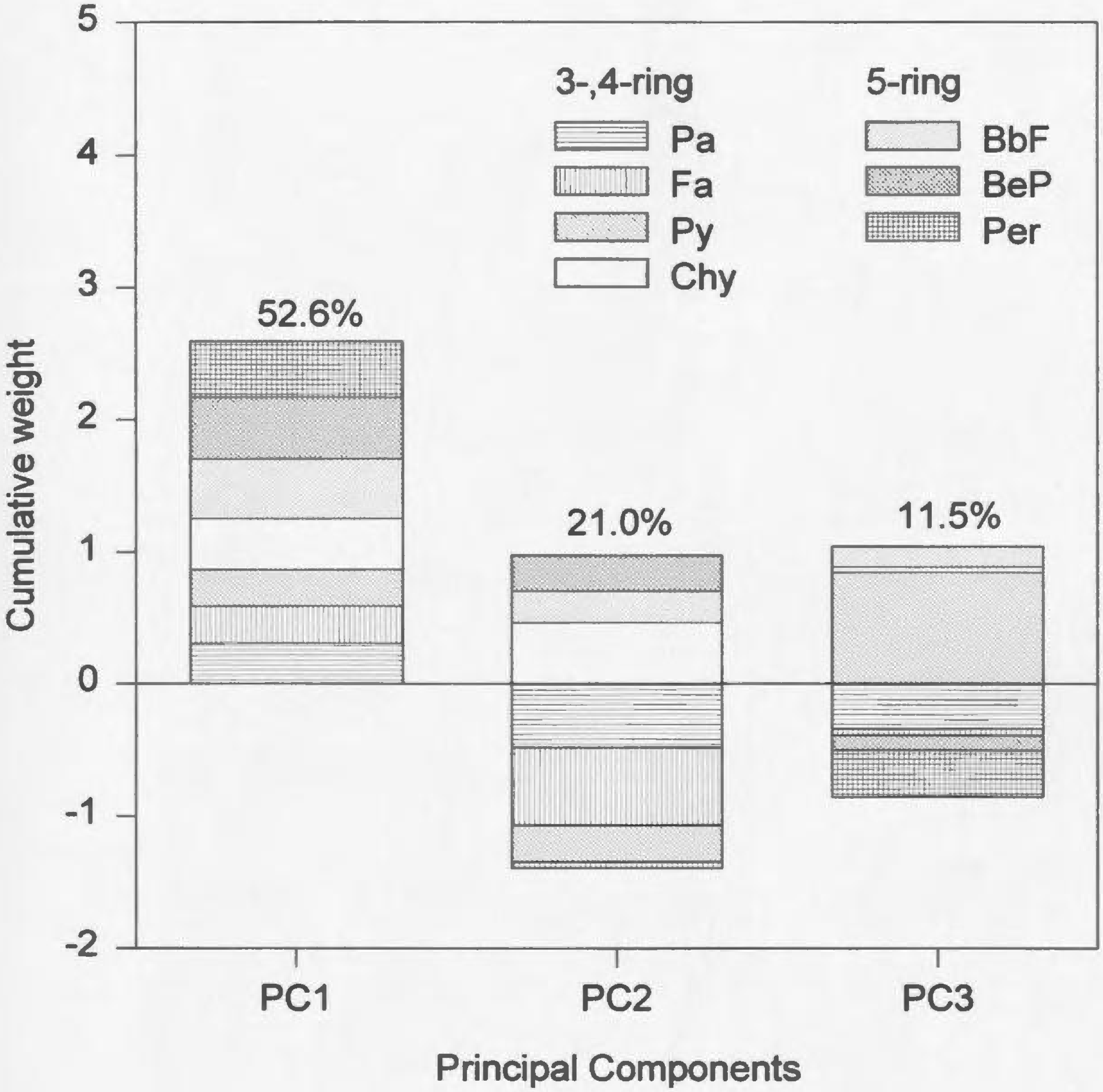
The western zone is characterized by the highest variability in isotopic values. The central-eastern zone generally exhibits ^{13}C depleted compounds. Conversely, the Buffalo zone shows extreme isotopic enrichment for all compounds. The signal at Detroit is characterized by the lightest isotopic values among the cities.

4.1.2.2 PCA for isotopic composition (spatial distribution)

Following the procedures performed for molecular composition, multivariate statistics was again employed in an attempt to statistically generalize the isotopic data (Appendix B2). The approach to this procedure is explained in detail in the chapter devoted to methods (Section 3.2.2). In a principal components analysis performed on 7 selected compounds with fewer missing values (Pa, Fa, Py, Chy, BbF, BeP, Per), the three first PCs explained 85.1% of total variance in samples. The three first components were further given interpretation based on respective variable weights.

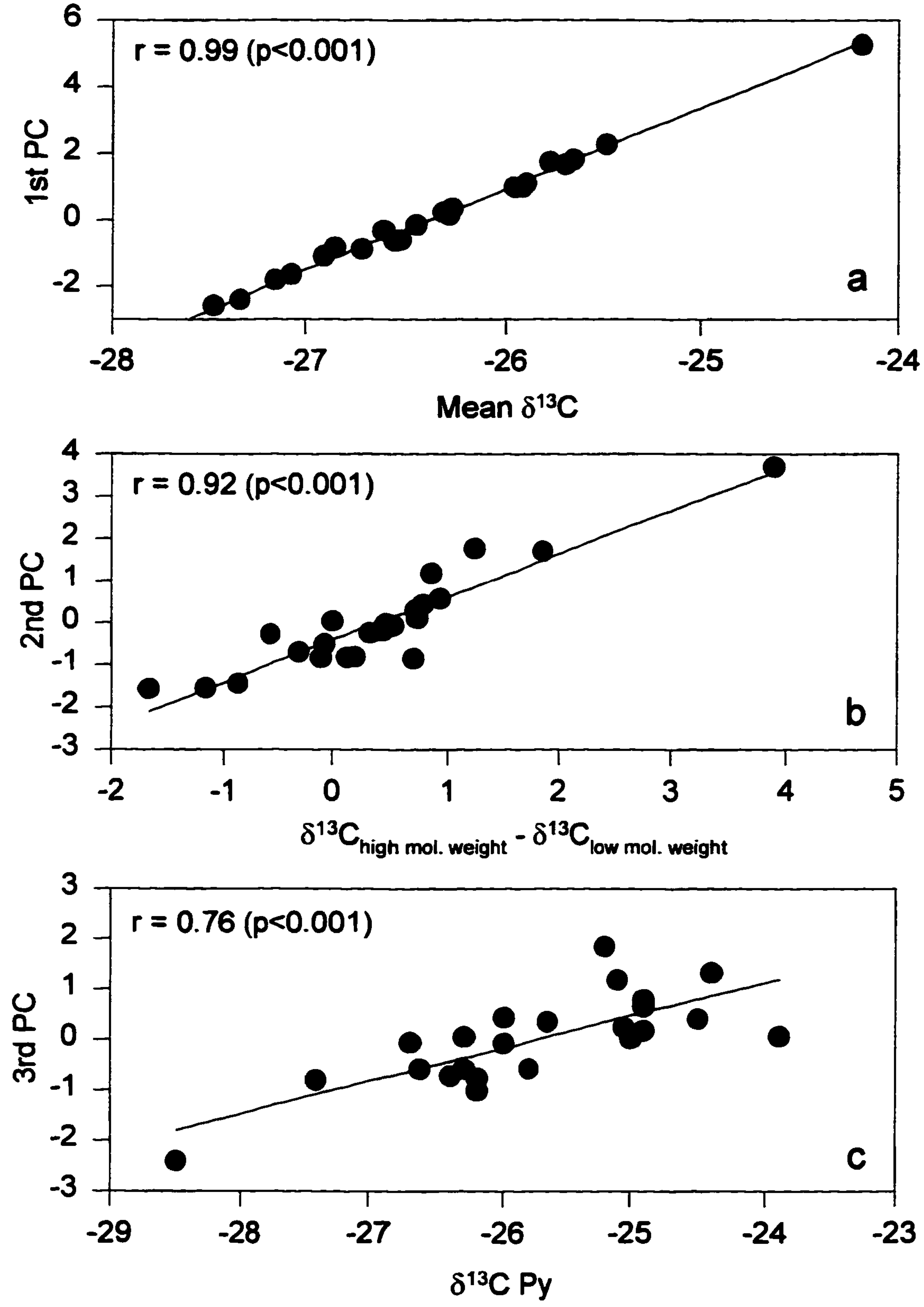
The first component explained 52.6% of total variance (Fig 4.1.6). It accounts for changes in isotopic composition of all utilized compounds which is proved by extremely high correlation ($r=0.99$; $p<0.001$) with their mean isotopic values (Fig. 4.1.7a). The station at Buffalo demonstrates an extreme positive value for PC 1(Fig 4.1.8a). This indicates that all compounds at this station are isotopically enriched. The other end of the component is occupied by a group of samples (966, Wh, 945, 951, 953) located close to the northern shore of the lake, station 966 being the extreme. The station at Cleveland (955) is the closest to Bf and demonstrates isotopically enriched compounds. This station is followed by stations 23, 1021, and 935 demonstrating isotopic composition similar to

Figure 4.1.6 Weights of variables (compounds) in 3 first PCs extracted by PCA utilizing $\delta^{13}C$ values of 7 selected compounds (Pa, Fa, Py, Chy, BbF, BeP, Per). Three first PCs explained 85.1% of total variance in samples.



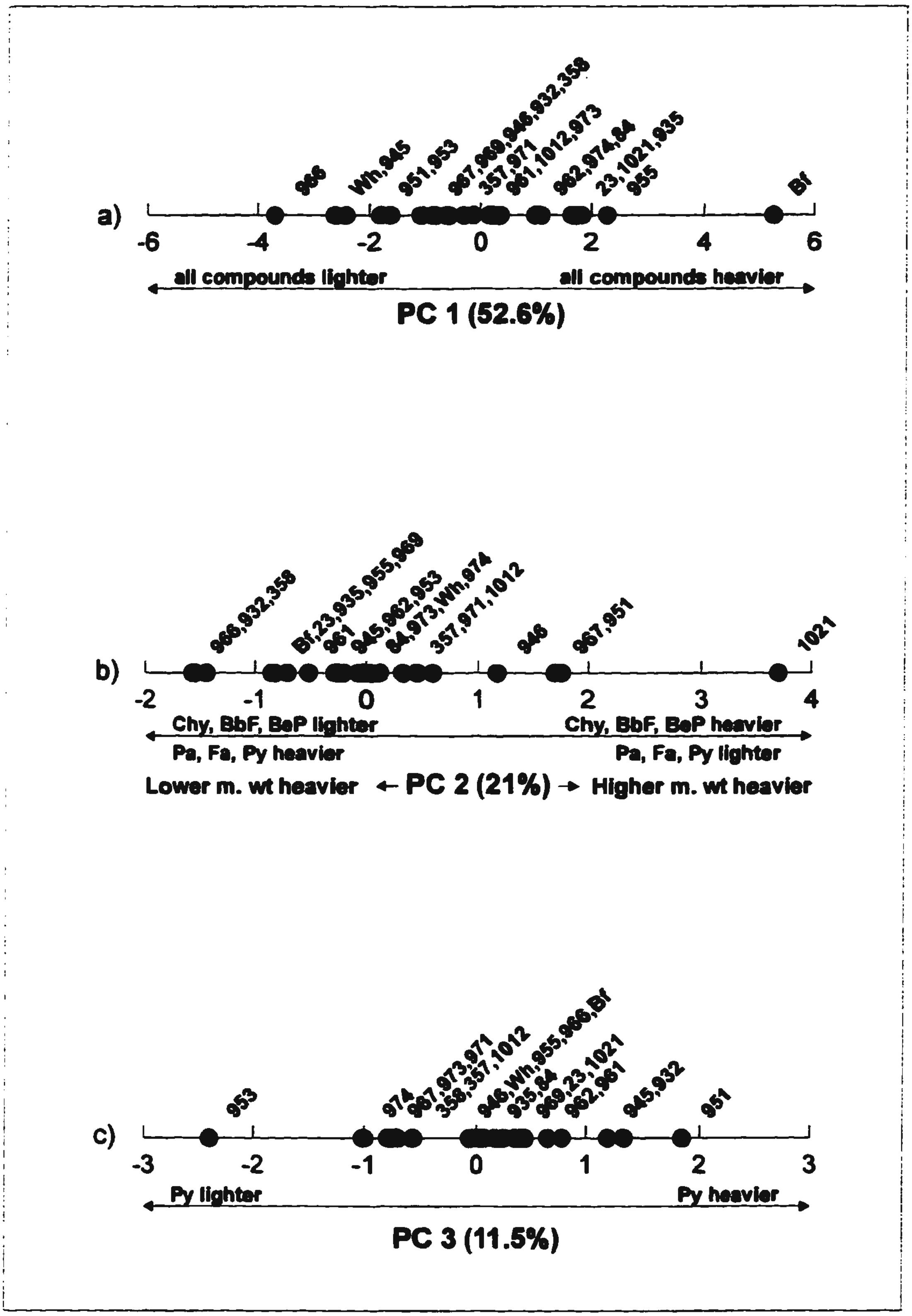
5
4
3
2
1
0
-1
-2
Cumulative weight
3-,4-ring
Pa
Fa
Py
Chy
5-ring
BbF
BeP
Per
52.6%
21.0%
11.5%
PC1
PC2
PC3
Principal Components

Figure 4.1.7. Regression of three first PCs on the parameters they are deemed to represent: **(a)** 1st PC vs. mean $\delta^{13}C$ of 7 selected PAHs used for the PCA (Pa, Fa, Py, Chy, BbF, BeP, Per); **(b)** 2nd PC vs. the difference between mean $\delta^{13}C$ of higher (Chy, BbF, BeP) and lower (Pa, Fa, Py) molecular weight compounds; **(c)** 3rd PC vs. $\delta^{13}C$ of Py. Correlation coefficients and significance levels are also shown.



r = 0.99 (p<0.001)
1st PC
6
4
2
0
-2
-28
-27
-26
-25
-24
Mean δ13C
a
r = 0.92 (p<0.001)
2nd PC
4
3
2
1
0
-1
-2
-3
-2
-1
0
1
2
3
4
5
δ13Chigh mol. weight - δ13Clow mol. weight
b
r = 0.76 (p<0.001)
3rd PC
3
2
1
0
-1
-2
-3
-29
-28
-27
-26
-25
-24
-23
δ13C Py
c

Figure 4.1.8 Distribution of samples along **(a)** 1st PC, **(b)** 2nd PC, and **(c)** 3rd PC identified by PCA utilizing $\delta^{13}C$ values of 7 selected PAH (Pa, Fa, Py, Chy, BbF, BeP, Per). Three first PCs explained 85.1% of total variance in samples.


a)
966
Wh,945
951,953
967,969,946,932,358
357,971
961,1012,973
962,974,84
23,1021,935
955
Bf
-6
-4
-2
0
2
4
6
all compounds lighter
all compounds heavier
PC 1 (52.6%)
b)
966,932,358
Bf,23,935,955,969
961
945,962,953
84,973,Wh,974
357,971,1012
946
967,951
1021
-2
-1
0
1
2
3
4
Chy, BbF, BeP lighter
Chy, BbF, BeP heavier
Pa, Fa, Py heavier
Pa, Fa, Py lighter
Lower m. wt heavier ← PC 2 (21%) → Higher m. wt heavier
c)
953
974
967,973,971
358,357,1012
946,Wh,955,966,Bf
935,84
969,23,1021
962,961
945,932
951
-3
-2
-1
0
1
2
3
Py lighter
Py heavier
PC 3 (11.5%)

that at Cleveland. Conversely, Detroit sample (971) is located among the major group of stations showing average isotopic composition. Stations 961 and 84 seem to occupy intermediate position between the two cities.

The second component explains 21% of variance and can be attributed to an opposition in isotopic composition of higher (> 228) and lower (< 202) molecular weight compounds (Fig. 4.1.8b). Most stations demonstrate isotopically balanced compounds. However, station 1021 shows heavy values for Chy and BbF and light values for Fa.

The third PC accounts for 11.5% of total variance (Fig. 4.1.6). This component is most significantly influenced by the isotopic composition of Py (72%). The interpretation is confirmed by significant correlation ($r=0.76$; $p<0.001$) between this component and isotopic values of Py. Among the other compounds, Pa and Per exhibit the largest contributions which are characterized by the opposite sign (Fig. 4.1.6). The extremes are Site 953 with very light $\delta^{13}C$ for Py and Site 951 which demonstrates isotopically light Pa and Per.

Thus the results of PCA support the conclusions made on the basis of the isotopic profiles and allowed the relationships between different stations to be better understood. The station at Buffalo is characterized by extreme ^{13}C enrichment in all compounds utilized in PCA as shown by PC 1 (Fig. 4.1.8a). Conversely, the lightest isotopic values are demonstrated by stations 966, Wh, 945, 951, and 953 located in the northern part of the lake. Station 955 at Cleveland is the closest to that at Buffalo with respect to its isotopic composition. The isotopic values at Detroit (971) do not significantly differ from those at the majority of stations. Station 1021 is distinct due to the relationship between isotopic composition of lower and higher molecular weight compounds. Finally, stations 953 and 951 are marked by unbalanced isotopic values for Py and Pa, Per.

4.2 SOURCE IDENTIFICATION

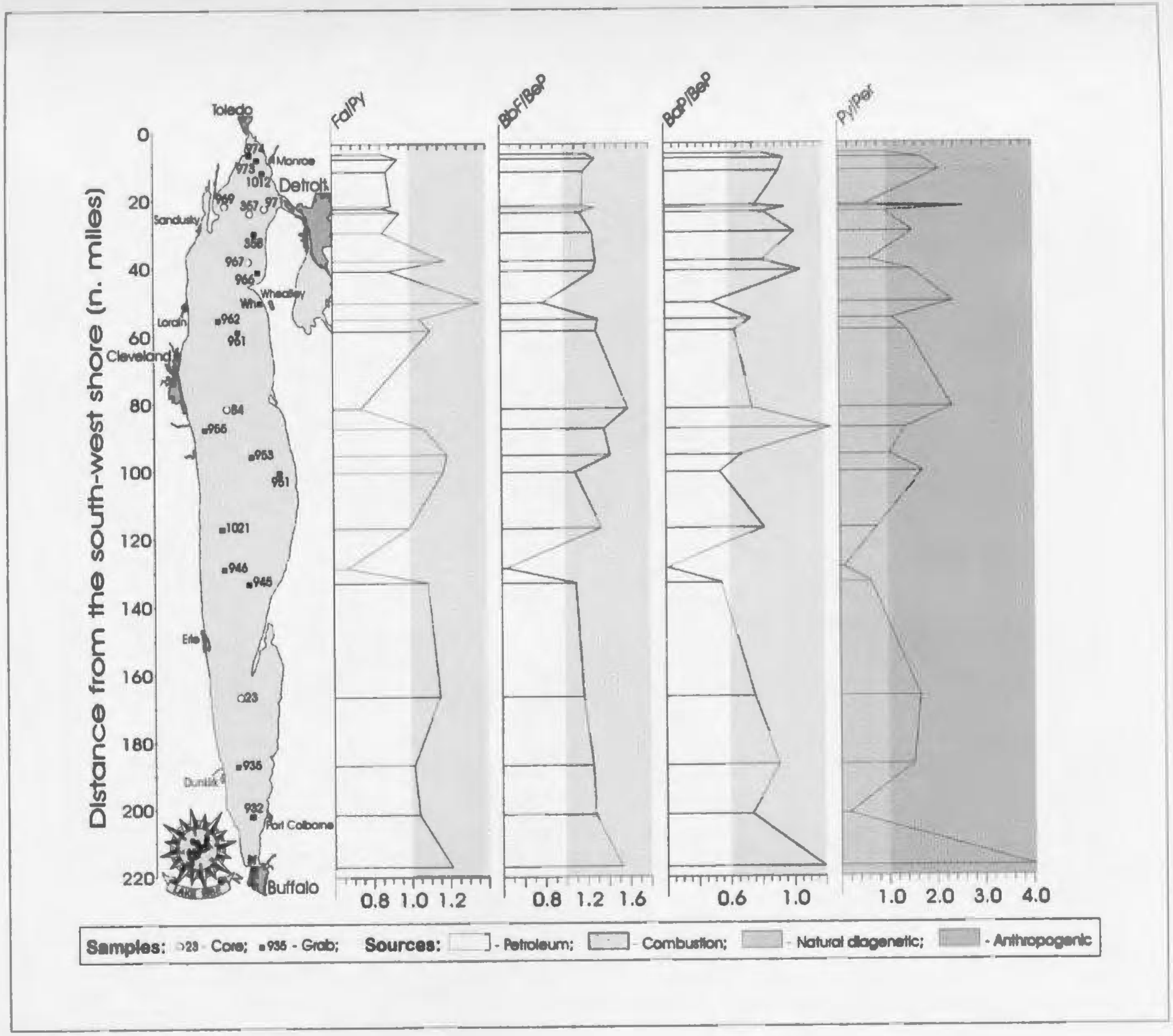
4.2.1 MOLECULAR COMPOSITION

4.2.1.1 Characteristic ratios and mixing curves

The ratios of kinetic to thermodynamic isomers have been found characteristic of the relative contribution of combustion and petroleum sources to the PAH assemblage (*e.g.*, Yunker and Macdonald, 1995; see also Appendix A5). In addition, Lipiatou and Saliot (1992) demonstrated that Py/Per ratio may serve as an indicator of the intensity of diagenetic processes. Following these ideas, three commonly used isomer ratios (Fa/Py, BbF/BkF, BaP/BeP) and the Py/Per ratio were calculated and plotted against the longest axis of the lake (Fig. 4.2.1). The general pattern that emerges from the consideration of the ratio profiles is that combustion sources dominate over petroleum input and anthropogenic production of PAH is more important than diagenetic sources throughout the lake. However, there are a few sites where petroleum related sources can play a significant role and/or the process of diagenesis might be intensive.

Although the isomer ratios may be ambiguous in some cases, a few regions with an increased importance of petroleum-related sources can be discerned across the lake. The ratio of Fa to Py consistently indicates petroleum presence in the Western Basin. The affected sites seem to be concentrated close to the mouth of the Detroit River (974, 973,

Figure 4.2.1 Ratios of selected 4-, 5-ring compounds compared to characteristic ratios of prominent primary sources (combustion vs. petroleum, and anthropogenic vs. natural diagenetic). Ratios of primary sources are those identified by O'Malley (1994) for an urbanized area in eastern Canada (see Appendix A5).


Distance from the south-west shore (n. miles)
0
20
40
60
80
100
120
140
160
180
200
220
Toledo
Monroe
Detroit
Sandusky
Lorain
Cleveland
Wheatley
Erie
Dunkirk
Port Colborne
Buffalo
974
973
1012
969
357
358
967
966
962
961
84
955
953
951
1021
946
945
23
935
932
Fal/Py
0.8 1.0 1.2
BbF/BeP
0.8 1.2 1.6
BaP/BeP
0.6 1.0
Py/Per
1.0 2.0 3.0 4.0
Samples: ○23 - Core; ■935 - Grab;
Sources: ☐ - Petroleum; ☐ - Combustion; ▨ - Natural diagenetic; ▨ - Anthropogenic

1012, 969, 971, 357, 358). In addition, at least a single ratio demonstrates significant contribution from petroleum sources at stations Wh, 951, 946, and 945 located in the northern part of the Central Basin.

Three zones of possible diagenetic production of Per can be detected in the lake. In the Western Basin, stations 974, 969, 357, and 967 seem to be affected by natural diagenesis. Stations 953, 1021, 946, and 945 demonstrate low Py/Per ratio in the Central Basin. Finally, in the Eastern Basin, intensive diagenetic processes can be detected at station 932.

The origin of PAH assemblage can further be tested using mixing relationship for prominent end members. Mixing curves were generated on the basis of molecular composition of major primary sources following the procedure described in Langmuir *et al.* (1978; see also Appendix A7). Five kinetic and thermodynamic compounds (Fa, Py, Chy, BeP, BaP) with available source signatures were chosen for this procedure. The mixing curves plotted for two permutations of compound ratios (Fig. 4.2.2, 4.2.3) allow an important conclusion regarding the origin of the PAH assemblage in samples to be drawn.

The plots indicate that the PAH assemblage at most stations was not derived from mixing of a single pair of sources utilized in the analysis. The major cloud of samples is shifted away from the curves connecting the prominent end members. The shift in both graphs seems to be directed towards the predominance of higher molecular weight compounds (Chy, BeP, BaP). Stations 946 and 967 are the most remote ones which

Figure 4.2.2 Samples and prominent primary and secondary sources on BaP/Py vs. Chy/Fa plot. Mixing curves are calculated using normalized concentrations (Appendix A3) in the two component mixing model described in Appendix A7.

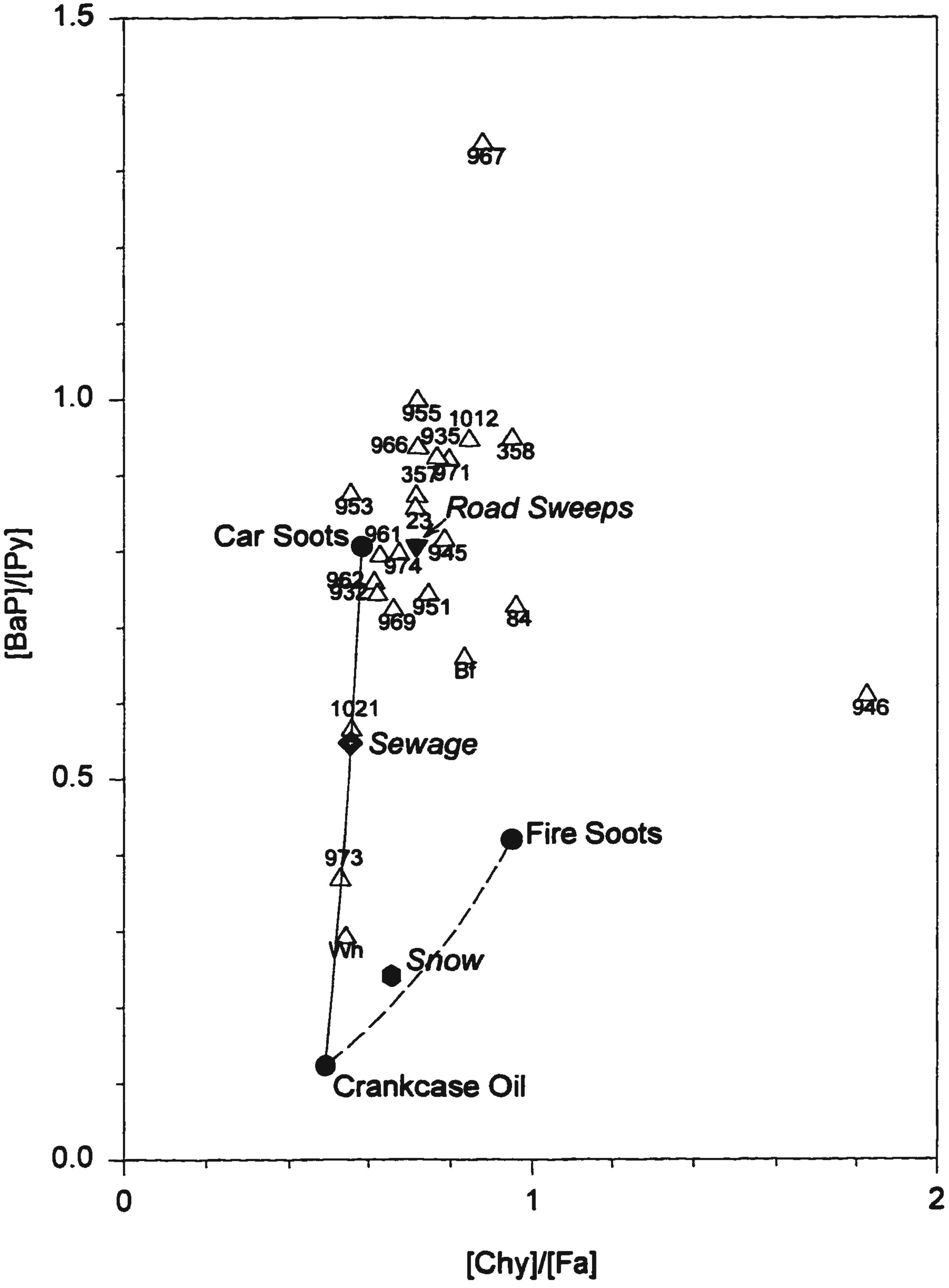
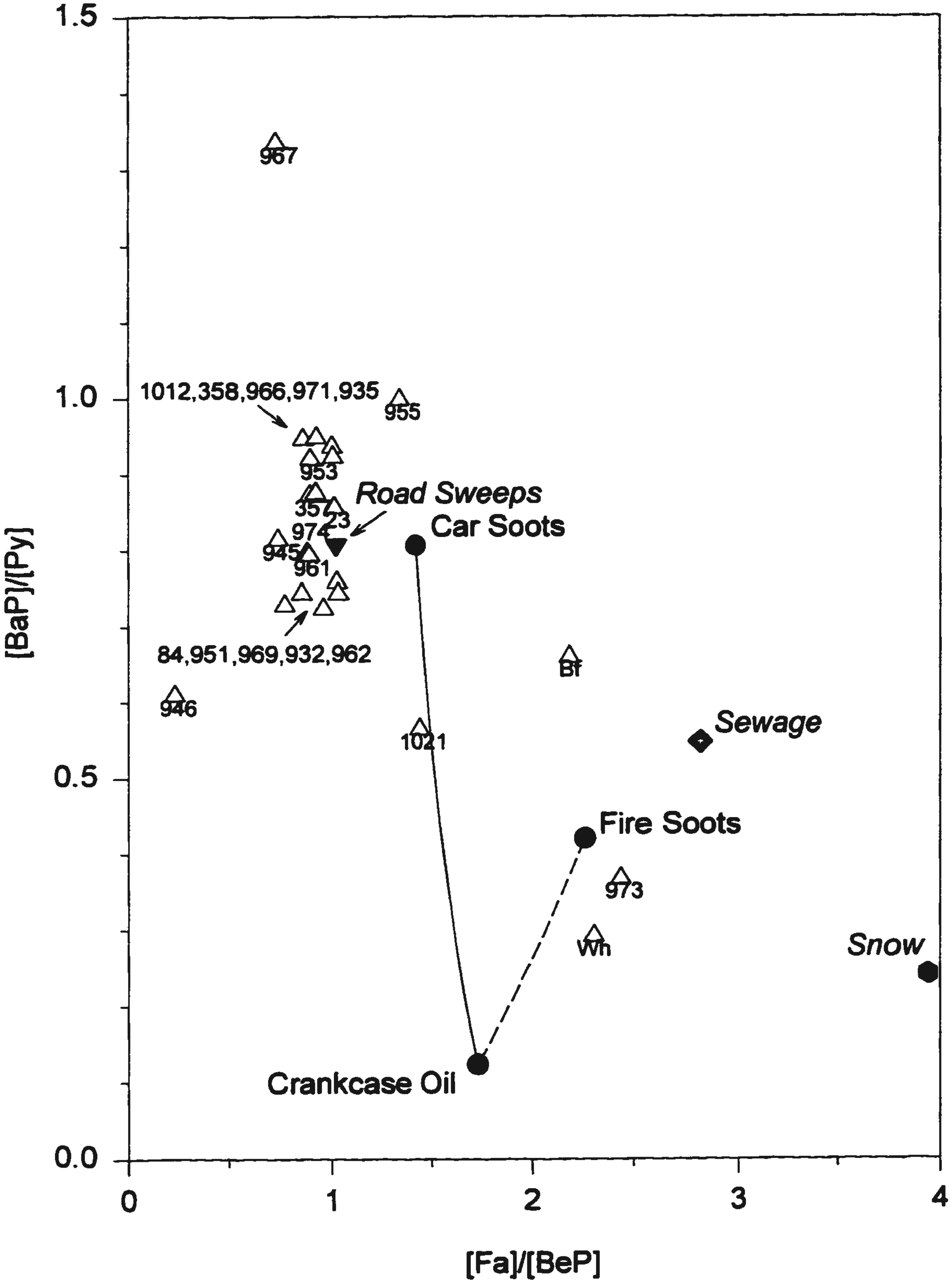

1.5
1.0
0.5
0.0
0
1
2
[BaP]/[Py]
[Chy]/[Fa]
967
955
1012
966
935
358
357
971
953
Road Sweeps
23
Car Soots
961
945
974
962
932
951
969
84
Bf
946
1021
Sewage
Fire Soots
973
Wh
Snow
Crankcase Oil

Figure 4.2.3 Samples and prominent primary and secondary sources on BaP/Py vs. Fa/BeP plot. Mixing curves are calculated using normalized concentrations (Appendix A3) in the two component mixing model described in Appendix A7.


1.5
1.0
0.5
0.0
0
1
2
3
4
[BaP]/[Py]
[Fa]/[BeP]
967
1012,358,966,971,935
955
953
Road Sweeps
Car Soots
357
23
974
945
961
84,951,969,932,962
Bf
946
1021
Sewage
Fire Soots
973
Wh
Snow
Crankcase Oil

implies that compounds there either entirely produced from a different source or strongly affected by a process altering the PAH assemblage in sediments. Only stations Wh, 973, 1021, and Bf tend to plot close to the curves demonstrating more affinity to the primary sources.

In summary, combustion sources, seem to be more important throughout the lake. However, sites close to the mouth of the Detroit River (974, 973, 1012, 969, 971, 357, 358) and stations in the northern part of the central basin (Wh, 951, 946, and 945) can be significantly affected by petroleum input. The origin of Per at most stations can be attributed to anthropogenic sources. Only a few stations, 974, 969, 357, 967(WB), 953, 1021, 946, 945 (CB) and 932 (EB), indicate possibility of intensive diagenesis. The consideration of mixing curves suggests a reduced abundance of lower molecular weight compounds (Fa and Py). This might be attributed to either presence of an unknown source depleted in this compounds or to a process stripping lower molecular weight PAH from the assemblage (weathering?). Stations Bf, Wh, 973, and 1021 seem to be affected by this process to a lesser degree.

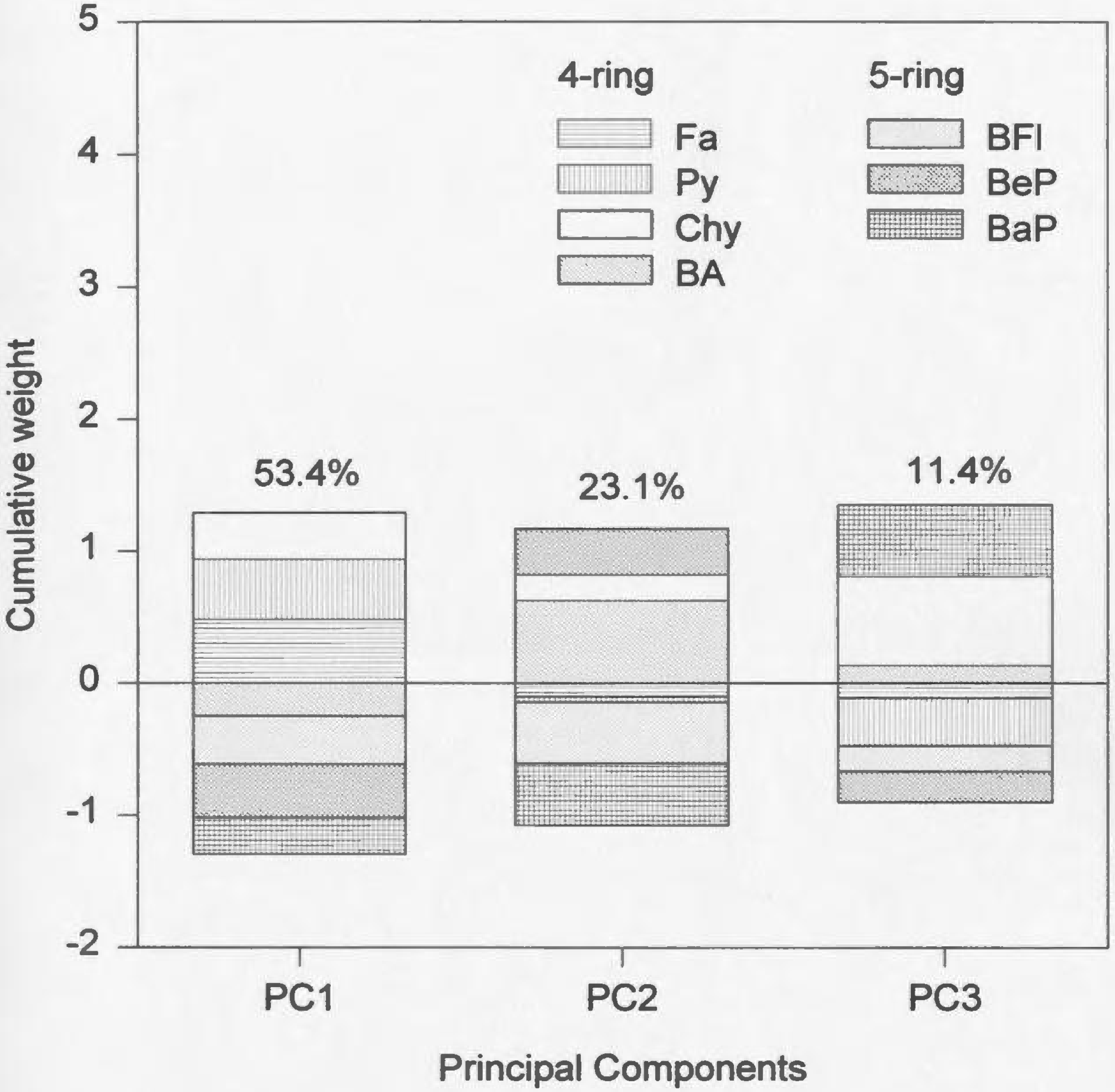
4.2.1.2 PCA for molecular composition (source identification)

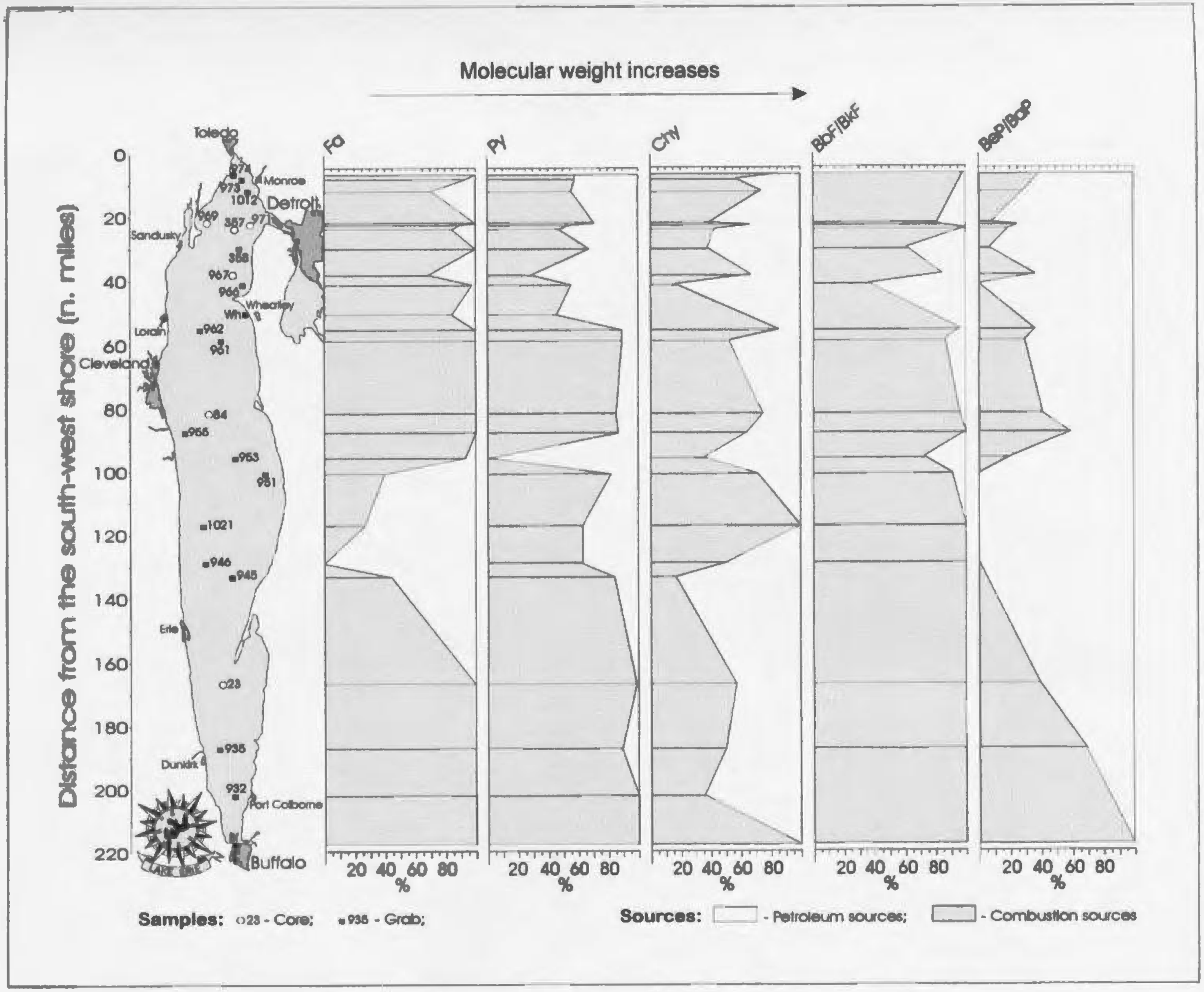
Further generalization of data on molecular composition was achieved through a principal components analysis performed on normalized concentrations of 7 selected 4-, 5- ring compounds (Fa, Py, Chy, BA, BFl, BeP, BaP; Appendix B3; see Section 3.2.2). Due to normalization, the effect of absolute loading of PAH in sediments was eliminated and consequently, the PCA primarily focused on the inter-compound variations. This analysis supported some of the previously observed patterns and allowed a few additional insights. The three first components explained 87.9% of total variance in samples.

The first component alone explains 53.4% of total variance (Fig. 4.2.4). This component represents an opposition of lower molecular weight (< 228) to higher (252) molecular weight compounds. All anthropogenic sources are grouped within the positive range of PC 1 indicating high importance of lower molecular weight compounds in the PAH assemblage (Fig. 4.2.5a). Stations 973 and Wh are mixed into the group of sources representing atmospheric influx, sewage and fire soots. Conversely, the majority of samples are shifted towards the negative values, away from the sources. This shift can be explained by overall predominance of high molecular weight compounds in the PAH assemblage. The extreme position here is occupied by stations 946 and 967.

The second component accounts for 23.1% of variance (Fig. 4.2.4). This component represents an opposition in the relative abundance of BA, BeP and BFl, BaP. The majority of stations and sources are grouped together in the range from -1.8 to 0.7 (Fig. 4.2.5b). Surprisingly, station 946 is shifted far away from the group towards extreme positive values. The position shows very high relative importance of BA and BeP at this station. Such a signature is not characteristic of any primary or secondary sources. The station at Wheatley exhibits some similarity to 946 with respect to the relative abundance of the above compounds. The latter is shown by its intermediate position between station 946 and the major group.

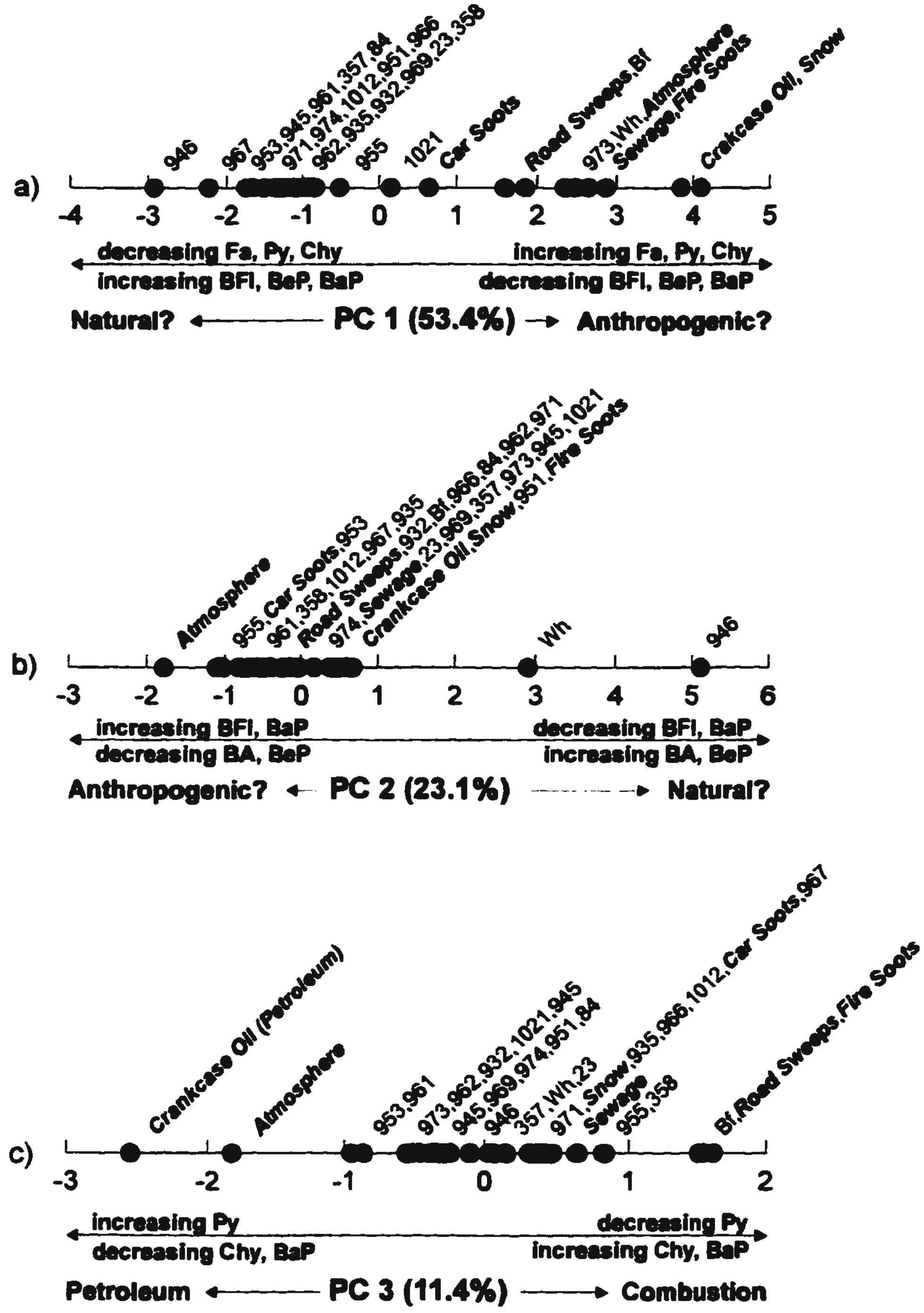
Figure 4.2.4 Weights of variables (compounds) in 3 first PCs extracted by PCA utilizing normalized concentrations of selected 4-, 5-ring PAH (Fa, Py, BA, Chy, BFl, BeP, BaP), with primary and secondary sources included. Three first PCs explained 87.9% of total variance in samples.


5
4
3
2
1
0
-1
-2
Cumulative weight
4-ring
Fa
Py
Chy
BA
5-ring
BFl
BeP
BaP
53.4%
23.1%
11.4%
PC1
PC2
PC3
Principal Components



Molecular weight increases
Fa
Py
Chy
BbF/BkF
BeP/BaP
Distance from the south-west shore (n. miles)
0
20
40
60
80
100
120
140
160
180
200
220
Toledo
974
Monroe
973
1012
Detroit
969
357
971
Sandusky
358
967
966
Wheatley
Wh
Lorain
962
961
Cleveland
84
955
953
951
1021
946
945
Erie
23
935
Dunkirk
932
Port Colborne
Buffalo
LAKE ERIE
20 40 60 80
%
Samples: ○23 - Core; ■935 - Grab;
Sources: ☐ - Petroleum sources; ▨ - Combustion sources

Figure 4.2.5 Distribution of samples and primary and secondary sources along **(a)** 1st PC, **(b)** 2nd PC, and **(c)** 3rd PC identified by PCA utilizing concentrations of 7 selected 4-, 5-ring PAH (Fa, Py, BA, Chy, BFl, BeP, BaP). Three first PCs explained 87.9% of total variance.


a)
946
967
953,945,961,357,84
971,974,1012,951,966
962,935,932,969,23,358
955
1021
Car Soots
Road Sweeps,Bf
973,Wh,Atmosphere
Sewage,Fire Soots
Crakcase Oil, Snow
-4
-3
-2
-1
0
1
2
3
4
5
decreasing Fa, Py, Chy
increasing BFl, BeP, BaP
increasing Fa, Py, Chy
decreasing BFl, BeP, BaP
Natural?
PC 1 (53.4%)
Anthropogenic?
b)
Atmosphere
955,Car Soots,953
961,358,1012,967,935
Road Sweeps,932,Bf,966,84,962,971
974,Sewage,23,969,357,973,945,1021
Crankcase Oil,Snow,951,Fire Soots
Wh
946
-3
-2
-1
0
1
2
3
4
5
6
increasing BFl, BaP
decreasing BA, BeP
decreasing BFl, BaP
increasing BA, BeP
Anthropogenic?
PC 2 (23.1%)
Natural?
c)
Crankcase Oil (Petroleum)
Atmosphere
953,961
973,962,932,1021,945
945,969,974,951,84
946
357,Wh,23
971,Snow,935,966,1012,Car Soots,967
Sewage
955,358
Bf,Road Sweeps,Fire Soots
-3
-2
-1
0
1
2
increasing Py
decreasing Chy, BaP
decreasing Py
increasing Chy, BaP
Petroleum
PC 3 (11.4%)
Combustion

The third PC is responsible for 11.4% of sample variance (Fig. 4.2.4). This component accounts for relative abundance of Chy, BaP and Py. The two extremes here are occupied by petroleum related sources and fire soots (Fig 4.2.5c). The car soot sample is also located within the positive range. Consequently, this component represents relative contribution from combustion and petroleum sources. Most samples are shifted towards the combustion range. The sample from Buffalo indicates strong affinity to fire soot and road sweep samples. Relative to Buffalo, the Detroit station (971) is slightly shifted towards the petroleum range and plots close to the snow, car soot, and sewage samples. Station 955 (Cleveland) occupies intermediate location between the other two cities and is found next to the sewage sample.

In summary, the statistical analysis of more stable 4-, 5-ring PAH confirms the previous suggestion that PAH in lake sediments are greatly influenced by an unknown source or (natural?) process. This influence caused the shift of samples away from major sources on the 1st PC (Fig. 4.2.5a). The unidentified source/process either tends to introduce a PAH assemblage depleted in lower molecular weight compounds or removes these compounds from sediments. Besides, the molecular composition of samples from Wheatley and especially from station 946 demonstrates an increased importance of BA and BeP (PC 2; Fig. 4.2.5b). This is not typical of any sources taken into consideration. The latter suggests that these two stations are affected by an additional source/process not important at other stations. Only the third component, which accounts for only 11.4% of total variance, represents the relative contribution of combustion and petroleum-related sources (Fig. 4.2.5c). This component again indicates that combustion sources dominate the PAH assemblage. The sample from Buffalo demonstrates molecular composition close to that of road sweeps and fire soots.

4.2.2 ISOTOPIC COMPOSITION

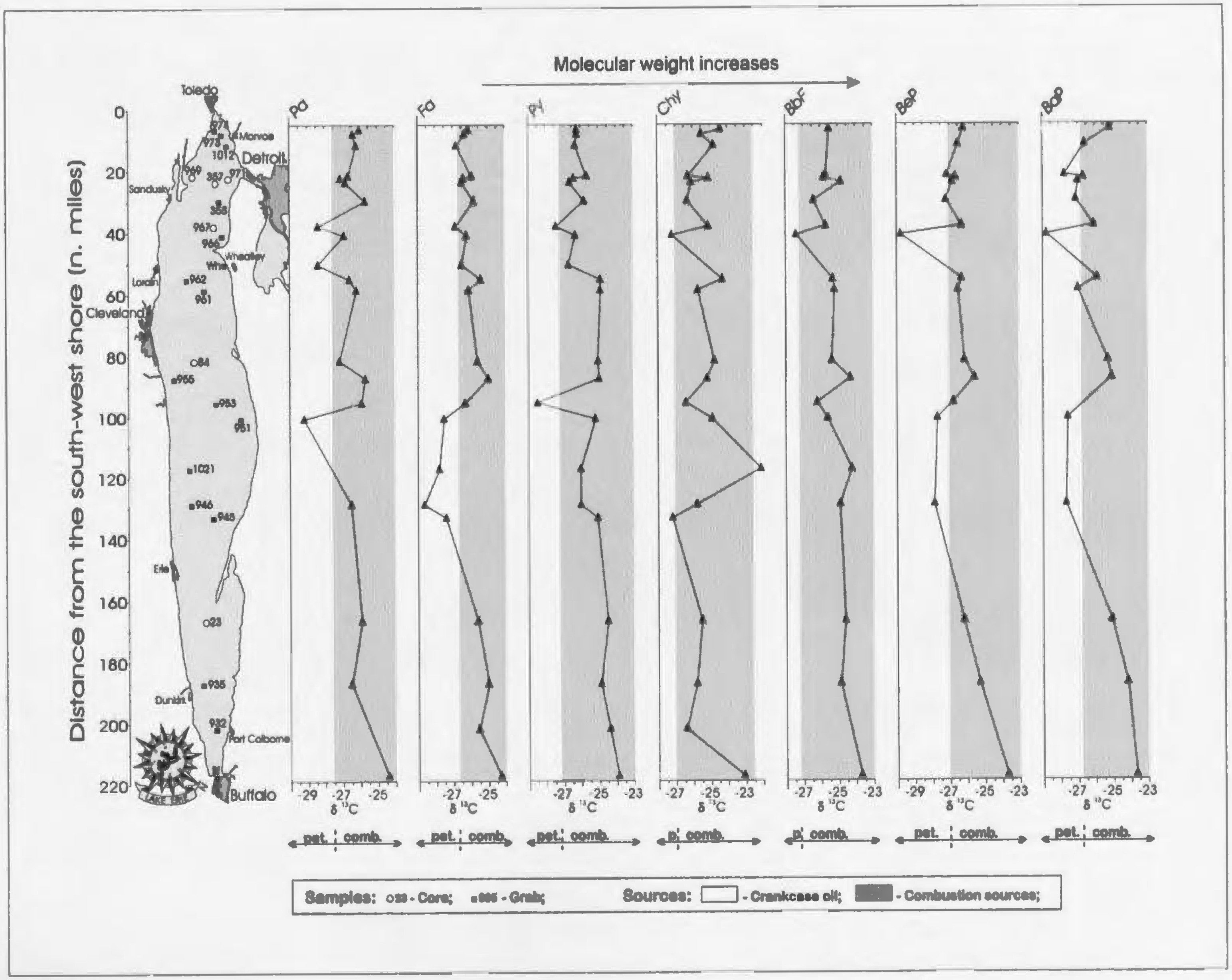
4.2.2.1 Comparison with characteristic signatures of primary sources and mass balance calculations

In isotopic data, the relative contribution of petroleum and combustion sources can first be elucidated through direct comparison of the composition of individual compounds with characteristic signatures of the major primary sources (Appendix A6; see also Section 3.2.2). The profiles of selected compounds fluctuate predominantly in the combustion range (Fig. 4.2.6). However, there are two major regions where contribution of petroleum sources may be important.

There is an indication of petroleum input in the Western Basin (Fig. 4.2.6). Stations 969, 967 and 966 demonstrate the highest contribution from petroleum-related sources in the region. At stations 966 and 969, this is indicated by high molecular weight compounds (BeP, BaP). Conversely, at station 967 the petroleum influence is shown by 3-. 4-ring PAH (Pa, Fa, and Py). The station at Detroit (971) plots close to the petroleum-combustion boundary on the Pa, Fa, BeP, and BaP graphs thus indicating possible input from petroleum-related sources at this site.

The second region demonstrating elevated relative importance of petroleum sources is located in the central part of the lake. Station 951 falls within the range of petroleum

Figure 4.2.6 Isotopic composition ($\delta^{13}C$) of 7 selected compounds (Pa, Fa, Py, Chy, BFl, BeP, BaP) compared to characteristic values of prominent primary sources (combustion vs. petroleum). Isotopic signatures of primary sources are those identified by Stark *et al.* (1995) for the lower Great Lakes region (Appendix A4).


Molecular weight increases
Distance from the south-west shore (n. miles)
0
20
40
60
80
100
120
140
160
180
200
220
Toledo
Monroe
Detroit
Sandusky
Wheatley
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
LAKE ERIE
Pa
Fa
Py
Chy
BbF
BeP
BaP
-29 -27 -25
-27 -25
-27 -25 -23
-27 -25 -23
-27 -25 -23
-29 -27 -25 -23
-27 -25 -23
δ 13C
pet. comb.
p. comb.
Samples: ○23 - Core; ■935 - Grab;
Sources: ☐ - Crankcase oil; ▨ - Combustion sources;

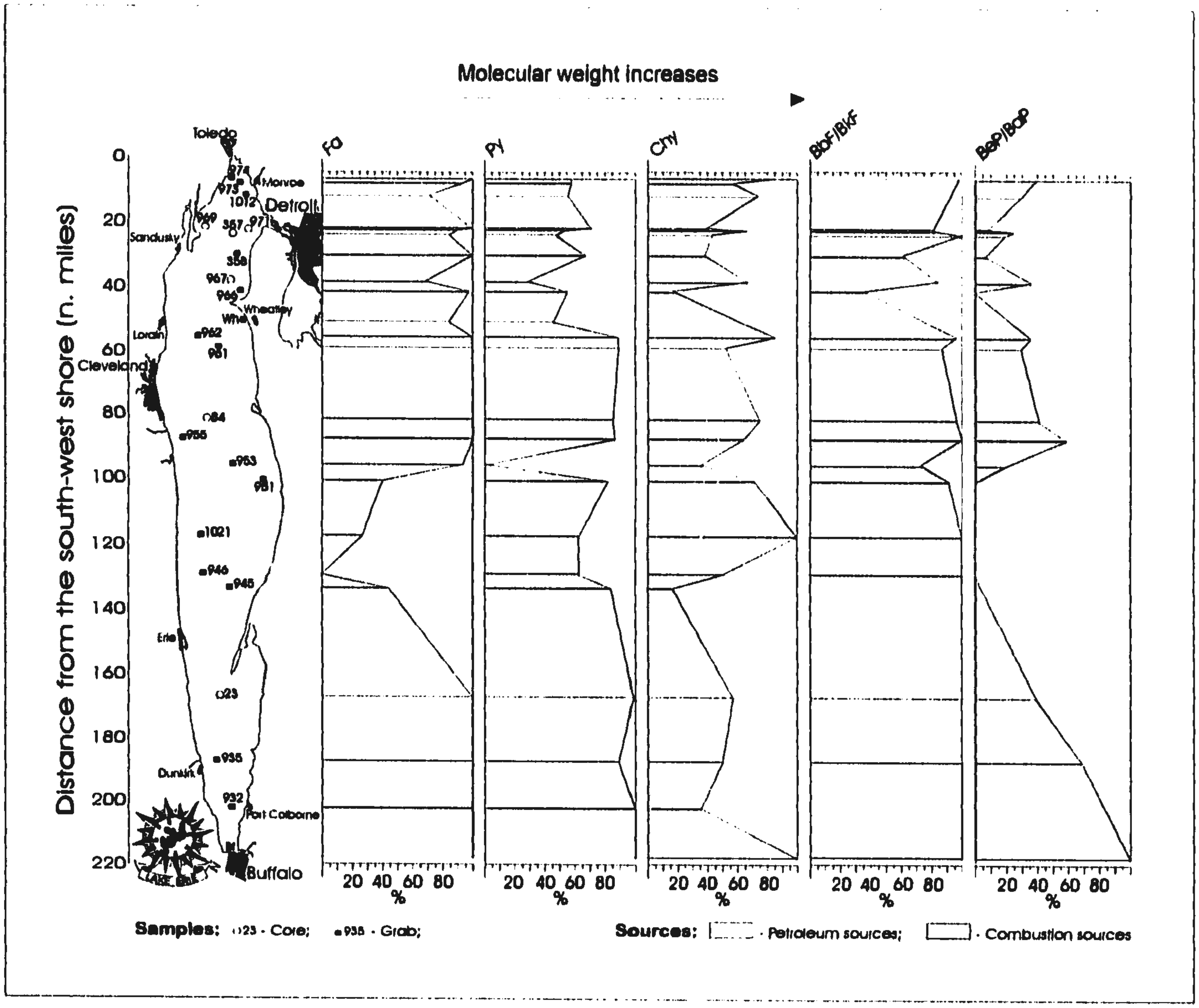
sources on the graphs for Pa, Fa, BeP, and BaP. Three compounds (Fa, BeP and BaP) indicate influence of petroleum sources at station 946, while Fa and Chy show their presence at station 945. Finally at least a single graph demonstrates that petroleum contribution is possible at stations Wh (Pa), 953 (Py), and 1021(Fa).

A two component model mass balance analysis (Appendix A6) further allows the relationships between combustion and petroleum sources to be quantitatively estimated (Fig. 4.2.7). The pattern generated from the mass balance calculations is similar to the previously described, with two major zones of high petroleum input. However, this analysis indicates that petroleum sources might play even more important role than it was suggested by the isotopic profiles.

The first region of elevated petroleum importance is again the Western Basin (stations 974 through 966). At station 971 (Detroit), the significance of petroleum is demonstrated by all compounds, with BeP/BaP (75%) indicating the highest and Fa the lowest (10 %) contribution. Another station with elevated petroleum input (BeP/BaP=90%) is site 969 located close to the Ohio shore. Finally, the highest petroleum contribution (BeP/BaP = 100%) is seen at station 966 in the vicinity of the northern shore. Conversely, station 974 (Toledo), shows the least petroleum influence in the basin. However, three compounds, BeP/BaP (60%), Py (40%), and Chy (15%), still indicate its presence in the PAH assemblage.

Similar to the isotopic profiles, the contribution from petroleum sources also seems to be important in the northern part of the Central Basin (Wh, 953, 951, 1021, 946, 945).

Figure 4.2.7 The relative contribution of combustion and petroleum sources estimated using the two-component mass balance model (Appendix A6). The utilized isotopic signatures of primary sources are those reported by Stark *et al.* (1995) for the lower Great Lakes region (Appendix A4).


Molecular weight increases
Fa
Py
Chy
BbF/BkF
BeP/BaP
Distance from the south-west shore (n. miles)
0
20
40
60
80
100
120
140
160
180
200
220
Toledo
974
Monroe
975
1012
Detroit
969
357
971
Sandusky
358
967
966
Wheatley
Lorain
962
961
Cleveland
84
955
953
951
1021
946
945
Erie
23
935
Dunkirk
932
Port Colborne
Buffalo
LAKE ERIE
20 40 60 80
%
Samples: ○23 - Core; ■935 - Grab;
Sources: Petroleum sources; Combustion sources

These sources contribute as much as 100% to the formation of BeP/BaP at stations 951, 1021, and 946. At the same stations, 60%, 70%, and 100% respectively of Fa seem to have derived from petroleum. At station 953 the greatest influence of petroleum is demonstrated by Py (100%), and BeP/BaP (80%). Isotopic composition of only two compounds were utilized for mass balance calculations at Wheatley. However, both of them indicate presence of petroleum derived PAH (Py=50%, Fa=15%).

In addition, some petroleum influence can be detected in the Eastern Basin. Stations 23 and 935 demonstrate 45-50% and 30-60% of BeP/BaP and Chy produced from petroleum-related sources. At station 932, as much as 60% of Chy is formed from petroleum. Unfortunately, its relative contribution to the formation of higher molecular weight compounds cannot be estimated at this station due to missing values.

To conclude, the comparison of sample isotopic values to characteristic signatures of the primary sources and mass balance calculations showed that although combustion sources are predominant throughout the lake, two major zones of high relative importance of petroleum are observed. The first zone is located in the Western Basin. Here, stations 971, 969, and 966 seem to be affected the most. The second region is found in the northern part of the Central Basin. The sites within this zone demonstrate even greater relative contribution of petroleum. Finally, there is an indication of petroleum input in the Eastern Basin.

4.2.2.2 Mixing curves (isotopic composition)

Consideration of mixing relationships based on both molecular and isotopic composition of prominent primary and secondary sources again allows the assumption concerning the PAH origin in samples to be tested. In addition, further quantification of relative contribution of different sources can be achieved through this procedure. Finally, this analysis can also be considered as the next step to generalization of results as two variables are involved in the plotting procedure. Mixing curves for different permutation of selected 4- and 5-ring compounds were generated and plotted as shown in O'Malley (1994; see Section 3.2.1 and Appendix A7). The molecular and isotopic composition for prominent primary and secondary sources utilized for plotting can be found in Appendices A3 and A4, respectively. Samples were further superimposed on the ratio/ratio plots with the mixing curves (Fig. 4.2.8-4.2.17). The relative position of samples with respect to the end members and the curves allow some additional information on the origin of the PAH assemblage and the relative contribution of different combustion and petroleum sources to be obtained.

The majority of stations plot in the vicinity of the mixing curves and/or within the range of statistical variation for the end members. This implies that the PAH assemblage at these sites can be viewed as derived from the set of primary and secondary sources under consideration. However, some samples seem to be shifted away from the mixing arrays implying existence of an unidentified PAH source with unique isotopic composition. For example, stations 946, 951, 966, 969 frequently demonstrate a shift

Figure 4.2.8 Samples and prominent primary and secondary sources on Py vs. Fa plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.

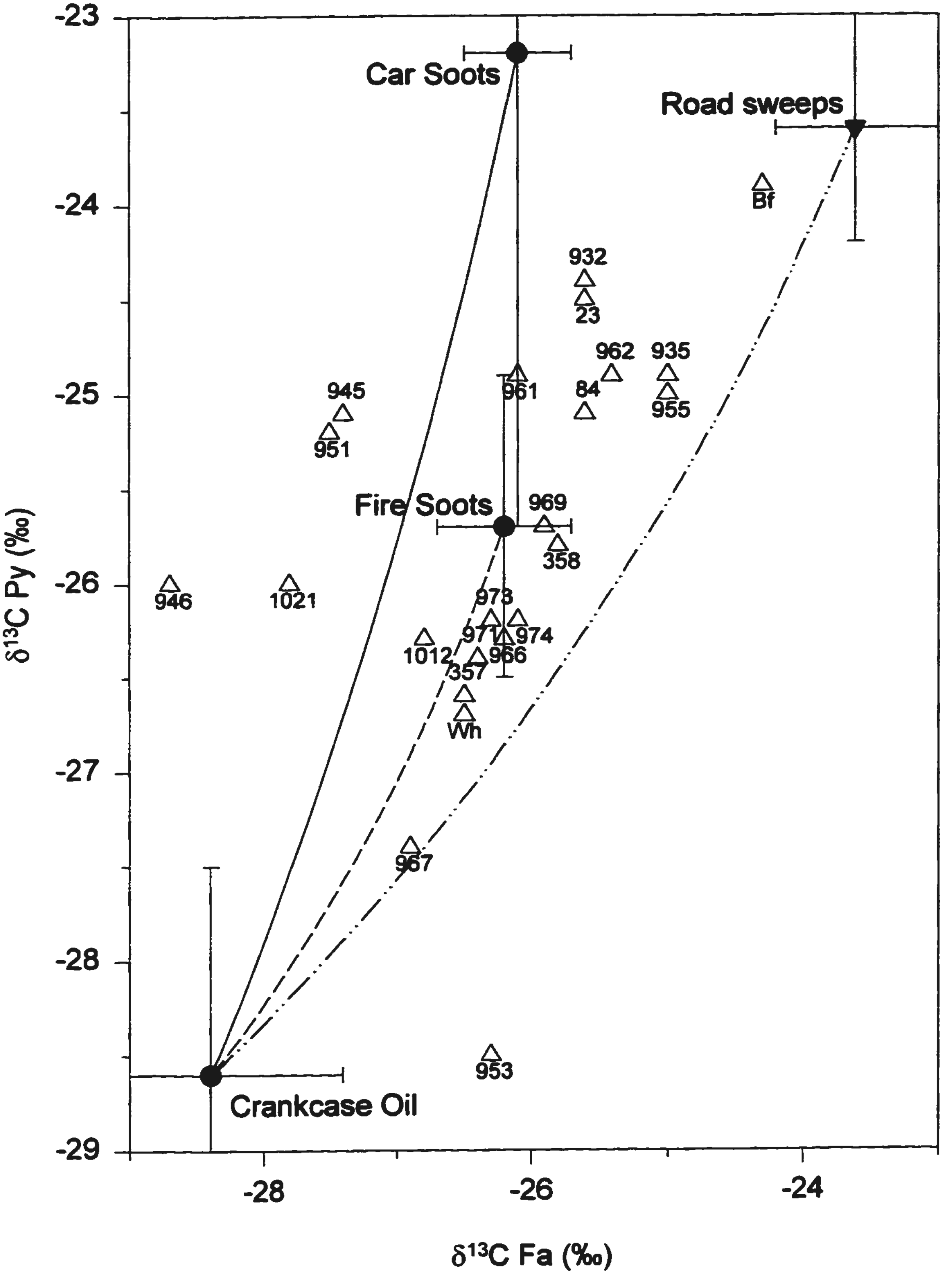
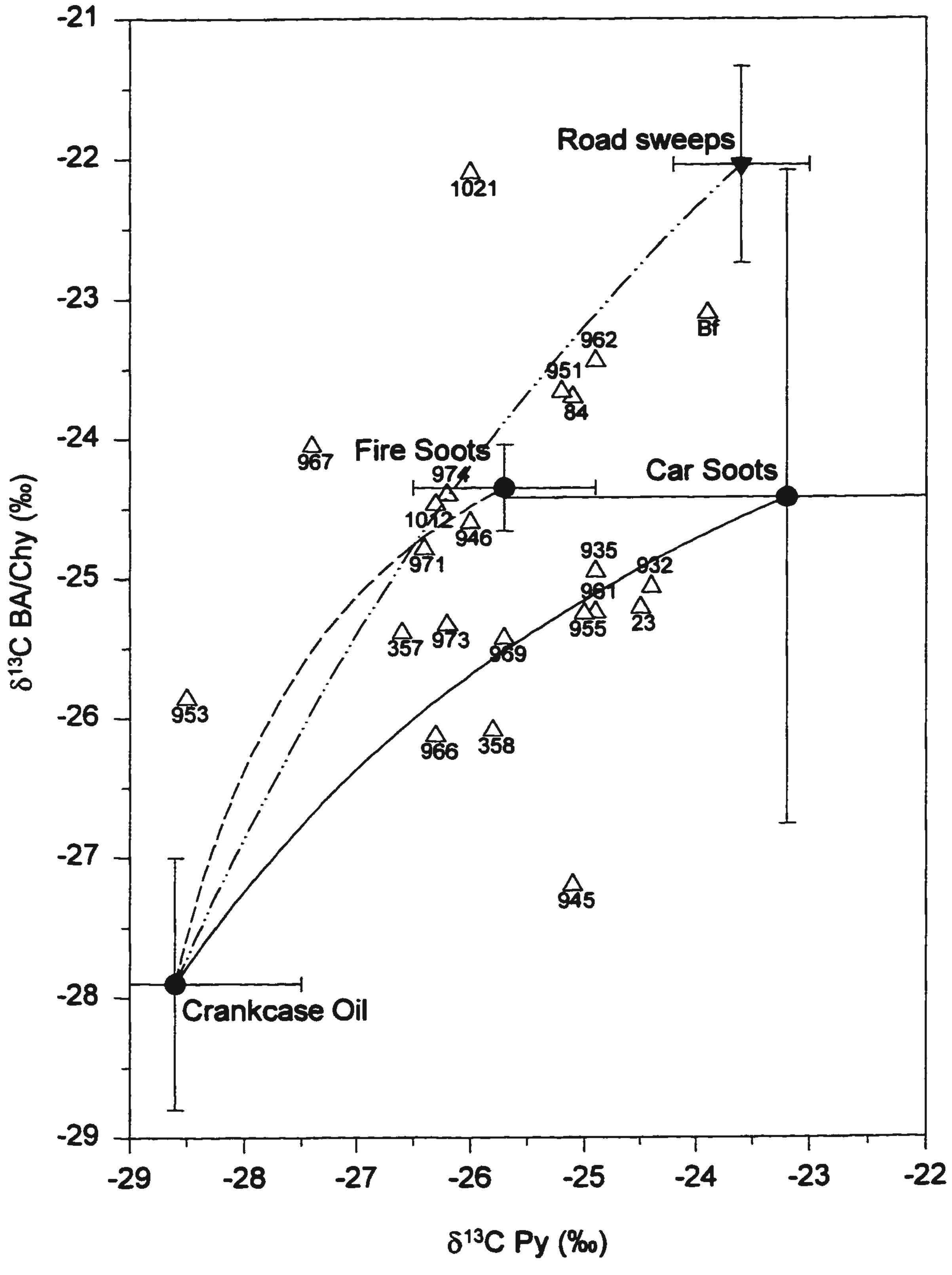

Car Soots
Road sweeps
Fire Soots
Crankcase Oil
Bf
932
23
962
935
945
961
84
955
951
969
358
946
1021
973
971
974
1012
966
357
Wh
967
953
-23
-24
-25
-26
-27
-28
-29
-28
-26
-24
δ13C Py (‰)
δ13C Fa (‰)

Figure 4.2.9 Samples and prominent primary and secondary sources on BA/Chy vs. Py plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.



-21
-22
-23
-24
-25
-26
-27
-28
-29
-29
-28
-27
-26
-25
-24
-23
-22
δ^{13}C BA/Chy (‰)
δ^{13}C Py (‰)
Road sweeps
1021
962
Bf
951
84
967
Fire Soots
974
Car Soots
1012
946
935
932
971
961
23
955
357
973
969
953
966
358
945
Crankcase Oil

Figure 4.2.10 Samples and prominent primary and secondary sources on BbF/BkF vs. Py plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.

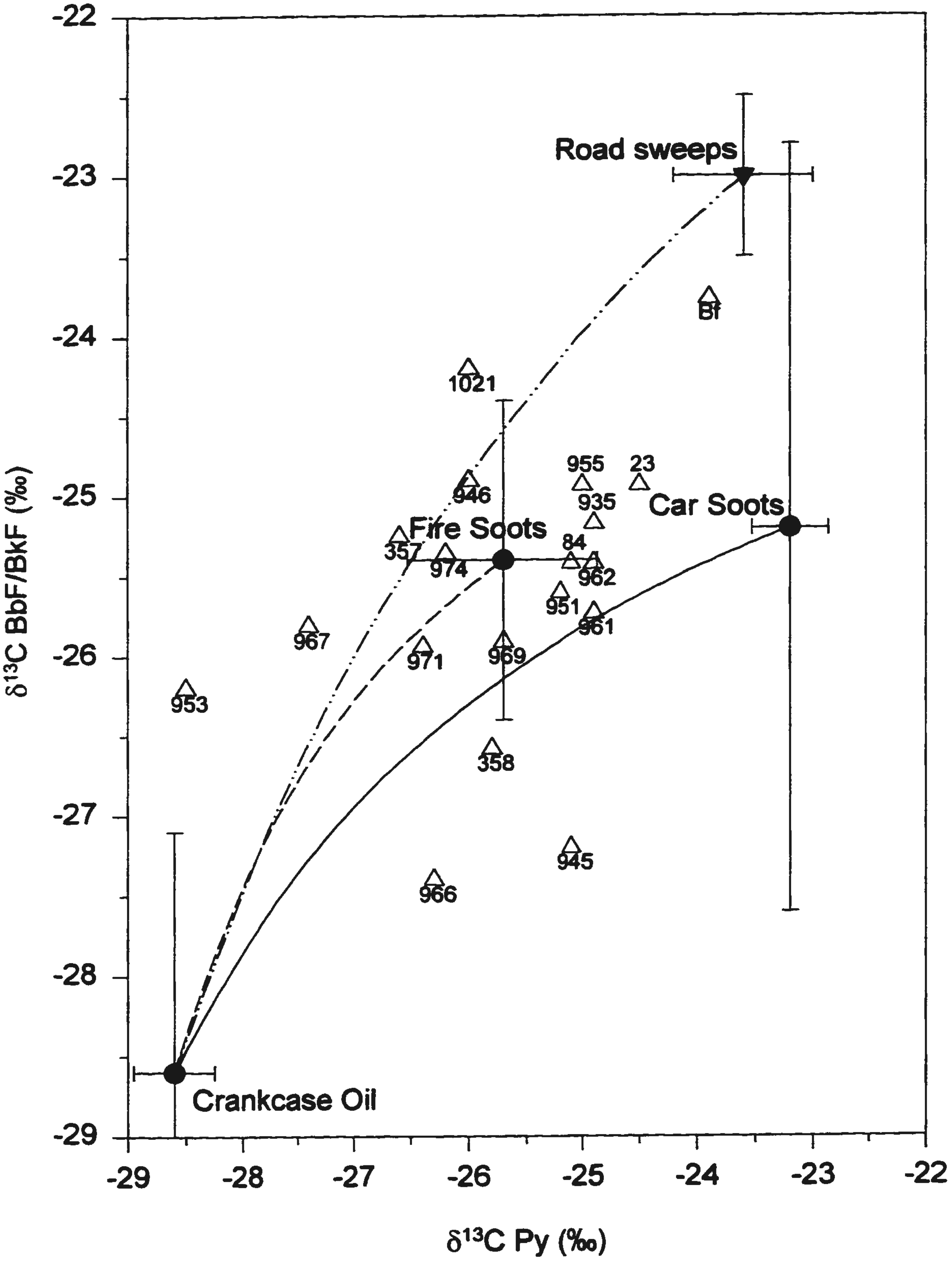
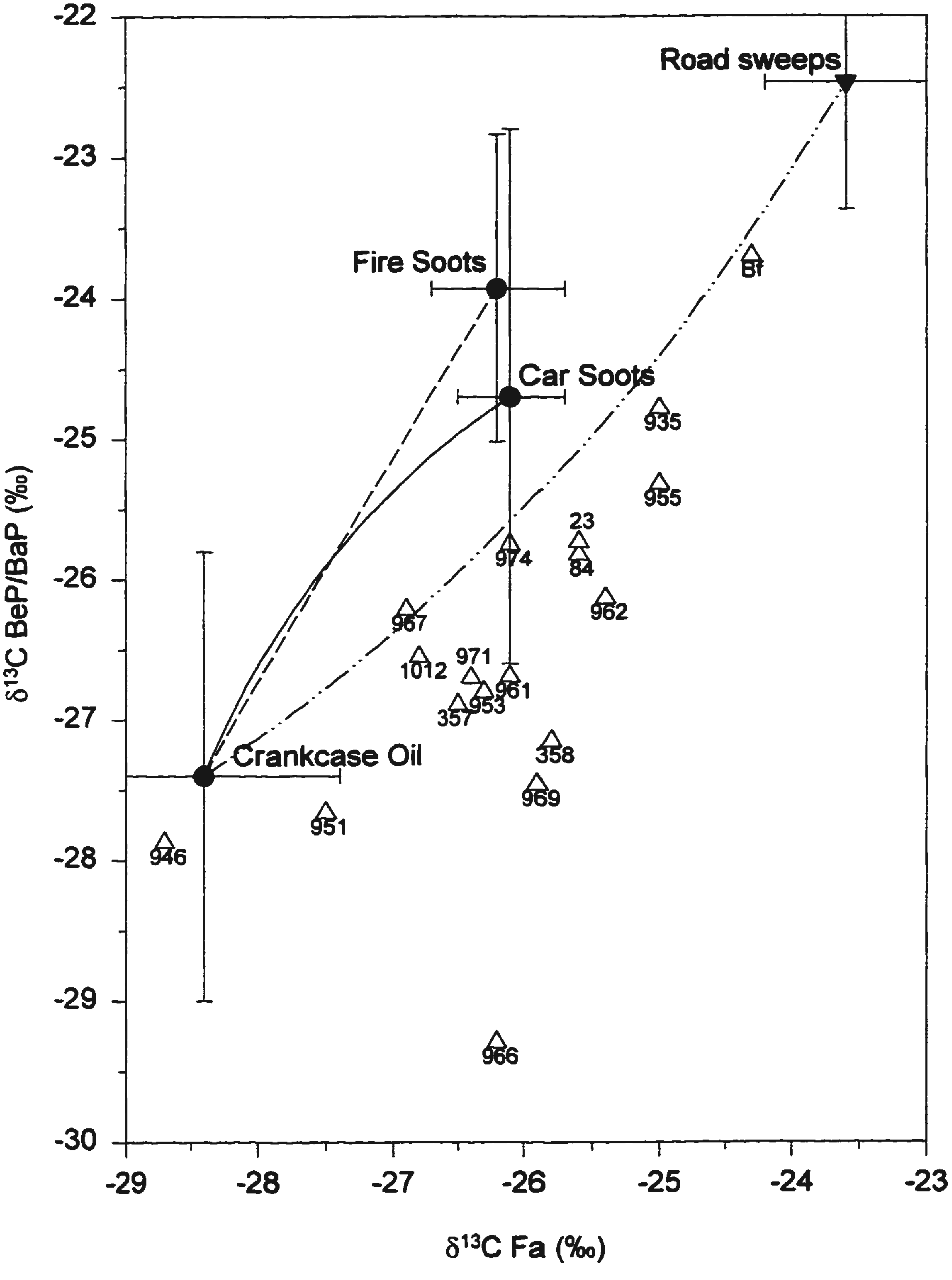
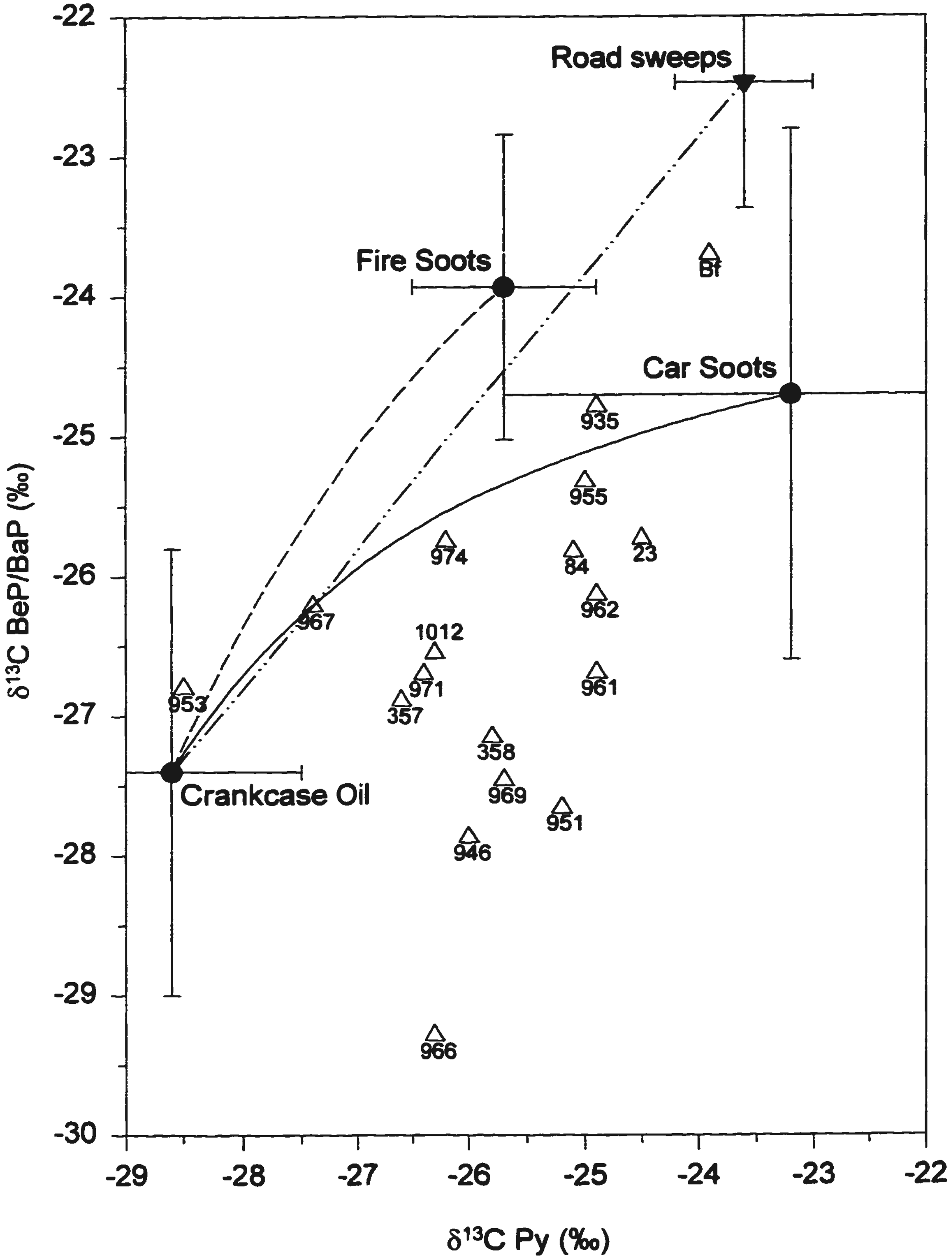

-22
-23
-24
-25
-26
-27
-28
-29
δ13C BbF/BkF (‰)
-29
-28
-27
-26
-25
-24
-23
-22
δ13C Py (‰)
Road sweeps
Bf
1021
955
23
946
935
Car Soots
Fire Soots
357
84
974
962
951
961
967
971
969
953
358
945
966
Crankcase Oil

Figure 4.2.11 Samples and prominent primary and secondary sources on BeP/BaP vs. Fa plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.



Road sweeps
Fire Soots
Car Soots
Crankcase Oil
Bf
935
955
23
84
974
962
967
1012
971
961
953
357
358
969
951
946
966
-22
-23
-24
-25
-26
-27
-28
-29
-30
-29
-28
-27
-26
-25
-24
-23
δ13C BeP/BaP (‰)
δ13C Fa (‰)

Figure 4.2.12 Samples and prominent primary and secondary sources on BeP/BaP vs. Py plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.



Road sweeps
Fire Soots
Car Soots
Crankcase Oil
Bf
935
955
974
84
23
967
962
1012
953
971
961
357
358
969
951
946
966
-22
-23
-24
-25
-26
-27
-28
-29
-30
-29
-28
-27
-26
-25
-24
-23
-22
δ13C BeP/BaP (‰)
δ13C Py (‰)

Figure 4.2.13 Samples and prominent primary and secondary sources on BeP/BaP vs. BbF/BkF plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.

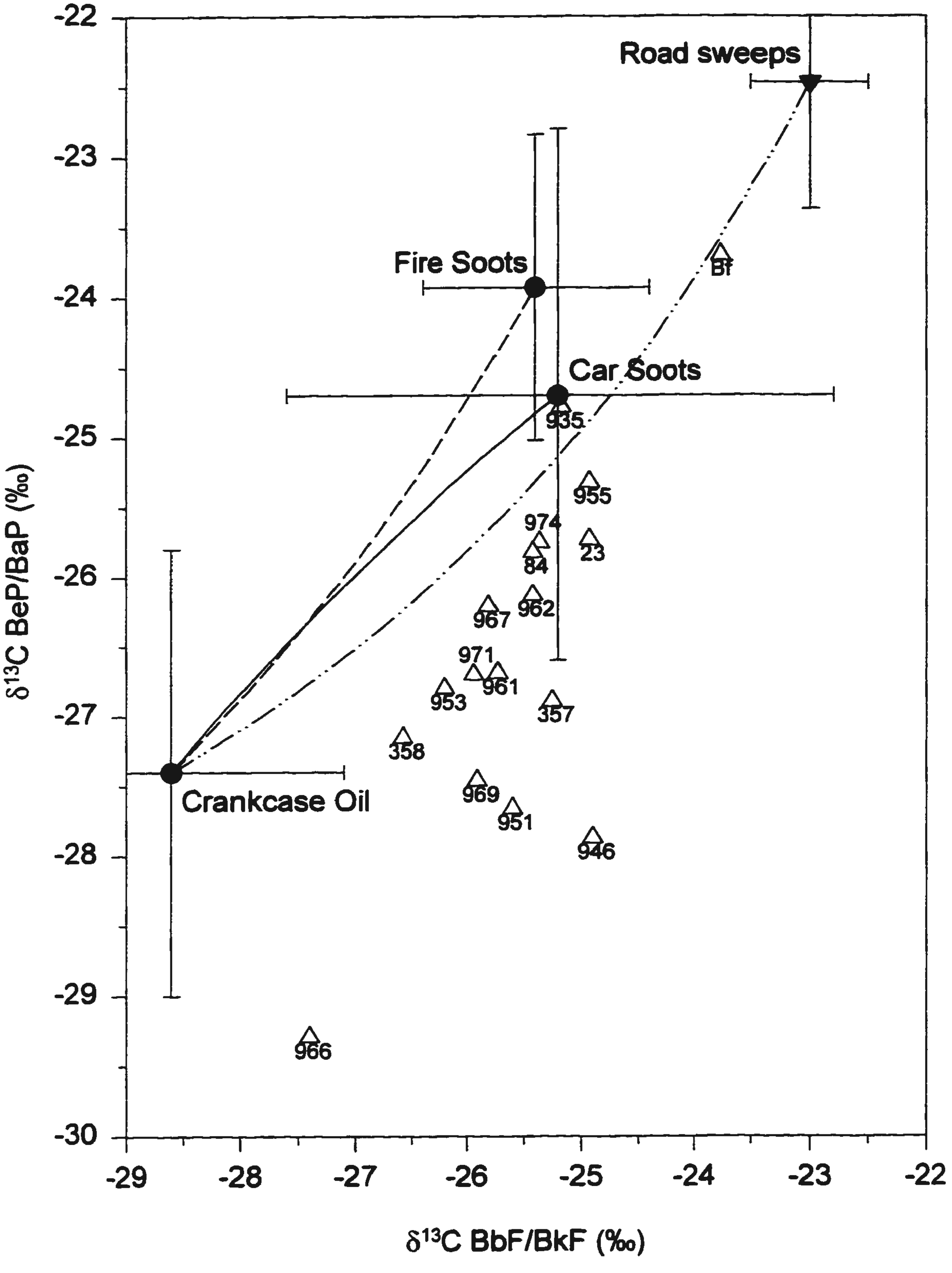

Road sweeps
Fire Soots
Car Soots
Crankcase Oil
Bf
935
955
974
23
84
962
967
971
961
953
357
358
969
951
946
966
-22
-23
-24
-25
-26
-27
-28
-29
-30
-29
-28
-27
-26
-25
-24
-23
-22
δ^{13}C BeP/BaP (‰)
δ^{13}C BbF/BkF (‰)

Figure 4.2.14 Samples and prominent primary and secondary sources on BeP/BaP vs. BA/Chy plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.

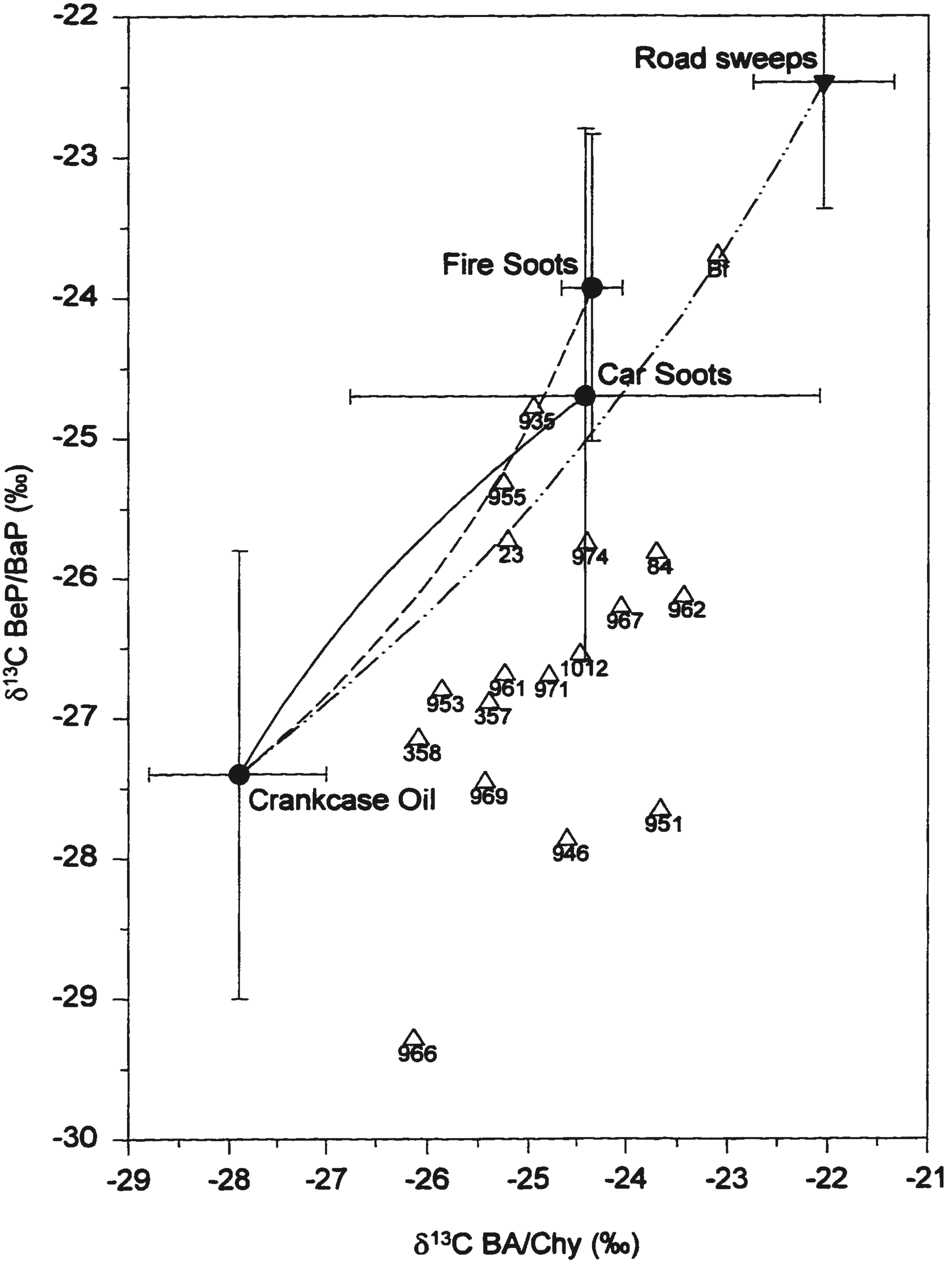
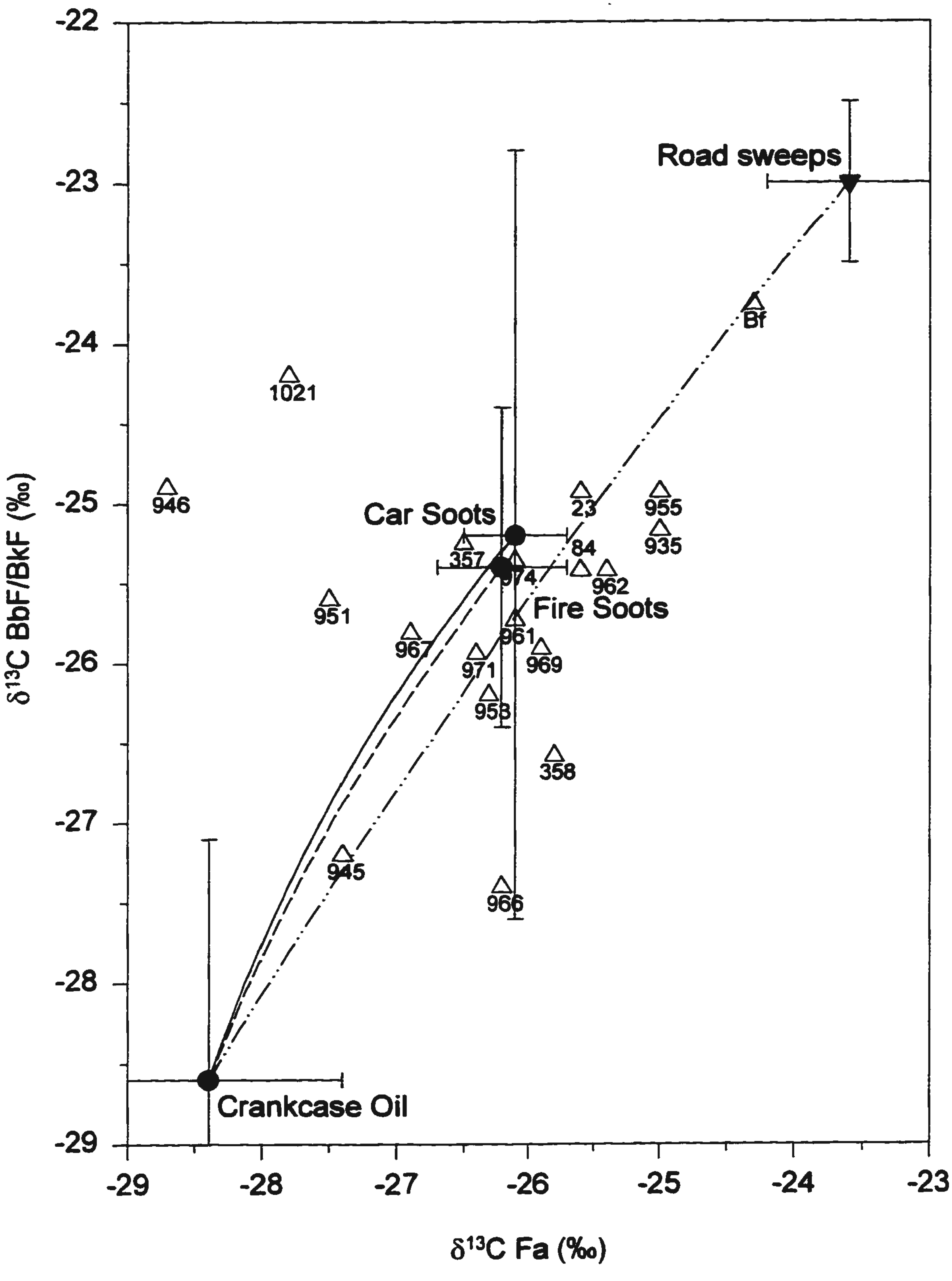
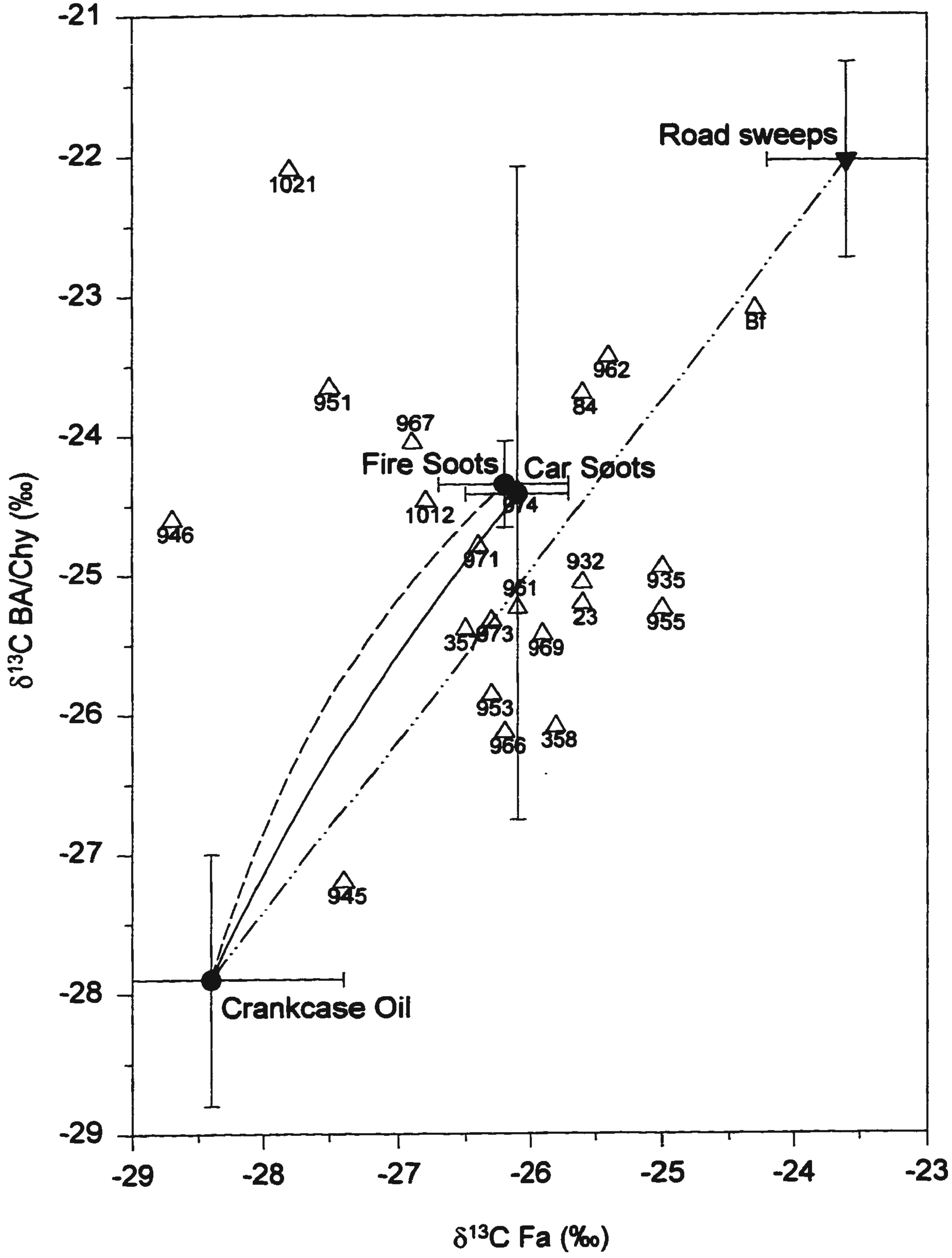

Road sweeps
Fire Soots
Car Soots
Crankcase Oil
Bf
935
955
23
974
84
962
967
1012
961
971
953
357
358
969
951
946
966
-22
-23
-24
-25
-26
-27
-28
-29
-30
-29
-28
-27
-26
-25
-24
-23
-22
-21
$\delta^{13}C$ BeP/BaP (‰)
$\delta^{13}C$ BA/Chy (‰)

Figure 4.2.15 Samples and prominent primary and secondary sources on BbF/BkF vs. Fa plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.



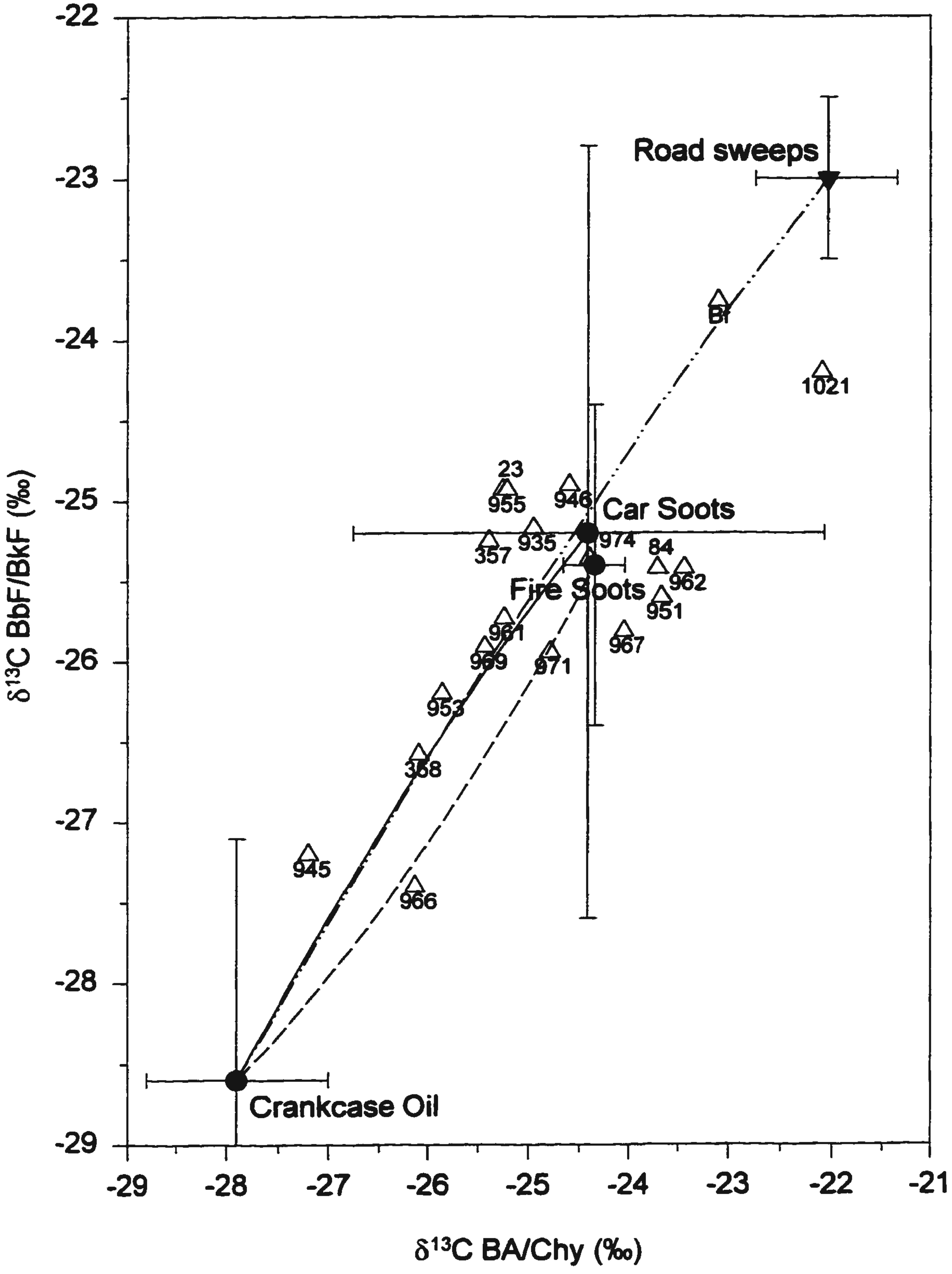
-22
-23
-24
-25
-26
-27
-28
-29
δ13C BbF/BkF (‰)
-29
-28
-27
-26
-25
-24
-23
δ13C Fa (‰)
Road sweeps
Bf
1021
946
Car Soots
23
955
84
935
357
974
962
Fire Soots
951
961
967
969
971
958
358
945
966
Crankcase Oil

Figure 4.2.16 Samples and prominent primary and secondary sources on BA/Chy vs. Fa plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.



-21
-22
-23
-24
-25
-26
-27
-28
-29
δ13C BA/Chy (‰)
-29
-28
-27
-26
-25
-24
-23
δ13C Fa (‰)
Road sweeps
Fire Soots
Car Soots
Crankcase Oil
1021
951
967
1012
946
974
971
932
935
951
23
955
357
973
969
953
966
358
962
84
Bf
945

Figure 4.2.17 Samples and prominent primary and secondary sources on BbF/BkF vs. BA/Chy plot. Mixing curves are generated using normalized concentrations (Appendix A3) and isotopic values (Appendix A4) in the two component mixing model described in Appendix A7. The error bars represent the range of statistical variations in end-members.



Road sweeps
Bf
1021
23
955
946
Car Soots
935
357
974
84
962
Fire Soots
951
961
969
971
967
953
358
945
966
Crankcase Oil
-22
-23
-24
-25
-26
-27
-28
-29
-29
-28
-27
-26
-25
-24
-23
-22
-21
δ13C BbF/BkF (‰)
δ13C BA/Chy (‰)

towards light values of BeP/BaP in all relevant graphs (Fig. 4.2.11-4.2.14). Station 953 plots outside the range due to extremely light isotopic composition of Py observed in the sample (Fig. 4.2.10). Samples from stations 946 and 1021 are shifted towards isotopically depleted Fa (Fig. 4.2.8, 4.2.11, 4.2.15, 4.2.16) and/or heavier isotopic values for BA/Chy (Fig. 4.2.16, 4.2.17).

Most samples demonstrate predominance of combustion-produced PAH. However, the influence of petroleum-related sources may be very important at some sites. Station 946 and 951 fall within the range of statistical variation for the crankcase oil end member on the BeP/BaP vs. Fa plot (Fig. 4.2.11). Station 953 is found within the oil range on the BeP/BaP vs. Py graph (Fig. 4.2.12). This station also plots closer to the crankcase oil end member on the BeP/BaP vs. Fa, BA/Chy, BFl (Fig. 4.2.11, 4.2.13, 4.2.14) and BA/Chy vs. Py (Fig. 4.2.9) graphs indicating petroleum contribution of 50-60%. The plots for BFl vs. BA/Chy (Fig. 4.2.17) and BFl, BA/Chy vs. Fa (Fig. 4.2.15, 4.2.16) show that for stations 945, and 966 contribution of petroleum sources might be over 50%. Another station that indicates significant (40-60%) petroleum contribution is 967 (Fig. 4.2.10-4.2.13). The station at Detroit (971) consistently demonstrates 20-30% of petroleum derived PAH (Fig. 4.2.8-4.2.17). At Cleveland (955) petroleum input is reduced to 10-20% and mostly demonstrated by higher molecular weight compounds, Chy/BA and BeP/BaP vs. Py (Fig. 4.2.9, 4.2.12). The only graph including the station at Wheatley (Py vs. Fa) indicates that as much as 30% of compounds could have been produced from petroleum related sources.

It is difficult to differentiate between the relative importance of car soot and fire soot end members. As the car soot member demonstrates the widest range of statistical variation, it always overlaps with the range for fire soots. However, an increased influence of road sweeps can be established for a number of stations. For example, the station at Buffalo consistently plots closer to the crankcase oil-road sweep mixing curve (Fig. 4.2.8, 4.2.11, 4.2.13-4.2.17). The graphs demonstrate that as much as 80-90% of PAH at this station derive from this secondary source. Contribution from the road sweeps may also be important at sites 955, 84, 962, 23, and 935 (Fig. 4.2.8, 4.2.11, 4.2.15, 4.2.16).

To conclude, the PAH assemblage in most samples can be attributed to mixing of four primary and secondary sources. However, there are a few stations (especially 1021, 946, 966) where previously unidentified sources might influence the isotopic composition of PAH. The contribution from combustion sources seem to be predominant throughout the lake. Nevertheless, petroleum sources are important at some stations in the Western Basin and the northern part of the Central Basin. Finally, at stations located closer to the southern shore in the Central and Eastern Basins, the contribution of road sweeps can also be important (955, 84, 962, 23, and 935). This importance is especially well seen at Buffalo where it is close to 100%.

4.2.2.3 PCA for isotopic composition (source identification)

As in the case with molecular composition, the final step to generalization of results was made through application of multivariate statistics (Appendix B4; for more information see Section 3.2.2). A principal component analysis was performed on $\delta^{13}C$ values of 4-, 5-ring compounds with known signatures for primary and secondary sources (Fa, Py, BA/Chy, BbF/BkF, BeP/BaP). In this analysis, the 3 first PCs explained 92.9% of total variance in samples.

The first PC (66.4%) explained simultaneous changes in isotopic composition of all utilized compounds (Fig. 4.2.18). Road sweeps together with car soots and fire soots and crankcase oil are the extremes here (Fig. 4.2.19a). Therefore, this PC represents relative contribution of combustion and petroleum sources in samples. The station at Buffalo again demonstrates close affinity to open road sweeps and combustion sources. Further, stations 955 (off Cleveland), 962, 935, 84, and 23 are found strictly within the combustion range, while station at Detroit (971) and other stations of the Western Basin demonstrate a shift towards the petroleum source. The position closest to petroleum is occupied by stations 945, 966, 953, and Wh.

The second PC (16%) is attributed to an opposition in isotopic composition of Fa+Py. to BA/Chy+BFl (Fig. 4.2.18). This component represents deviation of samples from the major primary and secondary sources (Fig. 4.2.19b). All sources are lumped together in the vicinity of zero indicating well balanced isotopic composition for these compounds. Only two stations, 946 and 1021 are located in the range of extreme positive values and thus demonstrate significant deviation from the sources. This deviation indicates that BA/Chy and BFl are isotopically enriched in these samples while Fa and Py are characterized by light isotopic values.

Figure 4.2.18 Weights of variables (compounds) in 3 first PCs extracted by PCA utilizing $\delta^{13}C$ values of 5 selected 4-, 5-ring PAH (Fa, Py, BA/Chy, BbF/BkF, BeP/BaP), with primary and secondary sources included. Three first PCs explained 92.9% of total variance in samples. The error bars represent the range of statistical variations in end-members.

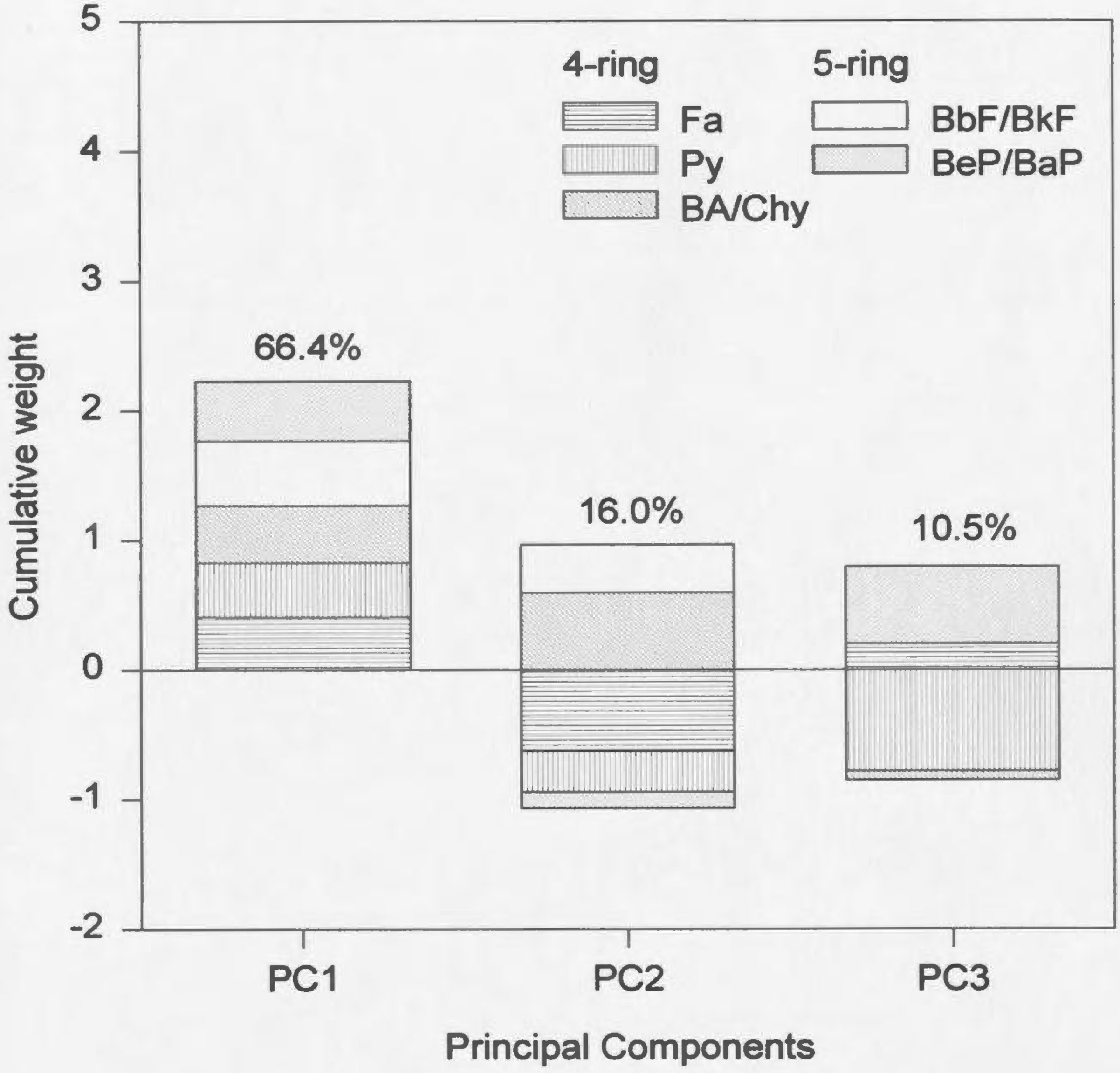
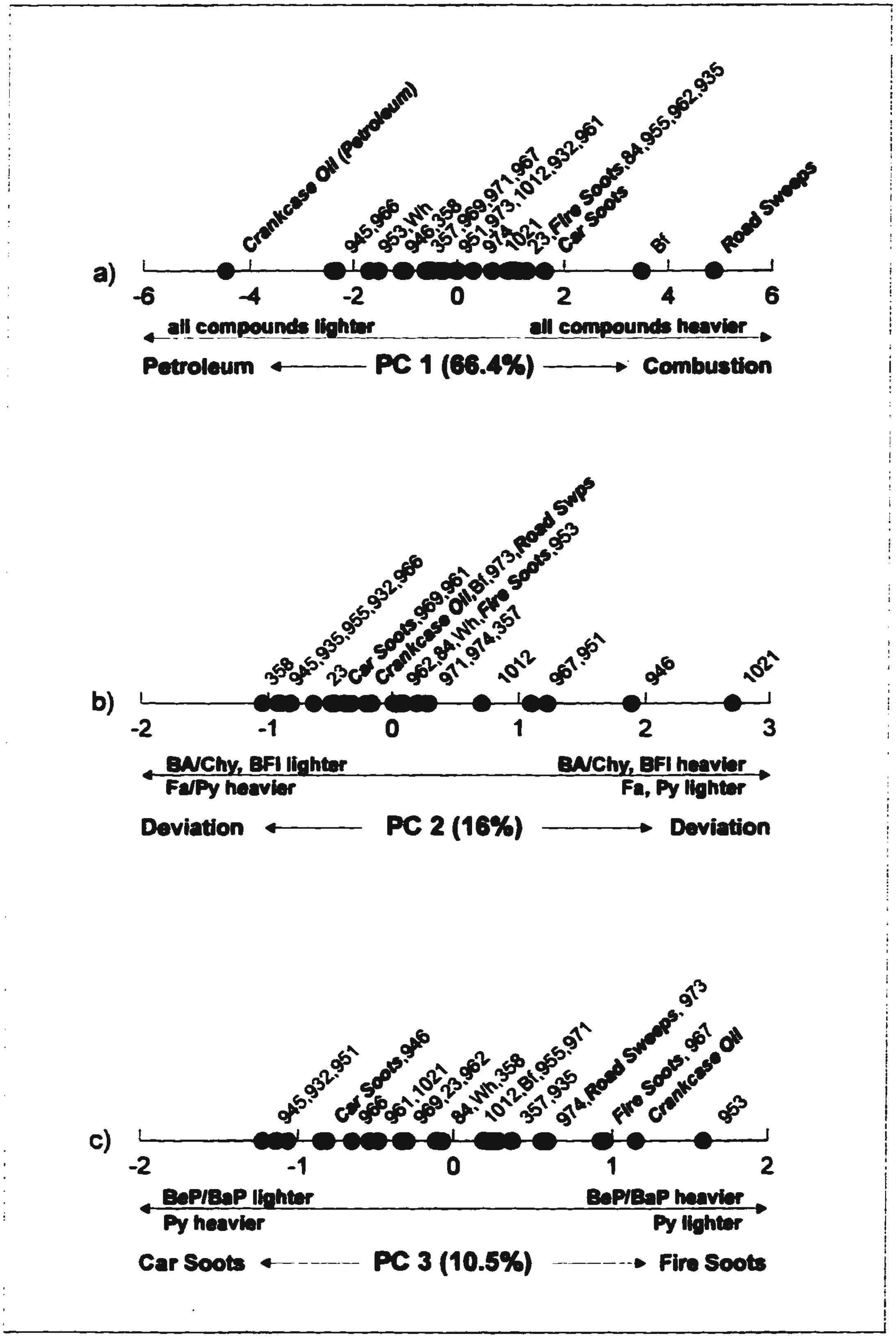

5
4
3
2
1
0
-1
-2
Cumulative weight
4-ring
5-ring
Fa
Py
BA/Chy
BbF/BkF
BeP/BaP
66.4%
16.0%
10.5%
PC1
PC2
PC3
Principal Components

Figure 4.2.19 Distribution of samples and primary and secondary sources along **(a)** 1st PC, **(b)** 2nd PC, and **(c)** 3rd PC identified by PCA utilizing $\delta^{13}C$ values for five selected 4-, 5-ring PAH (Fa, Py, BA/Chy, BbF/BkF, BeP/BaP). Three first PCs explained 92.9% of total variance.


a)
Crankcase Oil (Petroleum)
945,966
953,Wh
946,358
357,969,971,967
951,973,1012,932,961
974
1021
23,Fire Soots,84,955,962,935
Car Soots
Bf
Road Sweeps
-6
-4
-2
0
2
4
6
all compounds lighter
all compounds heavier
Petroleum
PC 1 (66.4%)
Combustion
b)
358
945,935,955,932,966
23
Car Soots,969,961
Crankcase Oil,Bf,973,Road Swps
962,84,Wh,Fire Soots,953
971,974,357
1012
967,951
946
1021
-2
-1
0
1
2
3
BA/Chy, BFl lighter
Fa/Py heavier
BA/Chy, BFl heavier
Fa, Py lighter
Deviation
PC 2 (16%)
Deviation
c)
945,932,951
Car Soots,946
966
961,1021
969,23,962
84,Wh,358
1012,Bf,955,971
357,935
974,Road Sweeps, 973
Fire Soots, 967
Crankcase Oil
953
-2
-1
0
1
2
BeP/BaP lighter
Py heavier
BeP/BaP heavier
Py lighter
Car Soots
PC 3 (10.5%)
Fire Soots

Another 10.5% of variance is explained by the third PC which mostly represents variations in $\delta^{13}C$ of Py (Fig. 4.2.18). As isotopic composition of Py is different in the two primary combustion sources (O'Malley, 1994) this component allows a better insight into their relative contribution to the PAH assemblage in samples (Fig. 4.2.19c). The distribution of samples along the axis shows that both combustion sources are important at most sites. The major cities (971, 955 and Bf) are of primary interest here. These samples show almost equal contribution from car emissions and fire places.

In summary, the results of PCA confirm the pattern seen in previous analyses. Station at Buffalo shows close affinity to combustion sources and open road sweeps. Further, a number of stations, 955 (off Cleveland), 962, 84, 935, and 23, was found to group together close to the combustion range. The station at Detroit (971) and most other stations in the Western Basin show significant contribution of petroleum-related sources. However, this contribution is especially strong at stations 945, 966, 953, and Wh located in the northern part of the lake. Stations 1021 and 946, previously shown to deviate from the mixing curves, are also shifted away from the primary sources on PC 2 indicating isotopically light lower molecular weight compounds (Fa, Py) and heavy BA/Chy, BFl. This points to presence of an additional source close to these stations. Finally, isotopic composition of Py (PC 3) shows that PAH assemblage at all cities is characterized by almost equal contribution of car soots and fire soots.

5. DISCUSSION

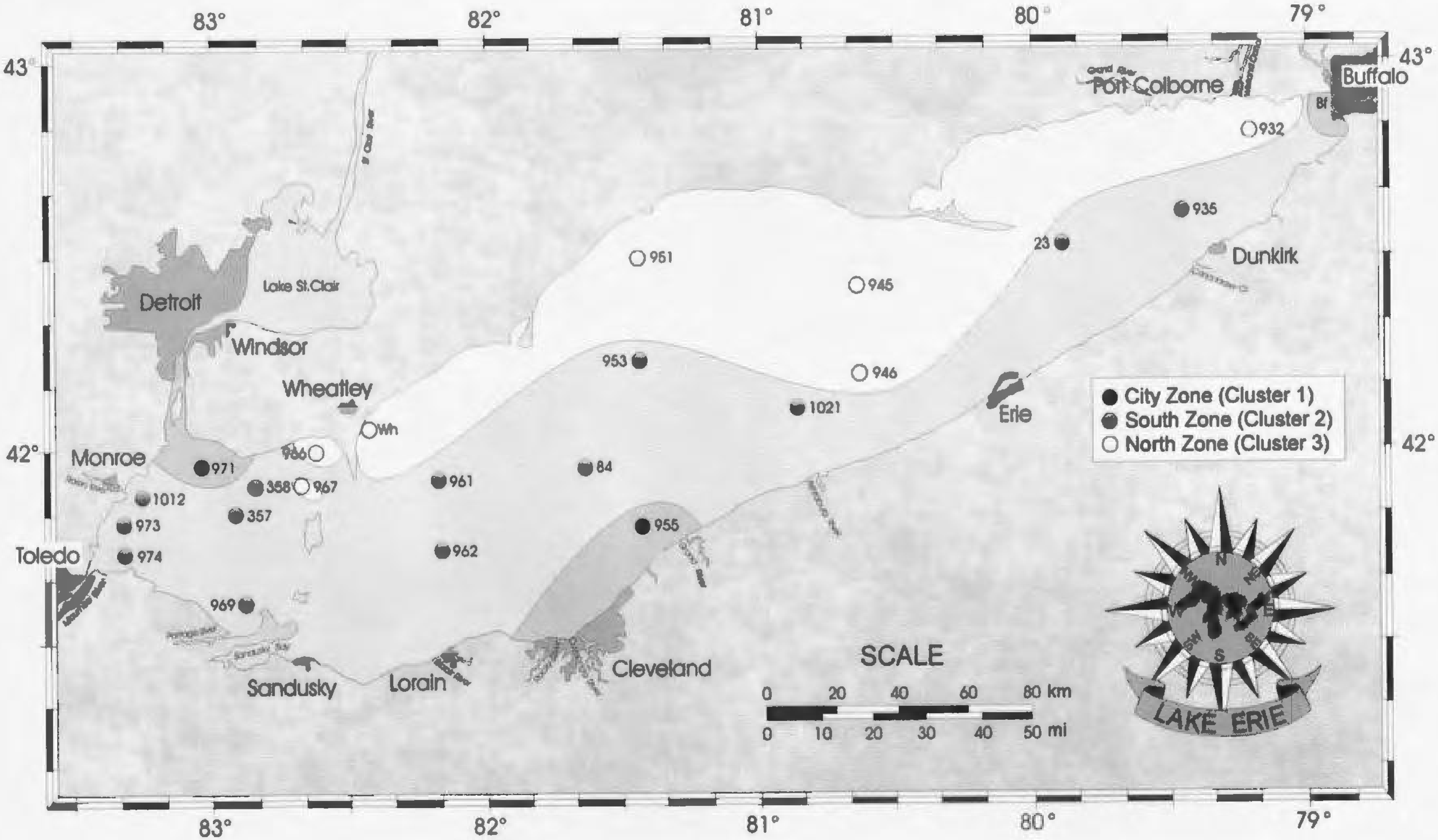
5.1 SPATIAL DISTRIBUTION

The patterns of spatial distribution emerging from the independent analyses of molecular and isotopic data exhibit strong resemblance. The lengthwise profiles showed that the lake can be split into three distinct zones with regard to both molecular and isotopic signatures. In addition, both principal components analyses showed that a certain crosswise pattern separating northern and southern stations exists in the central part of the lake. A generalized two dimensional pattern was statistically generated by clustering three principal components extracted from both molecular and isotopic data sets. A detailed description of the approach to the clustering procedure can be found in the chapter dealing with methods (Section 3.2.2). Prior to the analysis, the components were weighted with respect to the percentage of variance explained in each PCA (Appendix C1). The output of cluster analysis, which employed the non-hierarchical (K-means) technique, is presented in Appendix C1 and reproduced in Table 5.1.1. Sites associated with the identified clusters form three prominent zones which were named according to their relative position and proximity to the major industrial centers: the City Zone, the South Zone, and the North Zone (Fig. 5.1.1). Within each of these zones, the molecular and isotopic composition of PAH are broadly similar and can be interpreted in terms of transport and redistribution by primary and secondary circulation of lake contamination (introduced largely through fluvial input at major cities) superimposed on

Table 5.1.1 Three clusters identified by the non-hierarchical (K-means) clustering utilized for grouping of the first principal components extracted from molecular and isotopic data sets in the analysis of spatial distribution pattern. See also Appendix C1 (columns 0 and 8).

Stations	Clusters	Zones
St 971 St 955 Bf	1	City zone
St 974 St 973 St 1012 St 969 St 357 St 358 St 962 St 961 St 84 St 953 St 1021 St 23 St 935	2	South zone
St 967 St 966 Wh St 951 St 946 St 945 St 932	3	North zone

Figure 5.1.1 Zones coinciding with the three clusters identified by the non-hierarchical (K-means) clustering of first principal components previously extracted from molecular and isotopic data sets in the analysis of spatial distribution pattern.


83°
82°
81°
80°
79°
43°
42°
Buffalo
Bf
Port Colborne
932
935
23
Dunkirk
951
945
946
953
1021
Erie
Detroit
Lake St.Clair
Windsor
Wheatley
Wh
Monroe
971
986
358
967
1012
973
357
974
Toledo
961
84
955
962
969
Sandusky
Lorain
Cleveland
SCALE
0
20
40
60
80 km
0
10
20
30
40
50 mi
● City Zone (Cluster 1)
● South Zone (Cluster 2)
○ North Zone (Cluster 3)
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

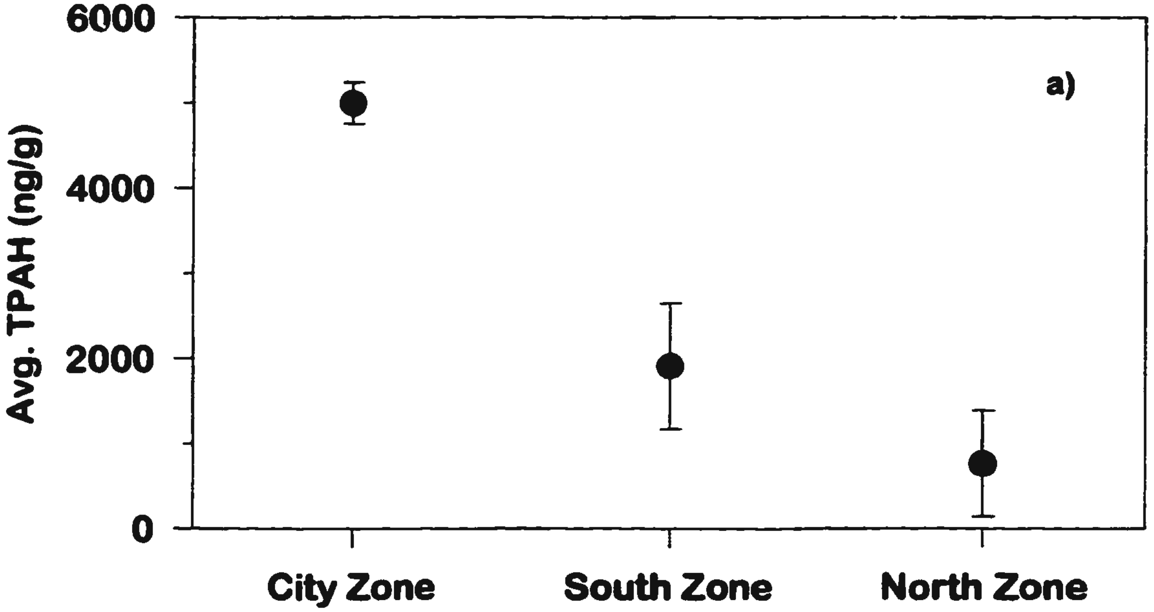
more pervasive background signature. Some compounds can also be generated internally, within the lake itself.

5.1.1 THE CITY ZONE

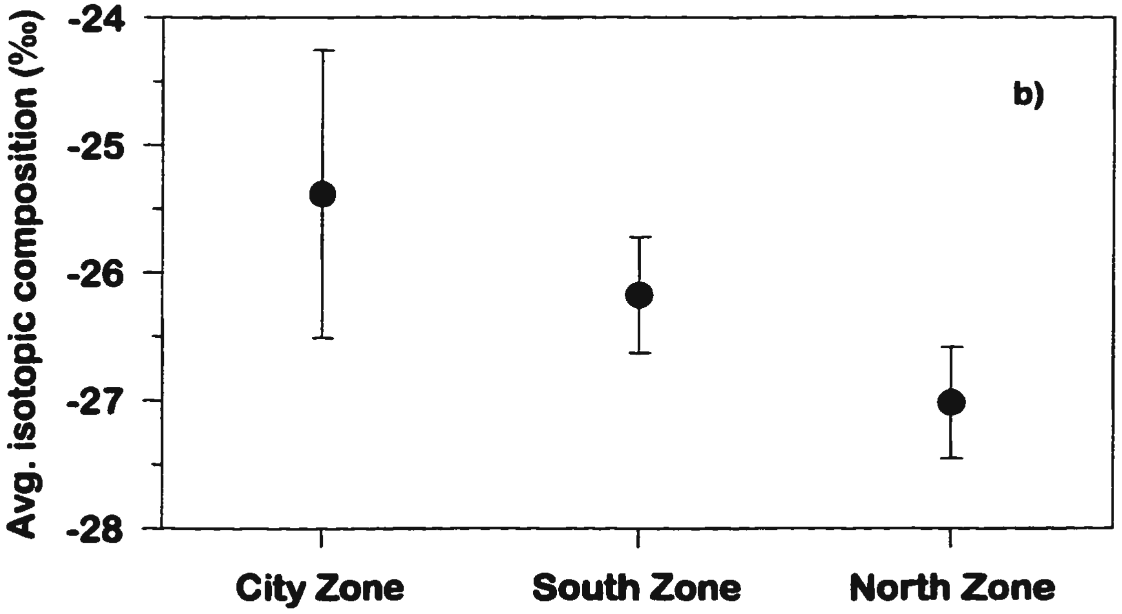
The City Zone (Cluster 1) consists of stations 971, 955, and Bf. The cluster is generally characterized by the highest levels of PAH contamination (avg. TPAH=4997.17 ng/g; σ=297.69 ng/g; Fig. 5.1.2a, 5.1.3) and the heaviest in the lake isotopic values (avg. mean $\delta^{13}C$=-25.38‰; σ=1.13‰; Fig. 5.1.2b, 5.1.4). There are within-cluster variations, the most noticeable of which is the light isotopic values at station 971(Detroit) relative to those at sites 955 (Cleveland) and especially Bf (Buffalo; Fig. 5.1.4; see also Fig. 4.1.5, 4.1.8a and Section 4.1.1). The station at Detroit was included into this cluster primarily due to the very high level of PAH contamination, a major characteristic feature of this cluster (Fig. 5.1.3; see also Fig. 4.1.1, 4.1.4a and Section 4.1.1). Another noticeable deviation is the somewhat different molecular signature at Bf from that at stations 971 and 955 as indicated by the concentration profiles and principal components analysis of molecular composition (Fig. 4.1.1, 4.1.4b, 5.1.3). Cluster 1 was probably formed by sediments directly deposited by the fluvial outflow at the three major cities, Detroit, Cleveland and Buffalo.

At station 971 the fluvial influence is suggested by the location of the site. The sample was collected approximately 10 kilometers south-east of the mouth of the Detroit River. The major flow of the river discharging tremendous volume of water (5,800 m^3s^{-1})

Figure 5.1.2 Average and range (± standard deviation) of **(a)** total PAH concentration and **(b)** mean isotopic composition for three zones identified by clustering in the analysis of spatial distribution.



a)
Avg. TPAH (ng/g)
6000
4000
2000
0
City Zone
South Zone
North Zone



b)
Avg. isotopic composition (‰)
-24
-25
-26
-27
-28
City Zone
South Zone
North Zone

Figure 5.1.3 Zones (clusters) in the space formed by 3 first PCs for molecular composition extracted in the analysis of spatial distribution.

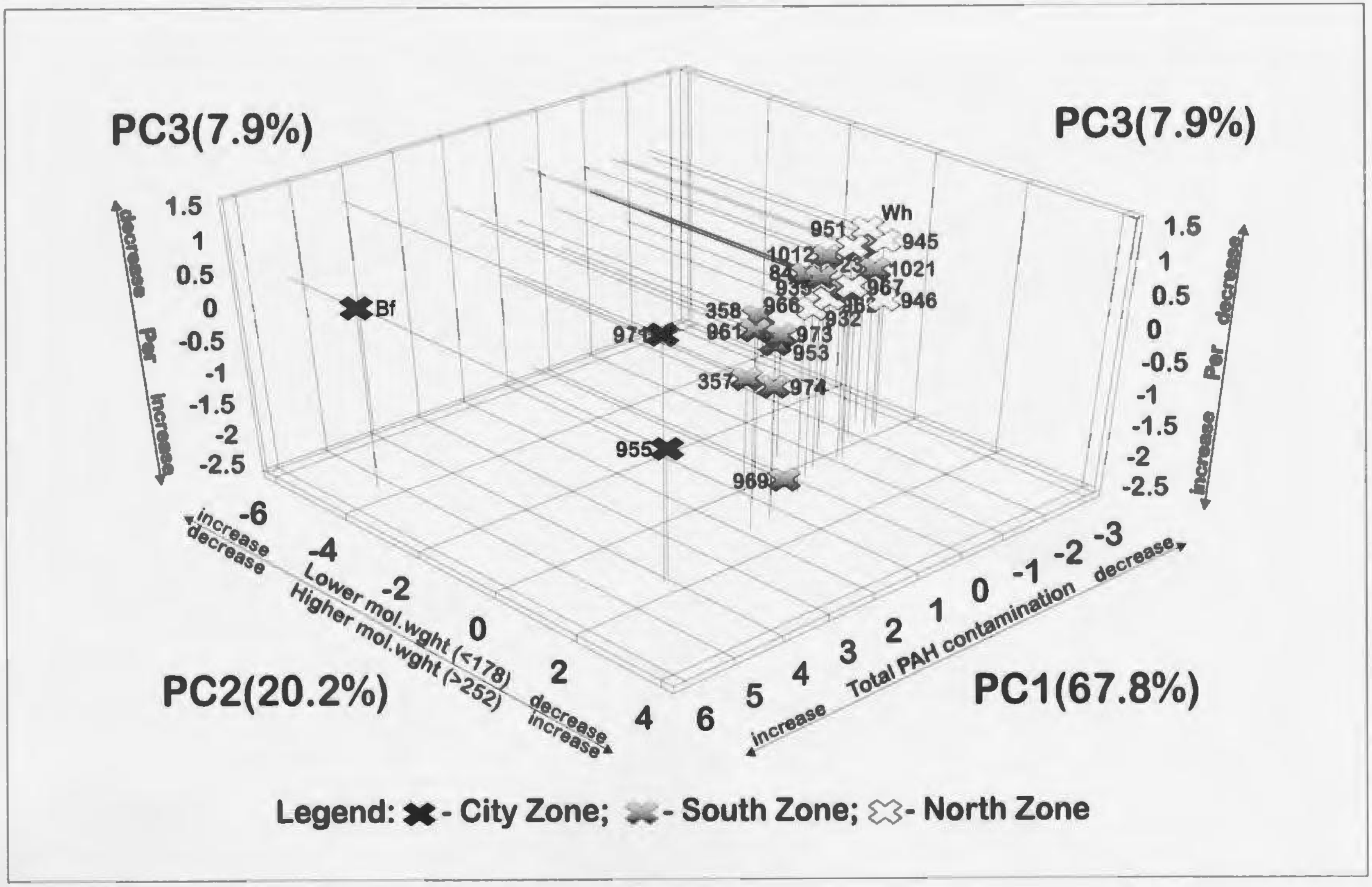
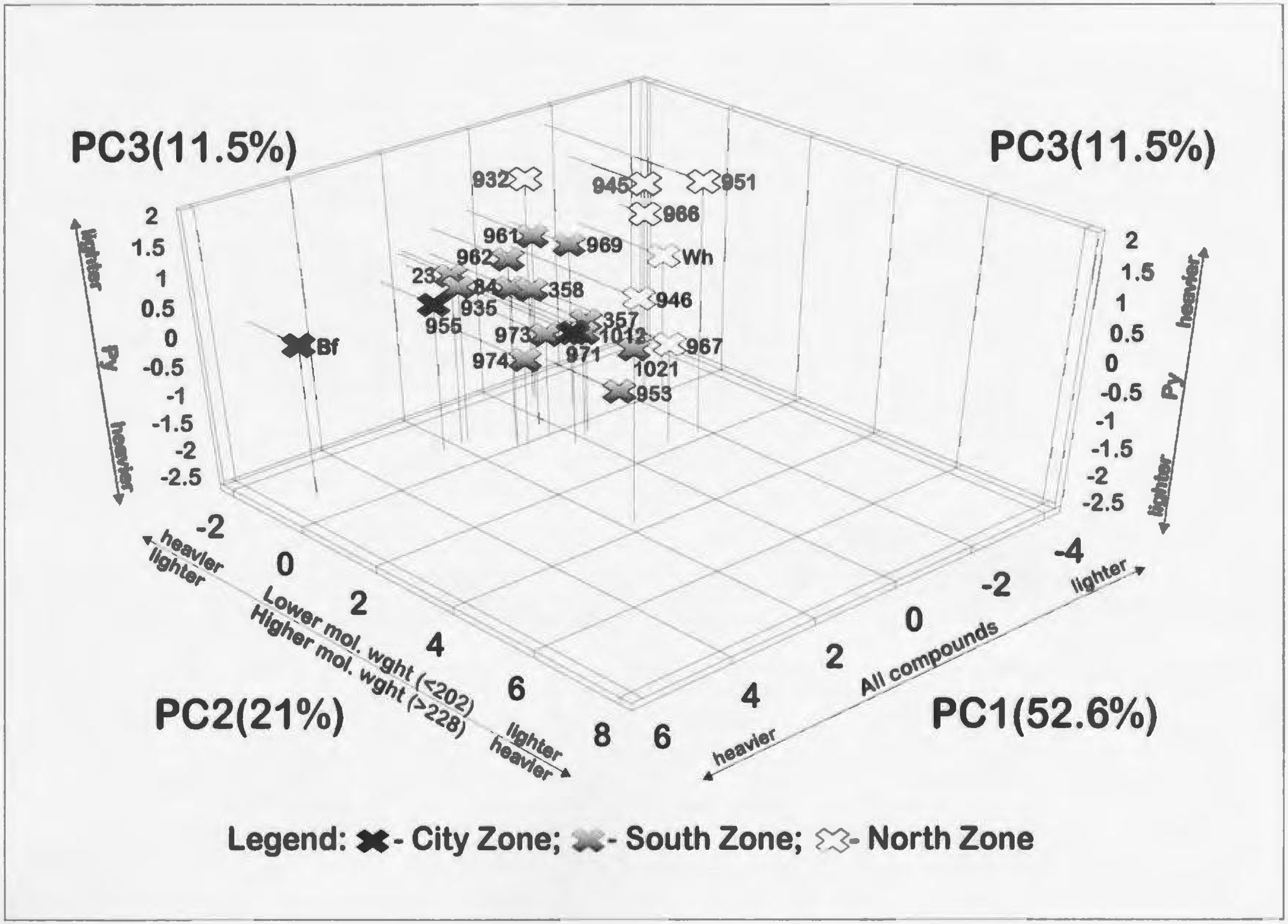

PC3(7.9%)
PC3(7.9%)
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
decrease Per increase
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
increase Per decrease
Bf
Wh
951
945
1012
23
1021
84
935
967
966
962
946
358
932
971
961
973
953
357
974
955
969
-6
-4
-2
0
2
4
increase
decrease
Lower mol.wght (<178)
Higher mol.wght (>252)
decrease
increase
PC2(20.2%)
6
5
4
3
2
1
0
-1
-2
-3
increase
Total PAH contamination
decrease
PC1(67.8%)
Legend: ✖ - City Zone; ✖ - South Zone; ✖ - North Zone

Figure 5.1.4 **Zones (clusters) in the space formed by 3 first PCs for isotopic composition extracted in the analysis of spatial distribution.**


PC3(11.5%)
PC3(11.5%)
PC2(21%)
PC1(52.6%)
lighter
Py
heavier
heavier
Py
lighter
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
heavier
lighter
Lower mol. wght (<202)
Higher mol. wght (>228)
lighter
heavier
-2
0
2
4
6
8
6
4
2
0
-2
-4
heavier
All compounds
lighter
932
945
951
966
961
969
962
Wh
23
84
358
955
935
946
357
973
1012
967
Bf
974
971
1021
953
Legend: ✖ - City Zone; ✖ - South Zone; ✖ - North Zone

is diverted in this direction (Fig. 5.1.5). This flow introduces as much as 1.4 x 10^6 metric tons per year of sediment into the lake (Kemp *et al.* 1976). The particles injected with the flow were found highly contaminated with different organic pollutants (Carter and Hites, 1992). Exclusively high rate of deposition in the vicinity of the station (7.4 mm yr^{-1}) has been determined in a study on sedimentation rates (Kemp *et al.*, 1977; Fig. 5.1.6). Thus the extreme level of contamination of rapidly deposited particles may possibly explain the highest PAH concentration observed at this site.

Although station 955 off Cleveland is located somewhat further east from the mouth of the Cuyahoga River (Fig. 3.1.1), strong fluvial input of contaminated sediments can also be suggested here. The Cuyahoga River, is notable for its polluted waters and is considered as an area of environmental concern (*e.g.*, Colbourn *et al.*, 1990). A strong easterly directed flow exists close the Ohio shore at this location (Hamblin, 1971). This flow can easily transport a significant part of suspended sediment load introduced by the river along the southern shore to deposit it a few tens of kilometers east of Cleveland. Kemp *et al.*, (1977) showed that sedimentation rates in the vicinity of this site are the highest in the Central Basin which indicates increased importance of fluvially introduced material (Fig. 5.1.6). Finally, the pollution signal in this area is different from that of Detroit in its isotopic composition (Fig. 5.1.4 see also Fig. 4.1.8a), and thus cannot entirely be attributed to long distance transport of polluted particles from the Western Basin.

Figure 5.1.5 **Direction of the mean surface flow in the western end of Lake Erie as deduced from drift card studies (1892-1967). (After Hamblin, 1971.)**

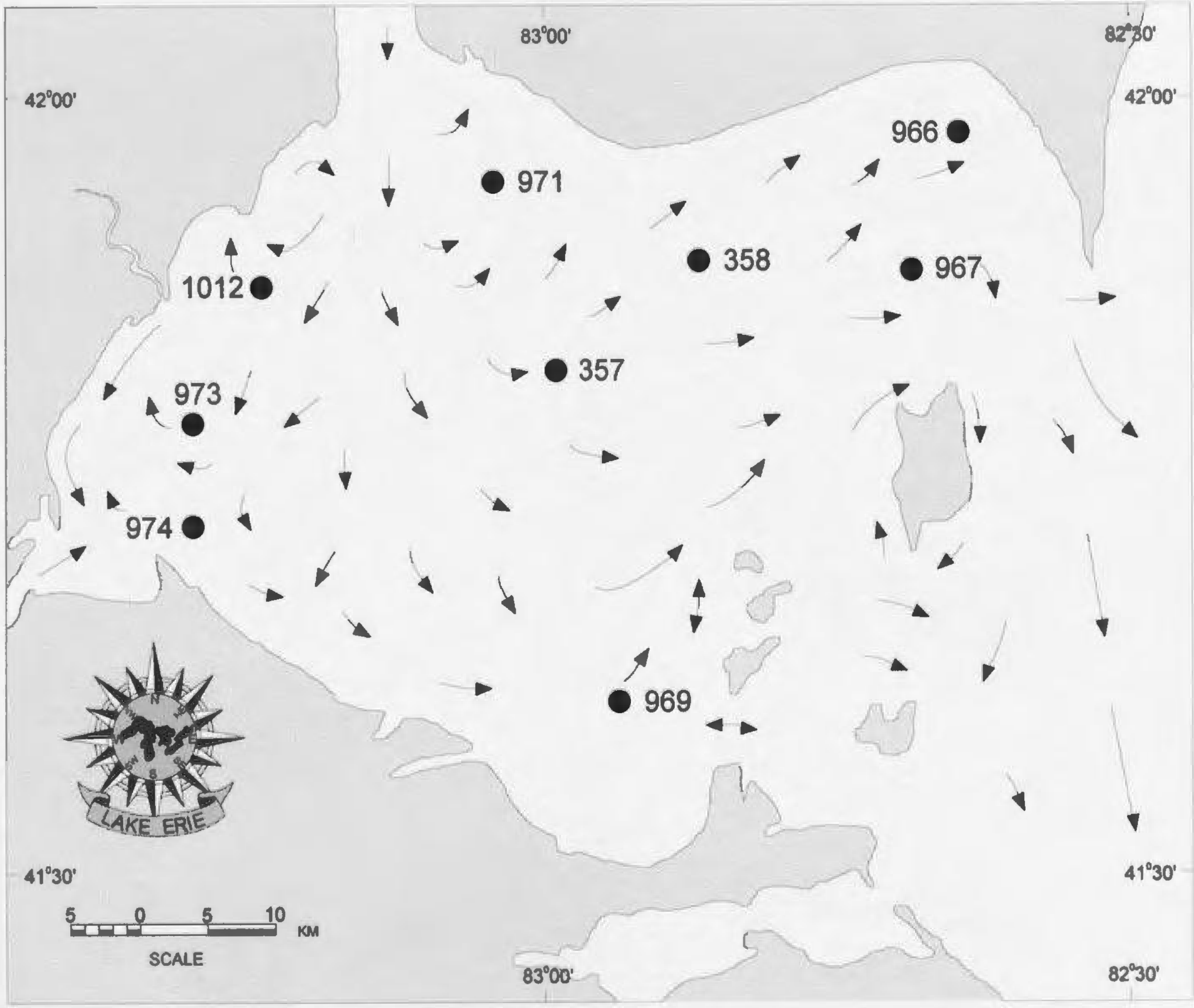
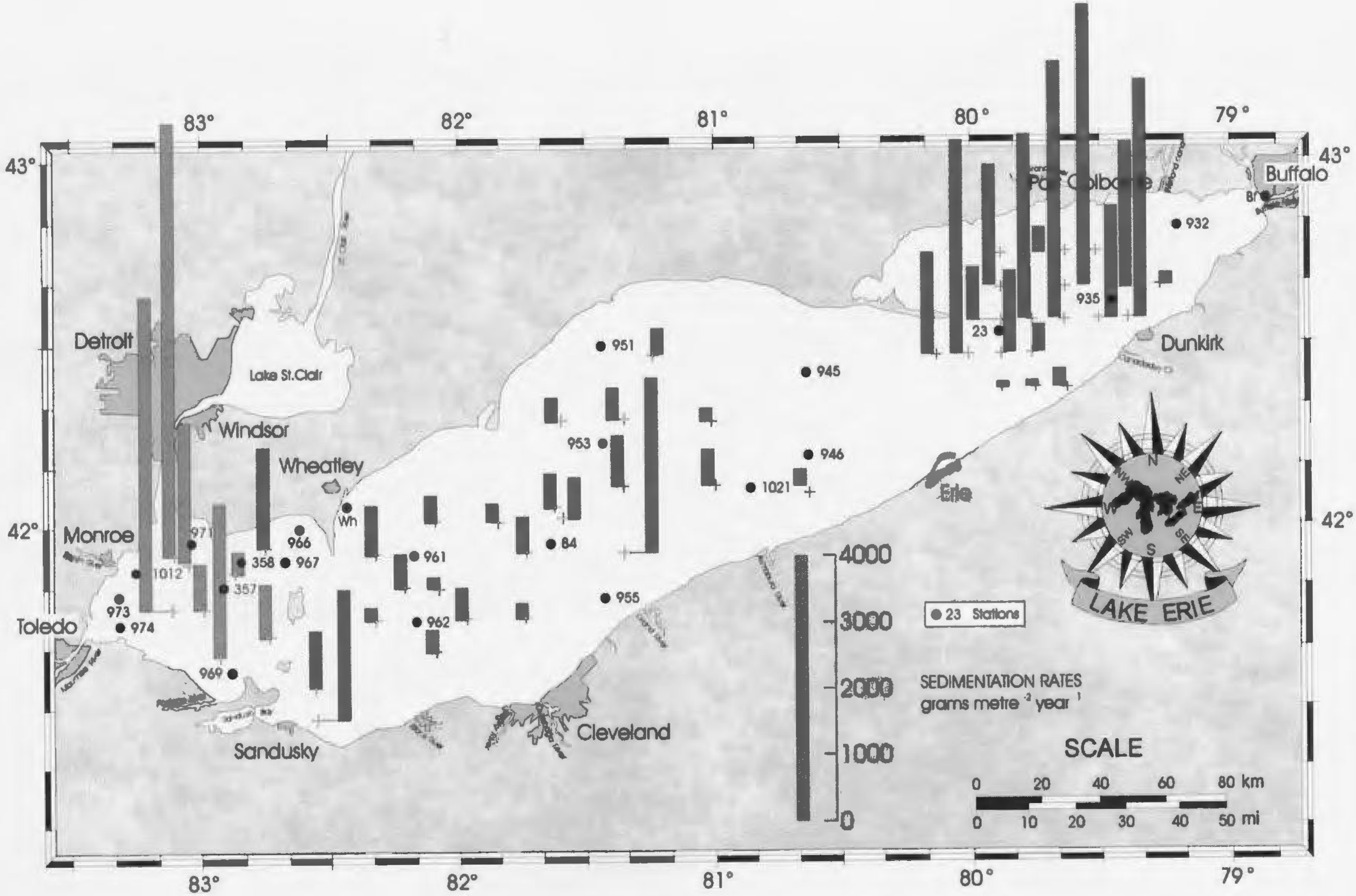

83°00'
82°30'
42°00'
42°00'
966
971
358
967
1012
357
973
974
969
LAKE ERIE
N
S
41°30'
41°30'
5
0
5
10
KM
SCALE
83°00'
82°30'

Figure 5.1.6 Station locations and sedimentation rates after Kemp *et al.* (1977). Note high sedimentation rates in the vicinity of stations 971 (Detroit), 955 (Cleveland) indicating fluvial input of sediment.


83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Wh
Monroe
Toledo
Sandusky
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
BR
951
945
953
946
1021
971
966
358
967
961
84
1012
357
973
974
962
955
969
23
935
932
4000
3000
2000
1000
0
23 Stations
SEDIMENTATION RATES
grams metre -2 year -1
SCALE
0
20
40
60
80 km
0
10
20
30
40
50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

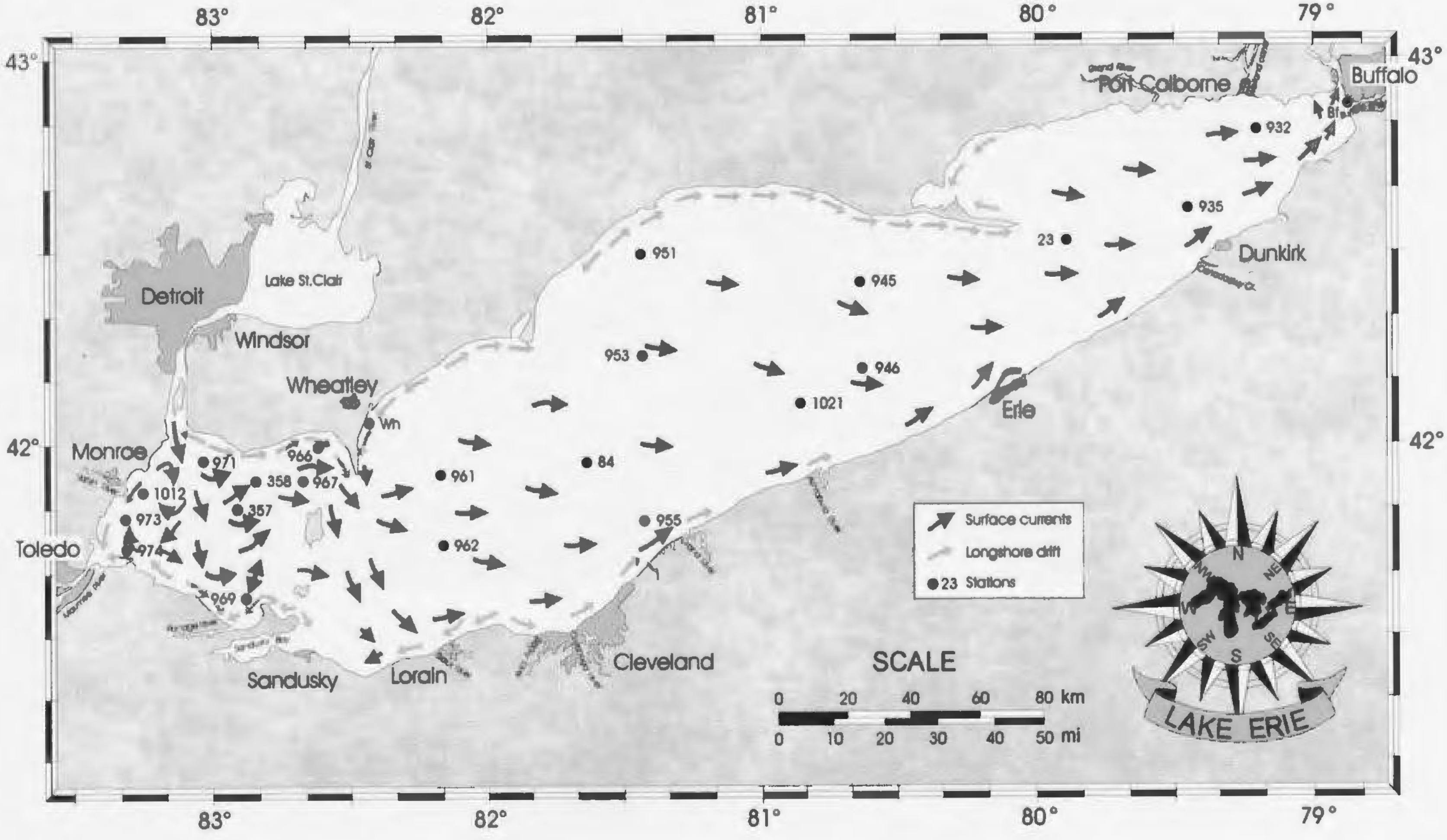
The location of the third station at Buffalo is suggestive of fluvially deposited PAH, possibly originating from direct city runoff. The site is actually located within the mouth of the Buffalo River and thus directly affected by fluvially introduced material. Since the river flows through the highly urbanized area extending to the very shore of the lake, the PAH pollutants might be introduced through direct city runoff. On entering the river the compounds are quickly sorbed on fluvially transported sediment particles, with the largest particles probably settling in quieter areas of the mouth not far from the place of entry. The close locations of PAH origin and deposition presumably results in the specific molecular and isotopic composition of compounds recovered from these sediments (Fig. 5.1.3, 5.1.4). However, these molecular and isotopic signatures are not apparently seen elsewhere in the Eastern Basin. The latter suggests that the polluted outflow of the Buffalo River is entirely diverted by strong hydraulic currents known to exist here (Hamblin, 1971) into the Niagara River and out of the lake.

5.1.2 THE SOUTH ZONE

The South Zone is the largest of three and contains stations 357, 358, 974, 973, 1012, 969, 961, 962, 84, 953, 1021, 23 and 935 separated into Cluster 2. This zone is generally characterized by average PAH concentrations (avg. TPAH=1914 ng/g; σ=768.83 ng/g; Fig. 5.1.2a, 5.1.3) and average isotopic values (avg. mean $\delta^{13}C$=-26.18‰; σ=0.45‰; Fig. 5.1.2b, 5.1.4). The within-cluster fluctuations are mostly attributed to variations in isotopic composition of compounds. The isotopic values at stations close to the mouth of the Detroit river (969, 358, 357) tend to be lighter than those in the Central and Eastern Basins (23, 1021, 935; Fig. 5.1.4; see also Fig. 4.1.8a). The stations 961, 1012, 973, 962, 974. 84 are transitional and demonstrate values close to the average of mean isotopic values (Fig. 5.1.4; see also Fig. 4.1.8a and Section 4.1.2). In addition, station 1021 demonstrates somewhat peculiar isotopic composition characterized by ^{13}C-enriched higher molecular weight compounds (Fig. 4.1.8b, 5.1.4). The only noticeable deviation in molecular composition is unusually high concentration of Per at station 969 (Fig. 5.1.3; see also Fig. 4.1.4c and Section 4.1.1). This cluster apparently was formed by transport and redistribution of diluted pollution signal from the cities by surface and bottom circulation. Some minor deviations from the general pattern can be attributed to the influence of local sources.

The contaminated flow of the Detroit River, spreads in the Western Basin and is partially diverted to the Central Basin. This flow veers in different directions, and might reach as far as the shore of Ohio (Hamblin, 1971). This is consistent with isotopic composition of sites 357, 358, and 969, which is similar to that of the station at Detroit (971: Fig. 4.1.5, 4.1.8a, 5.1.4). Three transitional stations (974, 973, 1012) are found in the basin (Fig. 4.1.8a), and their δ^{13}C values can possibly be attributed to somewhat different isotopic signature introduced by the Maumee and Rasin Rivers. Station 969 exhibits high concentrations of Per (Fig. 4.1.4c), which suggests that it might be affected by some local sources. Further, the major flow of the Detroit River is diverted eastward through the Pelee Passage to eventually enter the Central Basin (Fig. 5.1.5, 5.1.7). On

Figure 5.1.7 Station locations and the pattern of permanent surface circulation after Hamblin (1971) and Ristic and Ristic (1985). Note the easterly directed flow along the southern shore of the lake.


83°
82°
81°
80°
79°
43°
42°
Buffalo
Port Colborne
Grand River
Detroit
Lake St.Clair
Windsor
Wheatley
Wh
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Bf
932
935
23
951
945
953
946
1021
84
961
962
955
971
966
1012
358
967
357
973
974
969
Surface currents
Longshore drift
23 Stations
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

exiting the passage, the flow transporting remaining polluted particles splits into two parts (Fig. 5.1.5). The northern branch is injected eastward to the central part of the lake where the current slows down and deposition of fine sediment particles occurs. The southern branch of the flow crosses the lake and reaches the southern shore just before Cleveland (Hamblin, 1971). The influence of the Detroit River flow is observed as far east as stations 961, 962 and 84, which show isotopic composition close to that at Detroit and other stations in the Western Basin (Fig. 4.1.8a). The suggested pattern coincides with that described by Carter and Hites (1992), who on the basis of mass balance calculations indicated that at least 20% of sediment-bound pollutants originating from the Detroit River accumulate in the Central Basin.

The flow transporting the remaining pollutants from the Detroit River is joined at Cleveland by contaminated sediment load introduced by the Cuyahoga River and this combined flow proceeds further along the southern shore to exit the lake through the Niagra River. Some additional PAH contamination may also be introduced by other minor tributaries entering the lake along the southern shore such as the Black River and the Ashtabula River. Indeed, the major surface current in the Central and Eastern Basin is confined to the southern shore of the lake (Fig. 5.1.7). This current forms the so called 'south shore transportation route for sediment particles' (Thomas and Jaquet, 1976; Thomas *et al.*, 1976).. The transport and deposition along this route is exemplified by isotopic signature of stations 1021, 23, and 935 which show values close to that at Cleveland (955; Fig. 4.1.8a). The transitional isotopic signature of sites 961, 962, and 84

(Fig. 4.1.8a, 5.1.4) can also be attributed to some contribution of the isotopic signal from Cleveland characterized by isotopically heavier compounds. This northerly directed transport of a portion of contaminated sediments might be provided here by the compensatory bottom currents known to exist in the Central Basin (Hamblin, 1971; Fig. 5.1.8). The deviations in the isotopic composition of station 1021 (Fig. 4.1.8b, 5.1.4) can possibly be attributed to the outflow of the Ashtabula River located close to this site. Some temporary patterns of surface circulation can also significantly contribute to the redistribution of fluvially introduced polluted sediments within the Central Basin (Saylor and Miller, 1987; Fig. 5.1.9).

5.1.3 THE NORTH ZONE

The North Zone is formed by stations included in Cluster 3 and located in the northern part of the lake (966, 967, Wh, 951, 946, 945 and 932). The zone is generally characterized by low levels of PAH pollution (avg. TPAH=763.92 ng/g; σ=672.89 ng/g; Fig. 5.1.2a, 5.1.3) and relatively light isotopic composition of compounds (avg. mean $\delta^{13}C$=-27.02‰; σ=0.43‰; Fig. 5.1.2b, 5.1.4). The major within-cluster deviation is demonstrated by station 966. This station is characterized by fairly high level of contamination, characteristic of the majority of stations within the Western Basin (Fig. 4.1.1, 4.1.4a, 5.1.3; see Section 4.1.1). However, its extremely light isotopic composition especially for higher molecular weight compounds ($\delta^{13}C$ for BeP=-29.8‰; $\delta^{13}C$ for BaP=-28.8‰) resulted in its separation into this cluster (see also Fig. 4.1.5, 4.1.8a,b,

Figure 5.1.8 Station locations and direction of bottom currents after Hamblin (1971). Note that the northerly directed compensatory bottom currents do not penetrate to the northernmost parts of the lake.

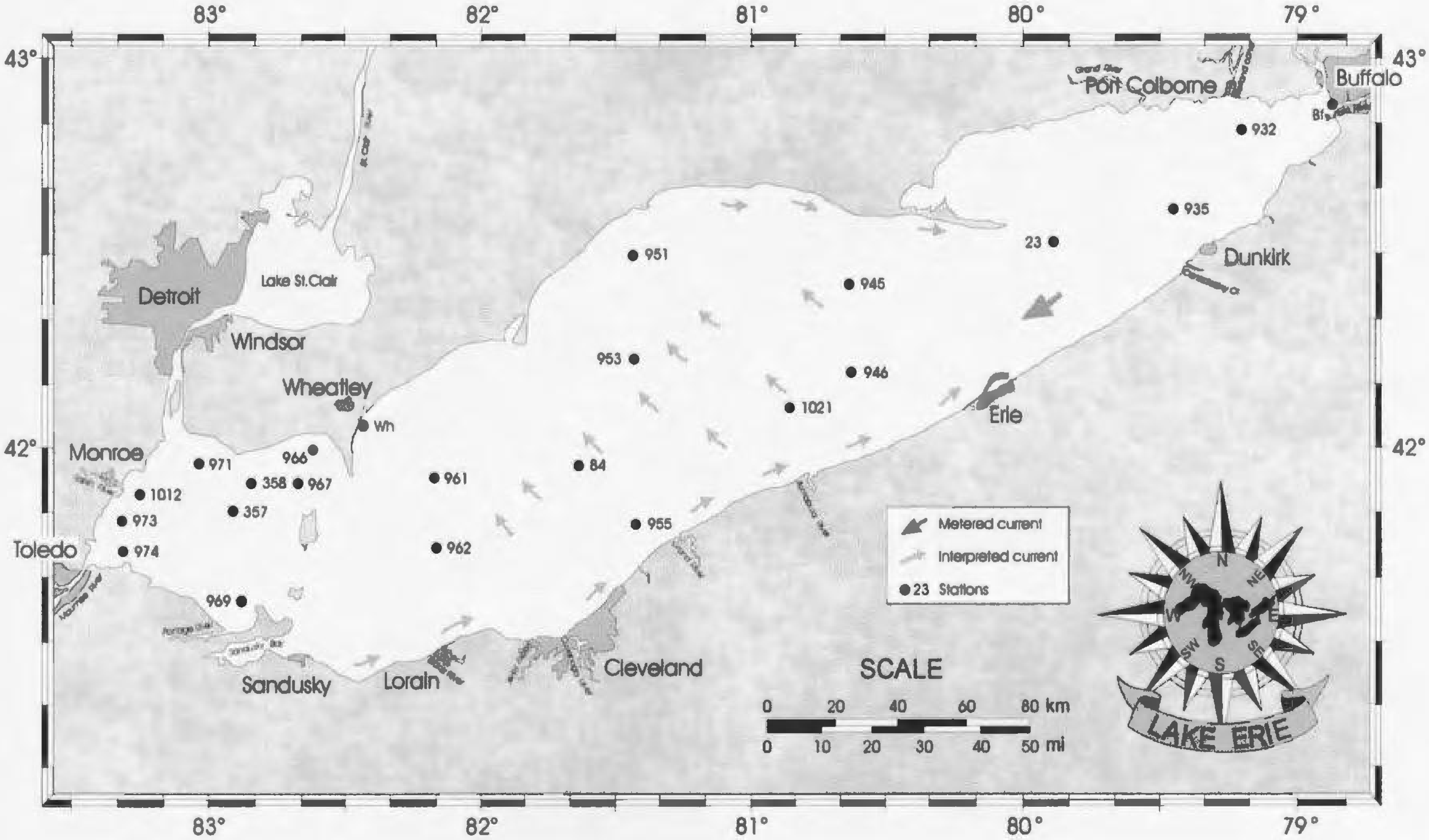
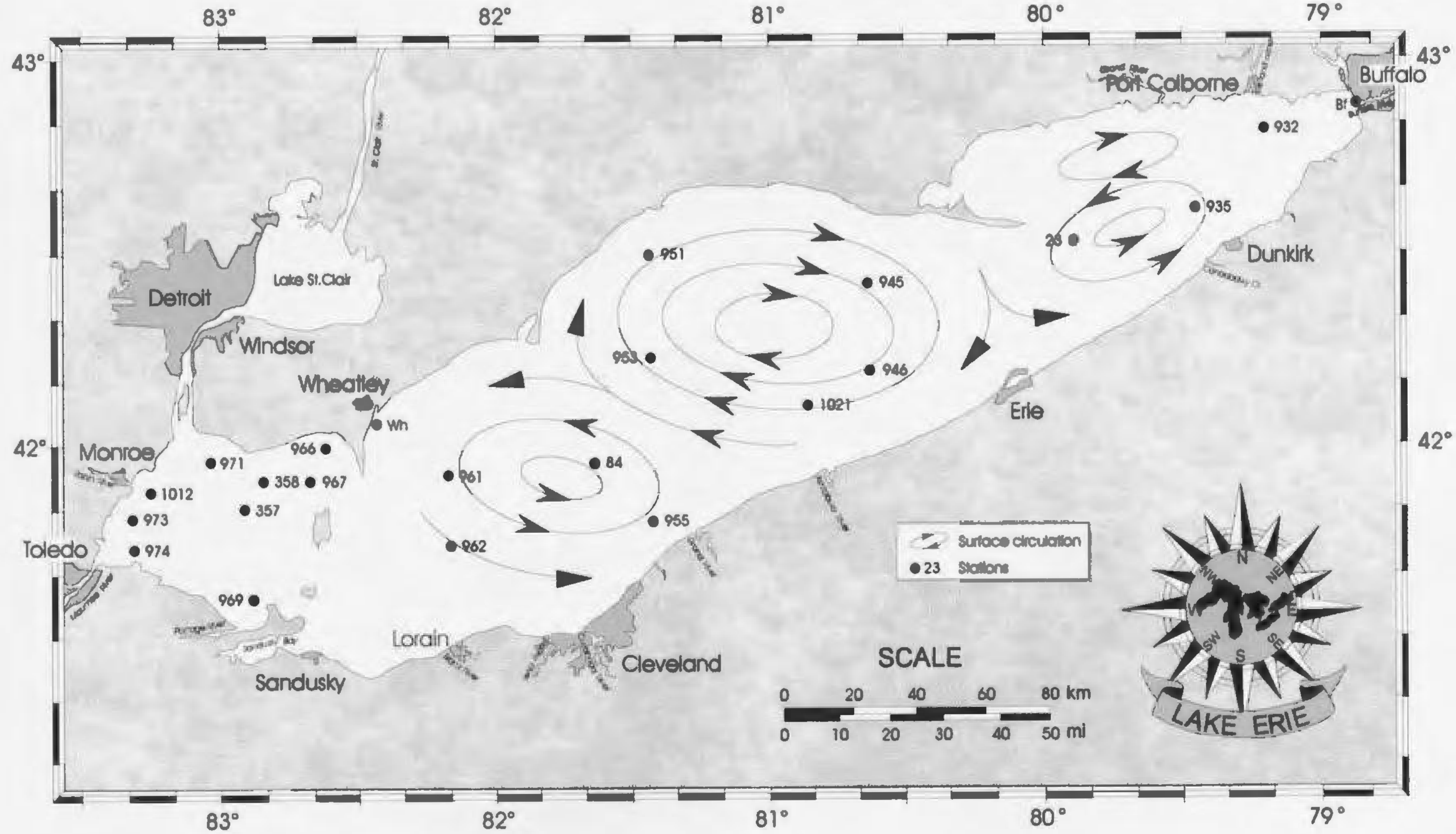

83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Wh
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Grand River
Buffalo
951
945
953
946
1021
84
955
961
962
966
971
358
967
357
1012
973
974
969
23
932
935
Metered current
Interpreted current
23 Stations
SCALE
0
20
40
60
80 km
0
10
20
30
40
50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Figure 5.1.9 Station locations and secondary patterns of surface circulation after Saylor and Miller (1987).


83°
82°
81°
80°
79°
43°
42°
Lake St.Clair
Detroit
Windsor
Wheatley
Wh
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
Bf
971
966
358
967
1012
973
357
974
969
961
962
84
955
951
953
945
946
1021
23
935
932
Surface circulation
● 23 Stations
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

5.1.4 and Section 4.1.2). This cluster is observed in all three basins and can generally be explained in terms of surface and bottom circulation patterns.

The incorporation of sites located in the Central Basin into Cluster 3 can be explained by the absence of major fluvial input along the shore and specific circulation pattern in this part of the lake. Most of the stations within the cluster are found in the northern part of the lake. There are no major rivers or cities along this shore which could introduce significant pollution signal. A study at Wheatley Harbor showed that minor tributaries are unlikely to significantly contribute to the PAH pollution of the offshore sediments (Appendix C3). The surface flow in the Central Basin is directed away from the northern shore (Fig. 5.1.10), while compensatory bottom currents intensive at the southern shore slow down and drop most of the suspended load by the time they reach the northern locations (Fig. 5.1.8). Furthermore, the longshore currents are directed in such a way that no pollution penetrates this part of the lake from the Western Basin (Fig. 5.1.7). The trace level PAH pollution observed within this cluster (Fig. 4.1.1, 4.1.4a, 5.1.3) can possibly be considered as some background characteristic of the lake sediments.

The inclusion of the two stations from the Western Basin into this cluster possibly has a different explanation. The isolated position of station 967 (Fig. 5.1.1) can again be explained in terms of surface circulation. Before entering the Pelee Passage the flow of the Detroit River splits into two arms due to the complicated bottom topography (Fig. 5.1.11) The northern branch passes closer to the shore while the southern part is deflected towards Pelee Island (Fig. 5.1.12). This pattern leaves site 967 relatively

Figure 5.1.10 Surface drifter tracks in the central and eastern parts of the lake. (After Saylor and Miller, 1987.) Note that the major surface flow is characterized by easterly and south-easterly directions which prevents penetration of contaminated particles introduced at major cities to the northern part of the lake.

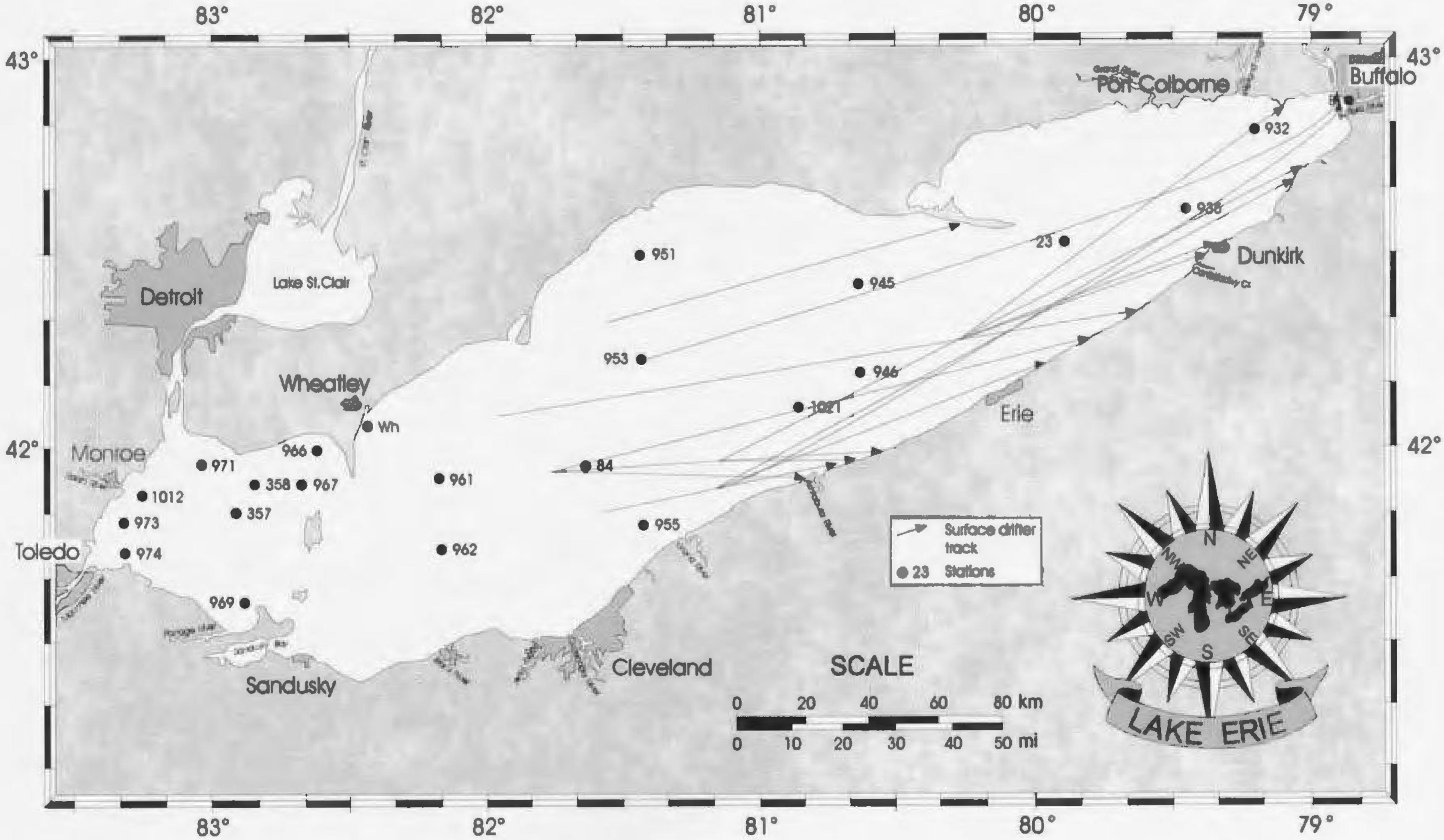

83°
82°
81°
80°
79°
43°
42°
Buffalo
Port Colborne
Detroit
Lake St.Clair
Wheatley
Wh
Monroe
Toledo
Sandusky
Cleveland
Erie
Dunkirk
932
938
23
951
945
953
946
1021
84
955
966
971
358
967
961
1012
973
357
974
962
969
Surface drifter track
23 Stations
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Figure 5.1.11 Station locations and bathymetry after Ristic and Ristic (1985). Note the complicated bottom topography in the northeastern part of the Western Basin.

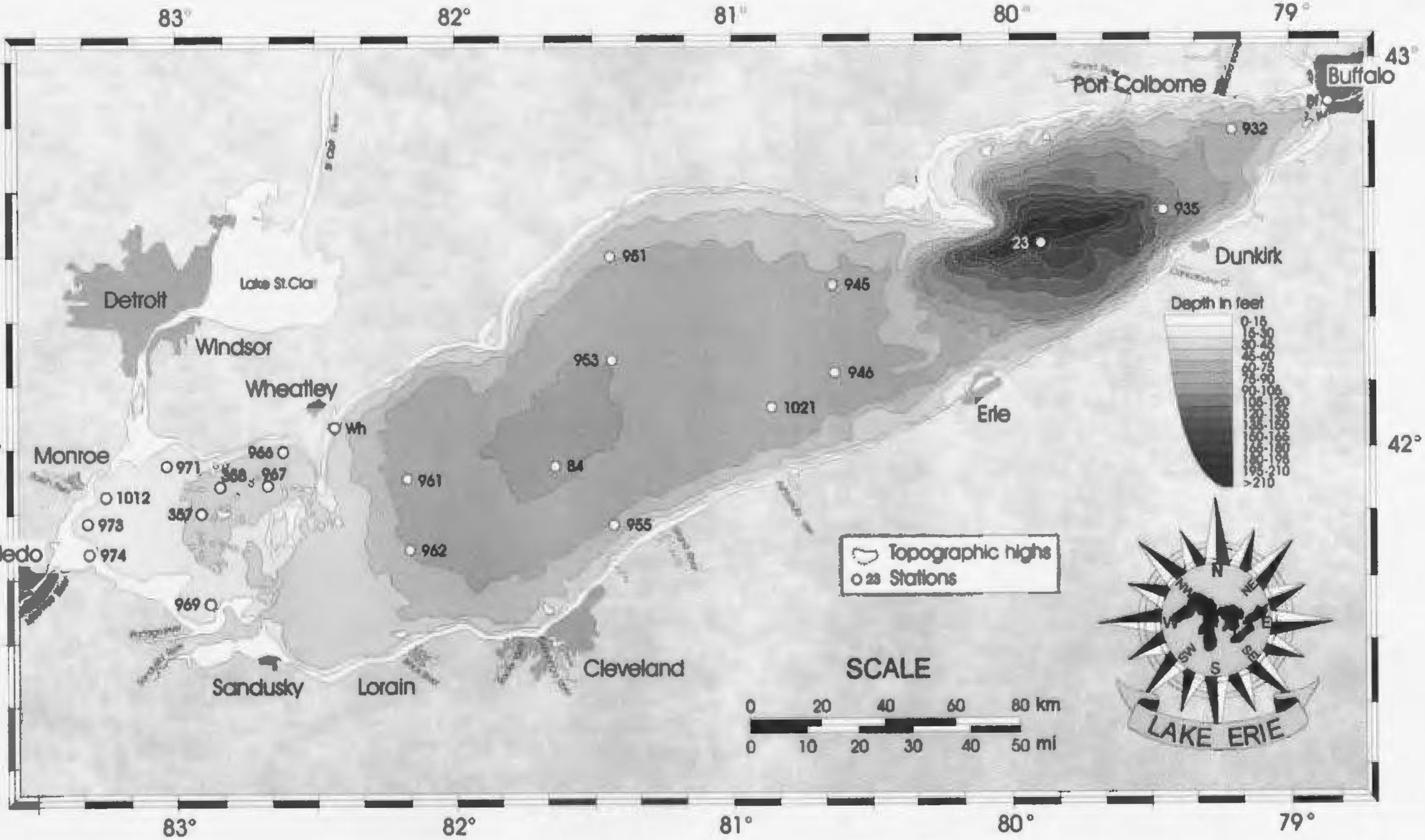
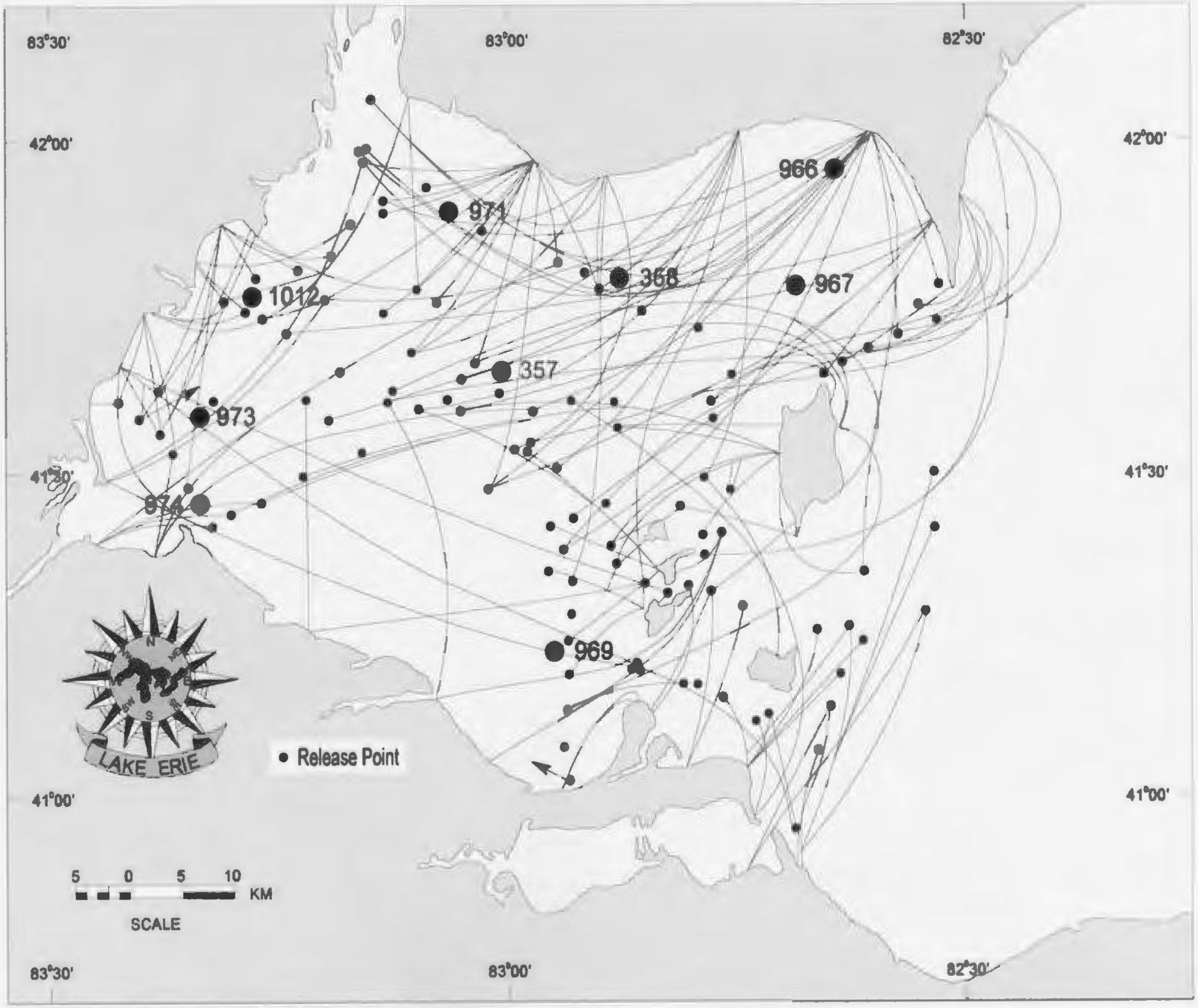

83°
82°
81°
80°
79°
43°
42°
Port Colborne
Buffalo
932
935
23
Dunkirk
951
945
Detroit
Lake St.Clair
Windsor
953
946
Wheatley
1021
Erie
Wh
Depth in feet
0-15
15-30
30-45
45-60
60-75
75-90
90-105
105-120
120-135
135-150
150-165
165-180
180-195
195-210
>210
Monroe
971
966
968
967
961
84
1012
357
973
955
974
962
Toledo
Topographic highs
23 Stations
969
N
NE
E
SE
S
SW
W
NW
Sandusky
Lorain
Cleveland
SCALE
0
20
40
60
80 km
0
10
20
30
40
50 mi
LAKE ERIE

Figure 5.1.12 Drift card trajectories in the western basin of Lake Erie (After Olson, 1950.) Note that the easterly flow splits into two parts just before it reaches station 967 leaving this site relatively unaffected.

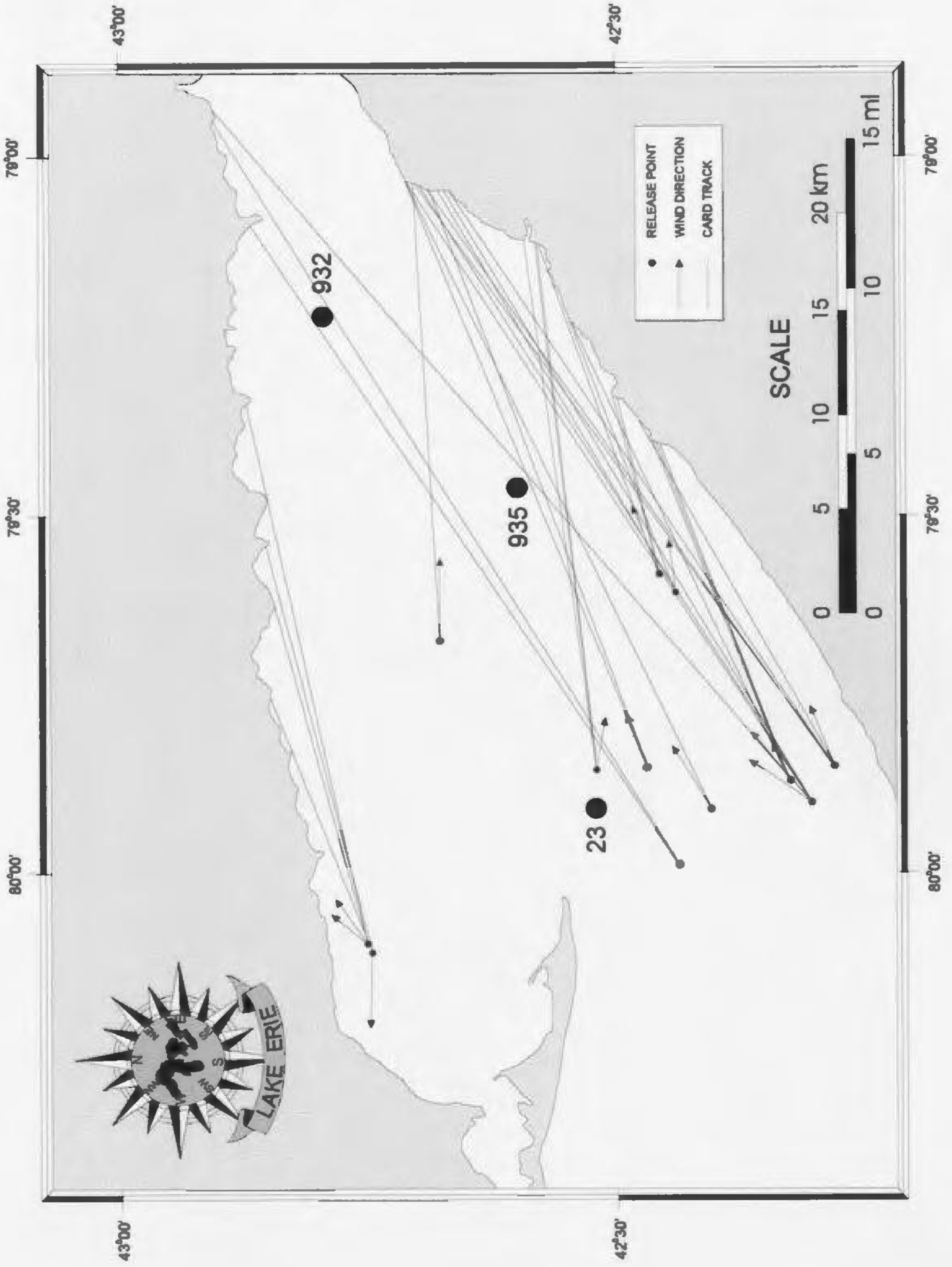

83°30'
83°00'
82°30'
42°00'
41°30'
41°00'
966
971
368
967
1012
357
973
974
969
N
S
LAKE ERIE
● Release Point
5
0
5
10
KM
SCALE

unaffected by the contaminated flow and results in lowest PAH concentration within the Western Basin (Fig. 4.1.1, 4.1.4a). The absence of sediment laden flow at this site is also confirmed by the low sedimentation rates observed here (Fig. 5.1.6). However, total PAH concentration at this station is somewhat higher that at the majority of sites within the cluster (Fig. 4.1.4a), while the isotopic composition of PAH assemblage resembles that at Detroit (Fig. 4.2.1a). This peripheral influence of the Detroit River flow seems to make this station transitional between clusters 2 and 3.

The incorporation of station 966 into this cluster (Fig. 5.1.1) can be attributed to somewhat different reasons. The flow of the Detroit River in this part of the Western Basin is deflected towards the shore and thus would inevitably hit the station. This is indicated by highly elevated PAH concentrations as compared to other stations in the cluster (Fig. 4.1.1, 4.1.4a). However, the isotopic composition of this station demonstrates the lightest values in the range (Fig. 4.1.5, 4.1.8a, 5.1.4). This characteristic signature implies presence of a local source of PAH pollution depleted in $\delta^{13}C$.

In the Eastern Basin, the incorporation of station 932 (Fig. 5.1.1) can again be attributed to the specific circulation pattern observed here. The flow of the only close fluvial system, the Grand River, does not seem to significantly affect this station. This is indicated by the directions of drift objects studied by Canada Center for Inland Waters (Hamblin, 1971; Fig. 5.1.13). The figures show instead that station 932 is affected by the flow originating in the central part of the Central Basin while the outflow of the Grand River seems to proceed along the northern shore towards the Niagara River outlet. Since

Figure 5.1.13 Drift object tracks in the Eastern Basin. (After Hamblin, 1971.) Note that the surface flow in the northern part of the basin is confined to the shore. Station 932 seems to be primarily affected by flow originating in the central part of the Central Basin.


43°00'
42°30'
79°00'
79°30'
80°00'
932
935
23
RELEASE POINT
WIND DIRECTION
CARD TRACK
SCALE
0
5
10
15
20 km
0
5
10
15 mi
LAKE ERIE
N
S

this station is the closest to the mouth of the Buffalo River, some influence of its outflow might be expected here. Indeed, the principal components analysis for molecular composition shows some remote similarity in the molecular composition of these stations (Fig 4.1.4b). However, the major flow in the basin is easterly directed, and somewhat similar pollution signal might indicate transport of contaminants by a mechanism different from water currents (*e.g.*, atmospheric deposition).

The major pattern of spatial distribution that emerges from the analyses of molecular and isotopic compositions of sediments can be summarized as follows. As the highest levels of contamination are found in the vicinity of three major cities and within zones controlled by fluvial sedimentation, the signal of PAH contamination seems to predominantly originate from fluvial input. The water circulation further distributes polluted particles introduced by the Detroit River around the Western Basin and partially transports them into the Central Basin. Here, the flow containing residual pollution signal is joined by the outflow of the Cuyahoga River at Cleveland and carried down the south shore transportation route towards the Niagara River outlet. This circulation scheme leaves the northern part of the lake isolated from the contaminated flow and results in background levels of PAH contamination. Some minor variations in this general pattern can possibly be caused by local input of PAH pollution. However, sources other than the major cities do not seem to play an important role on a lake-wide scale.

In conclusion, fluvial input of PAH appears to be very important. This is substantiated by the very close location of the lake to various pollutant discharges, with major sources of contamination located directly upstream along the connecting channel (Fig. 2.2.3). The importance of fluvial input as a pathway of various organic contaminants to the lake sediments was previously demonstrated by other researchers (*e.g.*, Strachan and Eisenrich, 1988; Kelly *et al.*, 1991; Carter and Hites, 1992). However, direct atmospheric influx should not be entirely ruled out as it was shown to contribute up to 21% of the total PAH inventory of the lake (Kelly *et al.*, 1991). The contaminated dust particles from pollution plumes of major cities can be deposited on the surface of the lake and transported and redistributed together with fluvially introduced PAH by the same circulation patterns.

5.2 PRIMARY AND SECONDARY SOURCES

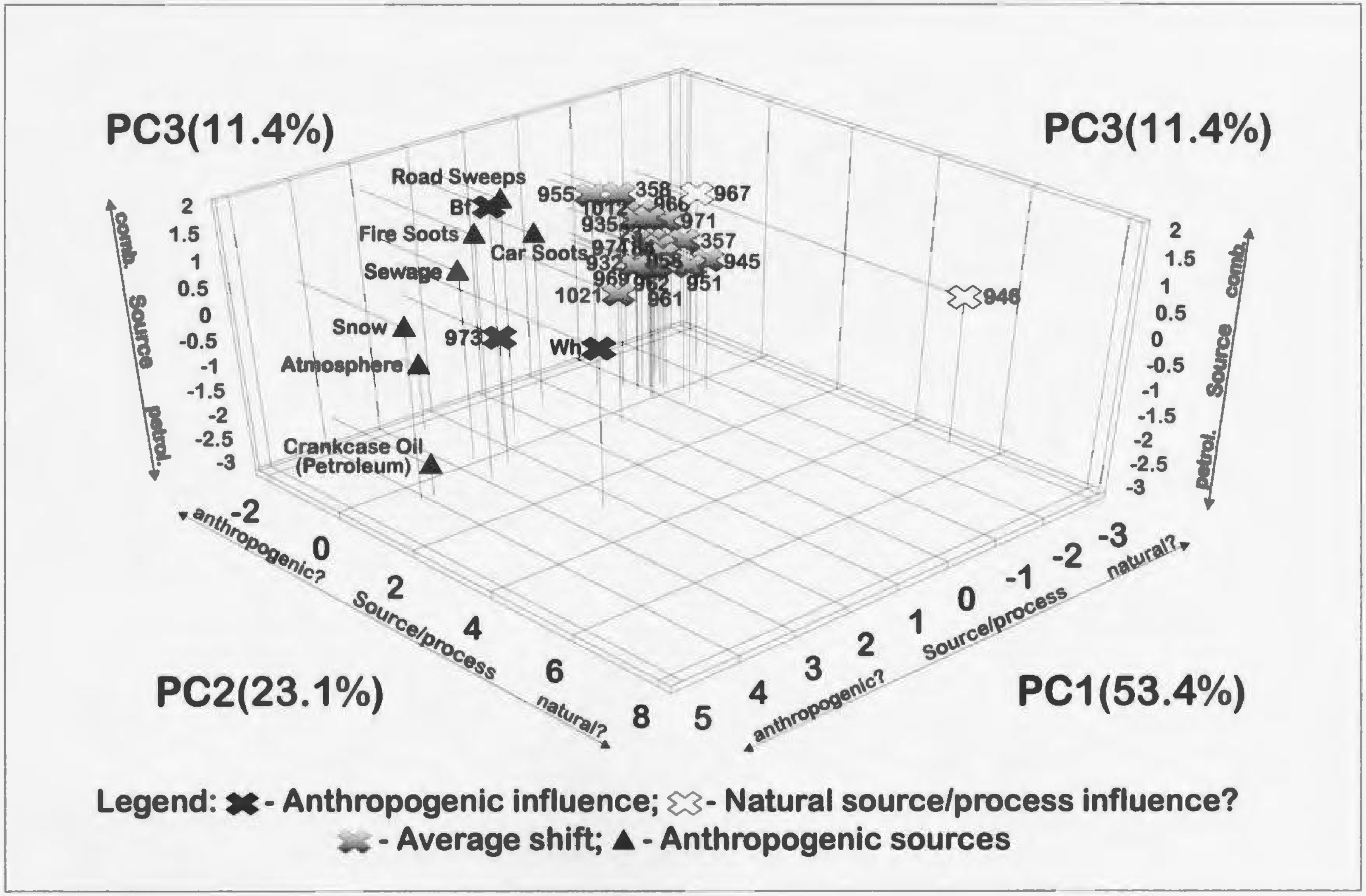
5.2.1 WEATHERING PROCESSES

After the whole lake was subdivided into three zones with generally similar molecular and isotopic composition, one can proceed further to investigate the ultimate sources and processes that contributed to the PAH assemblage of these zones. However, some additional discussion is required regarding the results of principal components analysis for molecular data. Three principal components were previously extracted for both normalized concentrations and isotopic composition of samples combined with prominent primary and secondary sources. Two first components in the analysis of molecular composition explained 76.5% (PC 1=53.4%; PC 2=23.1%) of total variance in samples and sources (Fig. 5.2.1 and 4.2.5a,b). The distribution of samples and sources along the two first PCs suggests presence of unaccounted sources or processes acting in lake sediments. A similar conclusion followed the analysis of the distribution of samples with respect to primary sources and mixing curves generated from normalized molecular composition of different compounds. It is possible that the pattern represented by the first and second PCs can be attributed to a variety of weathering processes known to affect PAH during their transport and after deposition.

A number of reasons point to the natural origin of the unidentified contributors. All known anthropogenic sources are concentrated on one end of both PCs (Fig. 5.2.1; see also Fig.4.2.5a,b and Section 4.2.1). On both components, they are at the opposite end of station 946 with the maximum contribution from the unidentified process/source. Site 946 is located very far from the areas subjected to direct anthropogenic influence and is characterized by a very low level of total PAH concentration (Fig. 4.1.1). Finally, station 946 exhibits very low Py/Per ratio (0.08; Fig. 4.2.1) which is indicative of natural origin of PAH assemblage (Lipiatou and Saliot, 1992; see also Appendix A5).

It can also be demonstrated that the observed changes in the PAH assemblage are more likely to be caused by an ongoing process rather than an additional source. The sites affected the most are located at considerable distance from each other (*e.g.*, 946 and 967, PC 1; 946 and Wh; PC 2; Fig. 4.2.5a,b). It is difficult to suggest a specific source selectively affecting different sites on a regional scale. Conversely, distance is not important for a process which can be initiated wherever the required conditions are met.

Figure 5.2.1 Cloud of samples and primary and secondary sources in the three-dimensional space formed by first PCs identified by PCA utilizing normalized concentrations of selected 4-, 5-ring PAH (Fa, Py, BA, Chy, BFl, BeP, BaP). Three first PCs explained 87.9% of total variance in samples.


PC3(11.4%)
PC3(11.4%)
comb. Source petrol.
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
Road Sweeps
Bf
Fire Soots
Car Soots
Sewage
Snow
Atmosphere
Crankcase Oil
(Petroleum)
973
Wh
955
358
967
1012
966
935
971
974
357
932
958
945
969
962
951
1021
961
946
-2
0
2
4
6
8
anthropogenic? Source/process natural?
PC2(23.1%)
5
4
3
2
1
0
-1
-2
-3
anthropogenic? Source/process natural?
PC1(53.4%)
Legend: ✖ - Anthropogenic influence; ✕ - Natural source/process influence?
✖ - Average shift; ▲ - Anthropogenic sources

There is yet another observation pointing to a natural process involved here. Stations with the lowest sedimentation rates seem to be affected the most. Thus the region of station 946 is characterized by the lowest sedimentation rates in the lake (Fig. 5.1.6). Another affected station, 967 (Fig. 5.2.1 and 4.2.5a), has the lowest sedimentation rates within the Western Basin and one of the lowest in the lake (Kemp *et al.*, 1977). Low sedimentation rates may result in a longer PAH residence time in the water column and at the sediment-water interface thus increasing the probability of alteration of the assemblage due to its extended exposure to light and oxygen.

A number of weathering processes are known to affect PAH after their release to the environment. These processes can result in significant alteration of the original assemblage (Neff, 1979; Wakeham *et al.*, 1980). It seems possible that the two first PCs (Fig. 4.2.5a,b) represent the combined action of different decomposition processes affecting PAH during transport and after deposition vs. immediate PAH input from anthropogenic sources. Weathering through biological, photolythic, and physico-chemical degradation was found an important factor of PAH decomposition in the aquatic realm (Neff, 1979). The major conditions necessary for the initiation of these processes can easily be met in Lake Erie. In shallow lakes like Erie (Fig. 2.1.3), the water column entirely warms up during the summer period. The resulting increase in sediment and water temperatures can greatly facilitate the processes of biological and chemical weathering (*e.g.*, Sherrill and Sayler, 1980; Lee *et al.*, 1978) and may also result in volatilization of compounds through the air-water interface (Kelly *et al.*, 1991). The increased amount of light easily penetrating the thin water column may further result in an increased rate of photolythic degradation in both water and upper sediments (*e.g.*, Neff, 1979). Further, the absence of stratification and mixing by storms provide additional access for oxygen to the sediments which might result in intensification of both bio- and chemical degradation (Barnsley, 1975; Mille *et al.*, 1988). Moreover, microbial activity has been shown to readily consume oil in sediments (Lee and Takahashi, 1977; Lee *et al.*, 1978). The presence of petroleum suggested by its high contribution to the formation of PAH assemblage at some stations (see Section 4.2) can substantially intensify the biological degradation. Finally, most of the processes were shown to preferentially destroy lower molecular weight compounds while leaving more stable higher molecular weight compounds intact (*e.g.*, Neff, 1979; Shiaris, 1989). The latter is the exact meaning of PC 1 which represents relative abundance of higher and lower molecular weight compounds in samples and sources (Fig. 4.2.5a; Section 4.2.1). The second component (PC2; Fig. 4.2.5b) also seems to reflect preferential degradation of certain compounds (BaP and BFl) and thus might be representative of a weathering process. It was shown, for example, that one of these compounds (BaP) is susceptible to the photolytic degradation (*e.g.*, Lee *et al.*, 1978).

Thus, although only more stable 4- and 5-ring compounds were utilized in the PCA analysis for molecular composition, the first two components taking 76.5% of sample variability appear to account for the alteration of PAH assemblage by weathering processes. Only the third component explaining as little as 11.4% of total variance deals with the relative contribution of different primary and secondary sources to the formation of the assemblage. The meaning of components produced by the PCA for isotopic composition was previously explained in the results chapter (see Section 4.2.2) and summarized again in Figure 5.2.2.

5.2.2 ANTHROPOGENIC SOURCES AND WEATHERING PROCESSES

A generalized pattern involving both molecular and isotopic composition was again generated through clustering first PCs obtained for both data sets. The percentage of total variance explained by each PC in the respective analysis was used in the weighting procedure performed prior to clustering. Since more detailed analysis was required to understand the inter-relationships between samples and sources, the number of clusters in this case was doubled. For detailed description of the clustering procedure the reader is referred to the chapter dealing with methods (see Section 3.2.2). The produced clusters (Table 5.2.1; see also Appendix C2) were further plotted in the space of first PCs for molecular and isotopic compositions (Fig. 5.2.3). In this graph, the horizontal axis is represented by PC 1 for molecular composition which was previously assumed to reflect various degree of PAH weathering in samples vs. the immediate input of compounds from primary and secondary sources. These relationships are in turn expressed by the relative abundance of lower vs. higher molecular weight compounds in samples and sources. The vertical axis demonstrates relative contribution of combustion vs. petroleum sources reflected by the isotopic composition of compounds and represented by PC 1 for isotopic composition. This more detailed approach indicates that although sediments in

Figure 5.2.2 Cloud of samples and primary and secondary sources in the three-dimensional space formed by first PCs identified by PCA utilizing $\delta^{13}C$ values for five selected 4-, 5-ring PAH (Fa, Py, BA/Chy, BbF/BkF, BeP/BaP). Three first PCs explained 92.9% of total variance in samples.

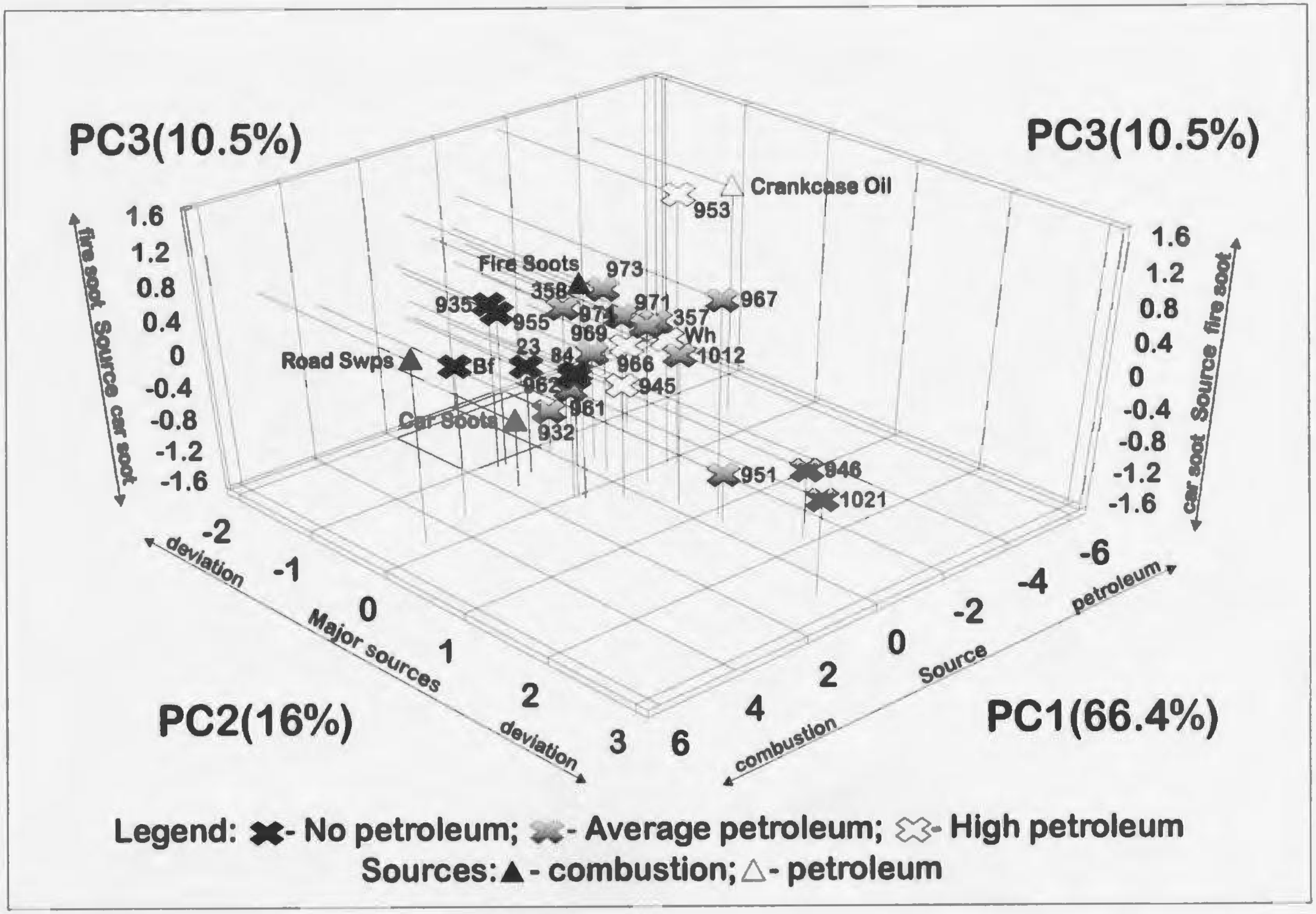
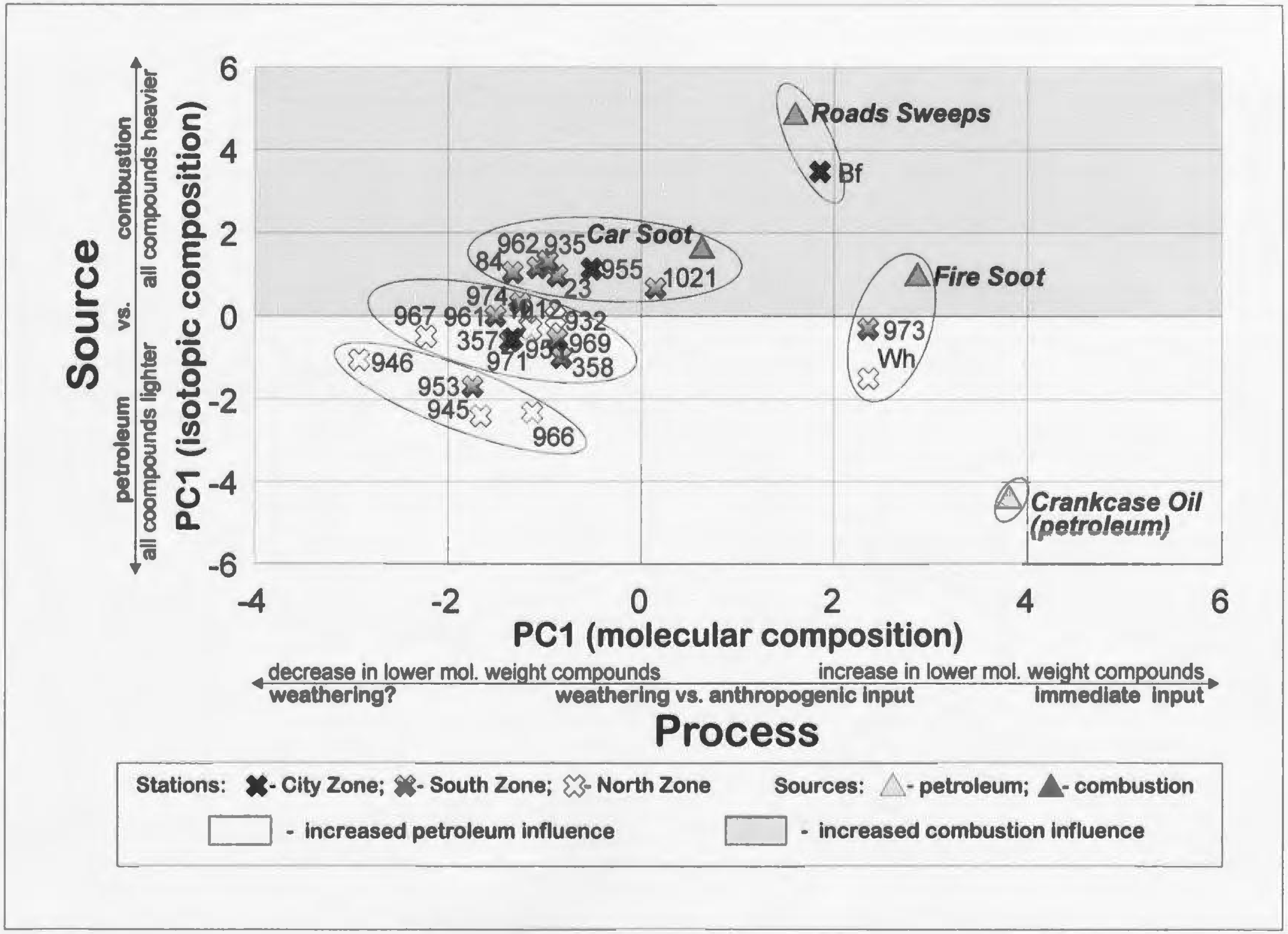

PC3(10.5%)
PC3(10.5%)
PC2(16%)
PC1(66.4%)
fire soot Source car soot
car soot Source fire soot
1.6
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
deviation Major sources deviation
-2
-1
0
1
2
3
combustion Source petroleum
6
4
2
0
-2
-4
-6
Crankcase Oil
953
Fire Soots
973
358
935
955
971
974
967
357
Wh
969
23
84
966
1012
Road Swps
Bf
962
945
961
Car Soots
932
951
946
1021
Legend: ✖- No petroleum; ✖- Average petroleum; ✖- High petroleum
Sources: ▲ - combustion; △ - petroleum

Table 5.2.1 Six clusters identified by the non-hierarchical (K-means) clustering utilized for grouping of the first principal components extracted from molecular and isotopic data sets during the source identification procedure. Zones are those identified in the previous analysis of spatial distribution. See also Appendix C2 (columns 0 and 8).

Samples/Sources	Zones	Clusters
St 966	North zone	1
St 953	South zone	1
St 946	North zone	1
St 945	North zone	1
St 973	South zone	2
Wh	North zone	2
Fire soots	-	2
St 974	South zone	3
St 1012	South zone	3
St 971	City zone	3
St 969	South zone	3
St 357	South zone	3
St 358	South zone	3
St 967	North zone	3
St 961	South zone	3
St 951	North zone	3
St 932	North zone	3
St 23	South zone	4
St 962	South zone	4
St 1021	South zone	4
St 84	South zone	4
St 955	City zone	4
St 935	South zone	4
Car soots	-	4
Bf	City zone	5
Road sweeps	-	5
Crankcase oil	-	6

Figure 5.2.3 Six clusters identified by the non-hierarchical (K-means) clustering of first principal components extracted from molecular and isotopic data sets during the source identification procedure.


Source
petroleum vs. combustion
all coompounds lighter all compounds heavier
PC1 (isotopic composition)
6
4
2
0
-2
-4
-6
-4
-2
0
2
4
6
PC1 (molecular composition)
decrease in lower mol. weight compounds
increase in lower mol. weight compounds
weathering?
weathering vs. anthropogenic input
immediate input
Process
Roads Sweeps
Bf
Car Soot
962
935
84
955
23
1021
974
1012
967
961
932
357
95
969
971
358
946
953
945
966
Fire Soot
973
Wh
Crankcase Oil
(petroleum)
Stations: ✖- City Zone; ✖- South Zone; ✖- North Zone
Sources: △- petroleum; ▲- combustion
☐ - increased petroleum influence
▨ - increased combustion influence

the three previously identified zones (Fig. 5.1.1) generally possess similar molecular and isotopic compositions of compounds, the relative contribution of various sources to the PAH assemblage and the degree of weathering at different sites might vary significantly within a single zone.

5.2.2.1 The City Zone

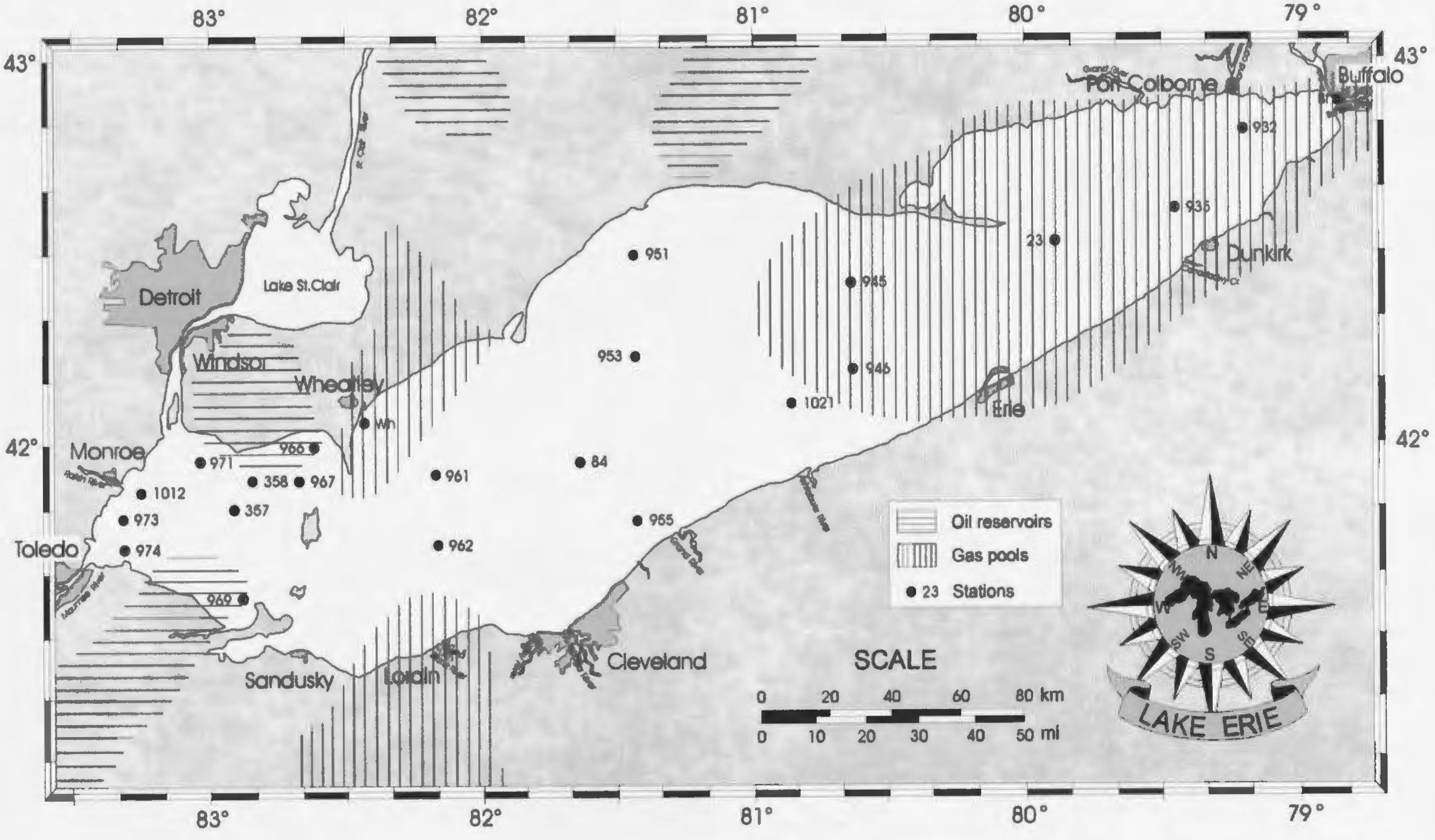
It was previously shown that although the major cities are included into a single cluster on the spatial distribution scheme (Fig. 5.1.1), certain within-cluster variations may occur. These variations can be attributed to somewhat different sources participating in the formation of the PAH assemblage and different degree of decomposition. The latter is demonstrated by the incorporation of stations representing the signal of major cities into three different clusters (Fig. 5.2.3).

Detroit (Station 971): The signal at Detroit seems to be largely formed from combustion sources but with non-negligible contribution from petroleum-related sources (Fig. 5.2.3). This is indicated by a shift of this site towards the petroleum range on PC 1 for isotopic composition (Fig. 4.2.19a). The isomer ratios also demonstrate that although generally in the combustion range, station 971 can be significantly affected by petroleum-related sources (Fa/Py; Fig. 4.2.1). In the principal components analysis for molecular composition, this station was also found closer to the petroleum end member than the other major cities (Fig. 4.2.5c). Finally, quantification of the relative contribution of these two sources utilizing mixing curves for $\delta^{13}C$ values showed that approximately 20-30% of PAH here can originate from petroleum sources (Fig. 4.2.8-4.2.17). However, the mass balance calculations show that this percentage may vary from 10% to 75% for different compounds (Fig. 4.2.7). The increased importance of petroleum sources in the formation of the PAH assemblage here might probably be attributed to spills and leaks of petroleum products from the harborside facilities and/or seeps of petroleum from an extensive oil reservoir located further upstream (Fig. 5.2.4; see also Meyers, 1984).

Both wood-burning and fuel combustion appear to have significantly contributed to the formation of the PAH assemblage at station 971, however car emissions may slightly dominate. This is demonstrated by the very few analyses that separate the two combustion sources which are almost always found together. Thus PC 3 for molecular composition separated the two sources by estimating the relative importance of Py vs. Chy and BaP (Fig. 4.2.5c). The position of station 971 on this component indicates slight predominance of car soots at this location. It was shown by O'Malley (1994) that isotopic composition of Py can also help differentiate between the two combustion sources. The analysis of $\delta^{13}C$ for Py (Fig. 4.2.19c) demonstrates almost equal contribution from both sources to the formation of this compound.

The PAH found at this station might have been introduced into the Detroit River waters with snow disposal and/or releases of city sewage. This is indicated by the position of this site in the vicinity of the average sample for road snow (Fig. 4.2.5c) obtained by O'Malley (1994) from an urbanized area in eastern Canada. The same compounds (Py vs. Chy and BaP; Fig. 4.2.5c) show an increased influence of city sewage at this location.

Figure 5.2.4 Station locations and major hydrocarbon reservoirs underlying the lake after Fuller and Shear (1995). Note that station 966 is situated within the oil field in the northern part of Western Basin.


83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Wh
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
951
953
945
946
1021
23
935
932
84
961
962
955
966
971
358
967
357
1012
973
974
969
Oil reservoirs
Gas pools
● 23 Stations
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

The processes of degradation might play an important role at station 971. This is shown by its position in the left part of the graph in Figure 5.2.3. The location indicates predominance of higher molecular weight compounds (BFl, BeP, BaP) over lower molecular weight PAH (Fa, Py; Fig. 4.2.5a). The ratio/ratio mixing curves for molecular composition also demonstrate that station 971 is shifted away from primary sources and their mixing arrays towards predominance of higher molecular weight compounds (Fig. 4.2.2, 4.2.3). The process of weathering could be enhanced here due to increased microbial activity resulting from possible presence of oil in sediments (Lee and Takahashi, 1977; Neff, 1979). The latter is indicated by the increased relative importance of petroleum-related sources in PAH supply. In addition, well oxygenated shallow water column (Fig. 5.1.11) and increased water temperatures in summer (Fig. 2.1.8) might also have facilitated various processes of decomposition at this site (Payne and Phillips, 1985; Mille *et al.*, 1988; Kelly *et al.*, 1991). Finally this station is located as far as 30 kilometers downstream from the City of Detroit and thus the PAH assemblage might undergo significant changes during its transport, prior to deposition in lake sediments.

Cleveland (Station 955): Petroleum sources seem to be less important at Cleveland than at Detroit. However they may still influence the formation of certain compounds. The overall predominance of combustion sources is indicated by the position of station 955 within the shaded (combustion) zone in Figure 5.2.3. This position is determined by relatively heavy isotopic values of all compounds as indicated by PC 1 for isotopic composition (Fig. 4.2.19a). In addition, none of the characteristic ratios indicates contribution from petroleum related sources at this site (Fig. 4.2.1). The comparison with characteristic ranges for $\delta^{13}C$ also demonstrates complete absence of petroleum influence in the assemblage (Fig. 4.2.6). However, mass balance calculations showed that as much as 10% of Py, 30% of Chy and 40% of BeP/BaP could still have been derived from petroleum related sources (Fig. 4.2.7). Further, the mixing curves for isotopic composition also indicate that 10-30% of the higher molecular weight compounds (Chy-BaP) might originate from petroleum (Fig. 4.2.9, 4.2.12 - 4.2.14).

Both wood burning and fossil fuel combustion sources have almost equally contributed to the formation of the PAH assemblage at Cleveland. This is first shown by PC 3 for molecular composition which demonstrates almost equivalent contribution of car emissions and fire soots to the formation of compounds (Fig. 4.2.5c). In addition, the isotopic composition of Py also indicates that PAH at this site are almost equally supplied by the two prominent contributors (Fig. 4.2.19c).

The PAH produced by the city might be further directed to the aquatic environment through city runoff and releases of sewers. The importance of these two pathways is indicated by the relative contribution of Py vs. Chy/BaP to the PAH assemblage at station 955 (Fig. 4.2.5c). In the mixing curves for $\delta^{13}C$ values, this station is also often shifted towards the road sweep end member (Fig. 4.2.8, 4.2.10, 4.2.11, 4.2.15). The latter again indicates the possible importance of direct city runoff as a pathway of PAH into the lake. The increased role of surface runoff as compared to that at Detroit may possibly be attributed to somewhat different precipitation regime of the two areas (Fig. 2.1.9).

Although less intensive than at Detroit, processes of decomposition may have affected the PAH assemblage at station 955. This influence is inferred from the slight shift of this station towards the left half of the graph (Fig. 5.2.3). The displacement results from slightly reduced abundance of lower molecular weight compounds (Fig. 4.2.5a). Similar to the station at Detroit (971), microbial activity here could be facilitated by the traces of petroleum in sediments resulting in somewhat increased weathering (Lee and Takahashi, 1977). In addition, station 955 is approximately 40 kilometers away from the mouth of the Cuyahoga River, the assumed major contributor of PAH contamination in the area (see Section 5.1). The extended transport of compounds to the site of final deposition may also have resulted in preferential losses of less stable compounds.

Buffalo (Station Bf): At Buffalo, the PAH assemblage seems to be formed strictly from combustion sources. Station Bf is found far in the shaded zone in Figure 5.2.3. This shift towards combustion sources is due to extremely heavy isotopic values for all compounds at this site (Fig. 4.1.5, 4.2.19a). Further, none of the characteristic ratios indicates any contribution by petroleum sources to the formation of the PAH assemblage (Fig. 4.2.1). This station also occupies an extreme position on PC 3 for molecular composition, where it is opposite the sample representing petroleum sources (Fig. 4.2.5c). In addition, the comparison of isotopic signal with characteristics $\delta^{13}C$ ranges for primary sources does not reveal any indication of petroleum influence (Fig. 4.2.6). The attempt to quantify the relative importance of two primary sources through mass balance calculations estimated contribution from combustion as 100% for all utilized compounds

(Fig. 4.2.7). Finally, this site consistently plots far in the combustion range in all graphs with mixing curves (Fig. 4.2.8-4.2.17).

The combustion sources at this station seem to be dominated by soots originating from fire places. For example, the relative importance of Py vs. Chy, BaP indicates that fire soots are largely responsible for the formation of the PAH assemblage at this site (Fig. 4.2.5c). However, isotopic values for Py suggest that fossil fuel combustion sources may also have significantly contributed to the isotopic composition of this compound (Fig. 4.2.19c).

The combustion-derived PAH were most likely introduced into the Buffalo River through direct city runoff. This is indicated by the constant association of the station at Buffalo with the average sample from open road sweeps. Station Bf is the only site clustered together with the road sweeps in Figure 5.2.3. This position is determined by very similar molecular and isotopic composition of both samples as follows from the results of the principal components analysis (Fig. 4.2.5, 4.2.19). In addition, this station is consistently found in the vicinity of the road sweep end member in all graphs with mixing curves for $\delta^{13}C$ values (Fig. 4.2.8-4.2.17). The close similarity in molecular and isotopic compositions of the PAH assemblage at this station and the open road sweep sample can possibly be attributed to an increased amount of precipitation characteristic of this area (Fig. 2.1.9). Frequent rain and snowfalls may result in PAH, constantly produced in the city, being washed off the paved roads and transported with direct runoff into the Buffalo River.

The processes of weathering do not seem to be important at this station. This is indicated by the position of site in the right part of the generalized graph together with a group of primary and secondary sources (Fig. 5.2.3). The latter is due to overall predominance of 4- over 5-ring compounds at this station as indicated by PC 1 for molecular composition (Fig. 4.2.5a). Site Bf also plots close to the end members and their mixing arrays in graphs with mixing curves for molecular ratios (Fig. 4.2.2, 4.2.3). The similarity of the PAH assemblage at this site to the signatures of prominent primary and secondary sources can possibly be attributed to the proximity of this station to the area of PAH production. This site is located close to a highly urbanized area (the City of Buffalo), hence a constant supply of low molecular weight compounds to the sediments may be suggested.

To summarize, the assemblage of PAH at major cities is generally dominated by combustion sources. The greatest contribution of petroleum-related sources is seen at Detroit and the least at Buffalo. The increased role of petroleum at Detroit may possibly be attributed to its spills and leaks from tankers and city harborside facilities, since petroleum products are a major part of the city's waterborne commerce. Possible seepage of oil originating from upstream reservoirs (*e.g.*, Meyers, 1984) may also have contributed to the increased importance of petroleum in the formation of the PAH assemblage close to the mouth of the Detroit River. Among combustion sources, car soots seem to be more important at Detroit while fire soots appear to dominate at Buffalo. Both sources have almost equally contributed to the PAH assemblage at Cleveland.

Snow melt and sewer releases seem to play an important role as pathways of PAH to the lacustrine environment at Detroit. At Cleveland, characterized by slightly increased amount of precipitation, direct city runoff starts to play more important role. Finally, enhanced precipitation regime at Buffalo results in direct city runoff being the major pathway of PAH to the Buffalo River and subsequently to the lake.

Degradation processes are fairly strong at Detroit and Cleveland which is probably attributable to the presence of oil available for co-metabolism in sediments of these sites and their relative remoteness from the areas of original PAH production. Increased water temperatures and shallow, well oxygenated water column may also have facilitated weathering processes at the mouth of the Detroit River. Conversely, decomposition processes do not seem to have significantly altered PAH at Buffalo. This is probably due to short transport path length from production to deposition at this site.

5.2.2.2 The South Zone

It was previously shown that the South Zone (Fig. 5.1.1) may possibly be attributed to dispersion of PAH contamination fluvially introduced at major cities. The stations in this zone are split into three clusters with regard to the relative contribution of petroleum and combustion sources to the PAH inventory (Fig. 5.2.3). In addition, these stations also significantly vary in the degree of weathering of PAH assemblage.

Petroleum vs. combustion (the South Zone): The South Zone was shown to likely be formed by distribution of contaminated sediment particles brought into the lake by fluvial outflow at Detroit and Cleveland (see Section 5.1). A separation of this zone into two subzones of influence was suggested. This separation is confirmed by Figure 5.2.3 and can be attributed to different relative importance of petroleum sources in the PAH assemblage generally dominated by combustion-produced compounds. The highest overall contribution from petroleum sources within this zone is demonstrated by station 953.

Stations affected by the Detroit River: As stations 357, 358, 969, 974, 1012, and 961 were shown to be affected by the outflow of the Detroit River, they are characterized by fairly significant contribution of petroleum-related sources to the PAH assemblage typical of this signal. This is indicated by their position in the lower half of Figure 5.2.3, characteristic of petroleum influence. The influence of petroleum-related sources is expressed in light isotopic values for all compounds (Fig. 4.2.19). These stations also show predominance of Py over Fa (Fig. 4.2.1) characteristic of petroleum input (*e.g.*, Yunker and MacDonald, 1995; Yunker *et al.*, 1995). The isotopic values for BeP, BaP and Fa for most stations fluctuate close to the characteristic petroleum range (Fig. 4.2.6). In addition, the mass balance calculations also indicate that relative contribution of petroleum is very high at these sites (Fig. 4.2.7). The greatest contribution of petroleum-related sources is seen at station 969 (BeP/BaP=90%; Fig. 4.2.7). This might be due to possible seepage of crude oil from the oil field located in this region (Fig. 5.2.4). On the contrary, station 974 demonstrates the least contribution of petroleum in the region. It is worth noting that this station may, to some extent, be affected by the outflow of the Maumee River at Toledo. This outflow might be characterized by an increased importance of combustion-derived PAH. Further, the location of this group of stations on the graphs for mixing curves also confirms the importance of petroleum in the formation of the PAH assemblage (Fig. 4.2.8-4.2.17). Finally, these stations occupy an intermediate position between petroleum and combustion sources on the third principal component for molecular data, responsible for their relative contribution (Fig. 4.2.5c).

Stations affected by the outflow at Cleveland: The PAH assemblage from stations 962,84,1021,23, and 935 demonstrate similarities to the pollution signal introduced by Cleveland in which combustion sources entirely dominate over petroleum. This is first indicated by the location of this group in the shaded zone in Figure 5.2.3. This position is explained by relatively heavy isotopic composition for all compounds (Fig. 4.2.19a). The characteristic ratios of kinetic compounds to their thermodynamic isomers demonstrate predominance of the less stable compounds for almost all the stations (Fig. 4.2.1). Only at station 84 the ratio Fa/Py is less than unity. This and somewhat lighter isotopic composition for Pa (Fig. 4.2.6) show that this site might still be affected by the petroleum signal introduced by the Detroit River. The minimum contribution of petroleum at most stations is also shown by their position on the mixing curve graphs (Fig. 4.2.8-4.2.17). Only the relative abundance of Py vs. Chy and BaP indicated possible minor influence of petroleum related sources (Fig. 4.2.5c). The isotopic composition of Station 1021 is somewhat different from the other stations within this subcluster. It demonstrates very light isotopic values for Fa while the composition of BA/Chy is enriched with respect to ^{13}C (Fig. 4.2.8, 4.2.9, 4.2.15-4.2.17). None of the sources employed in the present study possesses similar isotopic composition (Fig. 4.2.19b). This site might be affected by the Ashtabula River outflow entering the lake close to its location and probably introducing the signal of an unidentified primary source.

Station 953: Station 953 demonstrates the greatest contribution of petroleum in the South Zone. The isotopic composition here is light for all compounds (Fig. 4.2.19a). This in turn determines its location in Figure 5.2.3, where this site is found in the zone of increased petroleum influence. The mass balance calculations demonstrate that as much as 5% of Fa, 60% of Chy, 25% of BFl, 80% of BeP/BaP and 95% of Py could be formed here from petroleum-related sources (Fig. 4.2.7). The position of this station on the graphs for mixing curves also shows that as much as 30-60% of PAH could derive from petroleum sources (Fig. 4.2.8-4.2.18). In addition, this station is the closest to petroleum according to the relative abundance of Py vs. Chy and BaP (Fig. 4.2.5c). This increased importance of petroleum input might be attributed the close location of station 953 to the cluster boundary. The latter implies that sources controlling the PAH assemblage in the North Zone might be important here. The elevated importance of Py might also indicate its airborne origin. It was previously shown that the atmospheric influx in this region is characterized by an increased abundance of this compound (Eisenreich and Strachan, 1992). The possibility of atmospheric deposition at this station also follows from Figure 4.2.5c, where station 953 is the closest to the sample representing total atmospheric influx.

Intensity of degradation (the South Zone): Most stations of the South Zone indicate that processes of weathering can strongly impact on PAH in sediments at these sites (Fig. 5.2.3). The intensive degradation is demonstrated by a shift of these stations from the prominent end members and their mixing curves towards predominance of 5- over 4-ring compounds (Fig. 4.2.2, 4.2.3). The low values exhibited by these stations on PC 1 for molecular composition (Fig. 4.2.5a) are also indicative of preferential removal of lower molecular weight compounds from sediments and therefore, increased intensity of decomposition. Two major mechanisms seem to be involved in regulating these processes: presence of oil in sediments and sedimentation rates. These two mechanisms seem to determine the position of stations on the respective axis (Fig. 4.2.5a). Stations with relatively low sedimentation rates and characterized by importance of petroleum demonstrate the highest intensity of weathering (*e.g.*, St. 953). Since most sites in this zone meet at least one of the conditions, these processes seem to be generally important (Fig. 5.2.3).

A single station within this zone (973) exhibits slow rates of PAH decomposition (Fig. 5.2.3). Here, 4-ring compounds seem to dominate over 5-ring PAH (Fig. 4.2.5a). This station also plots very close to the mixing curves for molecular composition indicating little PAH contribution from sources other than those under consideration (Fig. 4.2.2, 4.2.3). The processes of weathering, at this site, can possibly be masked by continuous fresh supply of PAH from the closely located community (Monroe; Fig. 5.1.1). This supply can be provided through direct releases of sewage and atmospheric fallout of fire soots as indicated by Figures 4.2.5a and 5.2.3. In addition, a large plant using coal as the major fuel is located on the shore just opposite the station. Both combustion emissions and leachates from the coal storage built on the shore can be important as PAH sources (Eadie *et al.*, 1982).

To summarize, petroleum sources seem to be important at sites affected by the outflow of the Detroit River. On the contrary, stations affected by the fluvial input at Cleveland demonstrate reduced importance of petroleum derived PAH. Site 953 shows the greatest presence of petroleum across the zone which might possibly be attributed to its marginal position. The relative importance of two major combustion sources is difficult to discern since they contribute almost equally to the combustion signal introduced by both cities. Most sites within this zone are strongly affected by processes of PAH decomposition. Both sedimentation rates and presence of oil in sediments seem to regulate this process. At station 973 the process might be masked due to a constant fresh supply of four ring compounds from the closely located community and its facilities.

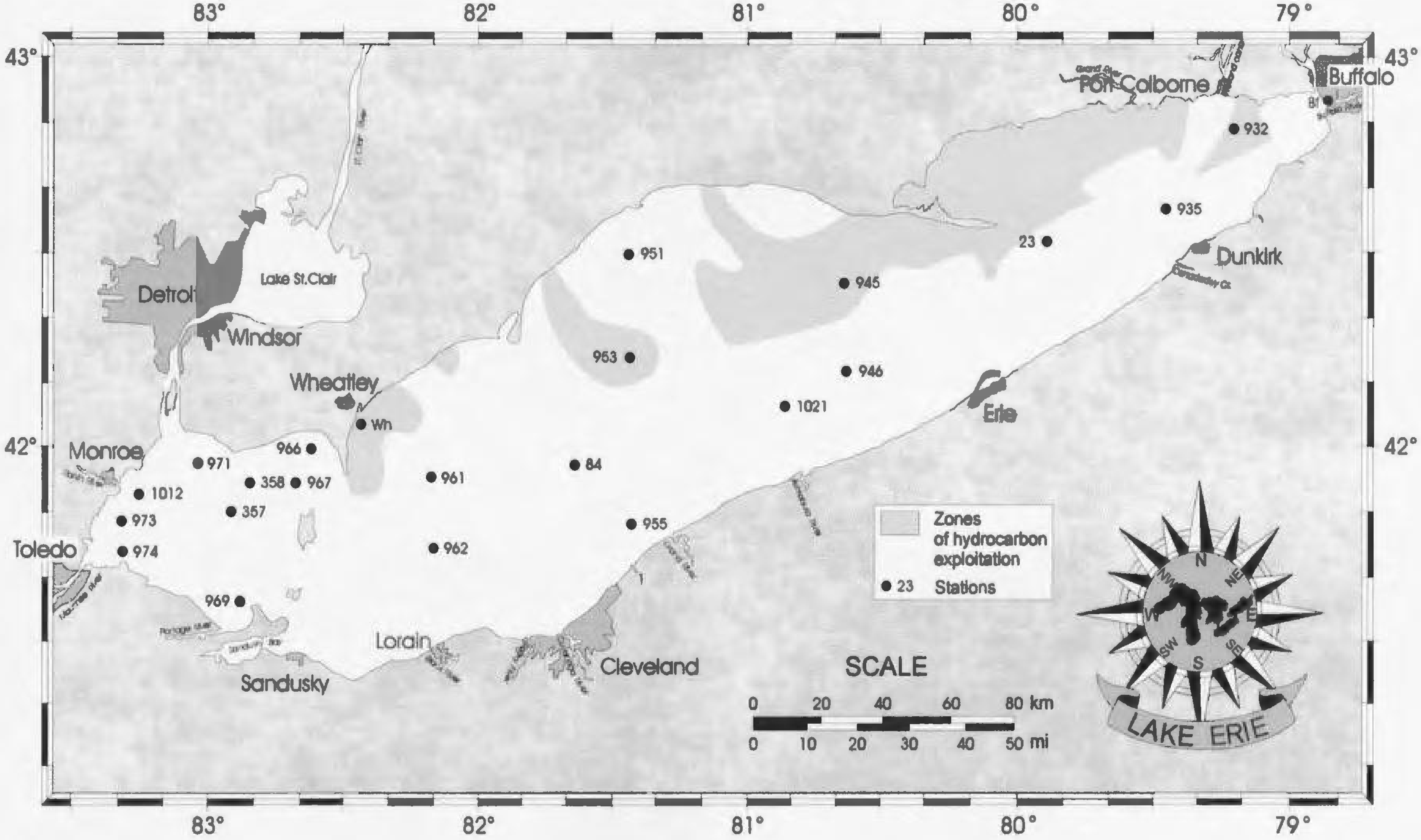
5.2.2.3 The North Zone

The origin of PAH recovered from the samples of the North Zone was previously attributed to a background level of PAH contamination existing in lake sediments. Samples from these sites are generally characterized by increased importance of petroleum-produced compounds. However, there are three stations (967, 951 and 932) where this importance is somewhat reduced. Decomposition rates are generally very high across the zone, the station at Wheatley being an exception (Fig. 5.2.3).

Petroleum vs. combustion (the North Zone): Both molecular and isotopic composition of the major group of stations (946, 945, 966, Wh) demonstrates high affinity to petroleum. This is shown by the position of these sites in Figure 5.2.3 which is in turn determined by very light isotopic values of all compounds. In addition, at least one ratio at each station shows petroleum origin of PAH (Fig. 4.2.1). The relative concentration of Py vs. Chy and BaP also demonstrates that contribution from petroleum related sources is very significant (Fig. 4.2.5c). Further, the comparison with characteristic isotopic values shows that 2-4 compounds at each station derived from petroleum-related sources (Fig. 4.2.6). The mass balance calculations indicate that up to 100% of Fa, 55% of Py, 80% of Chy, 60% of BFl and 100% of BeP/BaP at these stations could have derived from petroleum (Fig. 4.2.7). The graphs for mixing curves with isotopic ratios also indicate that 40-70% of compounds can be attributed to petroleum origin (Fig. 4.2.8-4.2.18). The high contribution of petroleum-related sources at these stations can probably be attributed to their location within or in proximity of an extensive hydrocarbon reservoirs existing in the lake. For example, station 966 is actually located in an area underlain by an oil field (Fig. 5.2.4). Possible seepage of oil from underlying reservoirs was previously found to be an important contributor to the PAH inventory of sediments elsewhere (*e.g.*, Steinhauer *et al.*, 1994). In addition, most stations of the North Zone are located within or in proximity of the areas of intensive gas exploitation confined to the northern part of the lake (Fig. 5.2.5). Seepage from well lubrication and transfer pipe coating and accidental oil spills during the operation procedures could also have resulted in the formation of this background characterized by high contribution of petrogenically produced compounds.

Although stations 967, 951 and 932 still demonstrate significant contribution from petroleum sources, somewhat greater input of combustion-derived PAH is observed here. The position of these cites in the vicinity of the shaded (combustion) zone in Figure 5.2.3 indicates that all compounds are somewhat heavier than those at the other stations within the zone. Moreover, only a single ratio (BeP/BaP at St. 951) demonstrates presence of petroleum derived PAH. The relative abundance of Py vs. Chy and BaP in the assemblage shows that combustion sources are very important at these sites (Fig. 4.2.5c). Although some compounds still demonstrate light isotopic composition, increased presence of isotopically enriched compounds again indicates the importance of combustion sources (Fig. 4.2.6). The mass balance analysis shows that from 80% to 100% of Fa, Py, and up to 70% of Chy, and 90% of BFl could be formed from combustion sources (Fig. 4.2.7). These stations are also located close to the prominent combustion sources on the mixing curve graphs which indicate that only 10-30% of assemblage can be ascribed to petroleum origin (Fig. 4.2.8-4.2.18). The increased importance of combustion sources at station 967 can possibly be attributed to the influence of the Detroit River. This site is actually incorporated into the South Zone (Fig. 5.1.1) and thus, although somewhat sheltered by irregularities in bottom topography (see

Figure 5.2.5 **Station locations and zones of intensive hydrocarbon exploitation (numerous production wells) in the northern part of the lake after Canadian Hydrographic Service (1993). Note that almost all stations of the North Zone are located within areas of hydrocarbon exploitation.**


83°
82°
81°
80°
79°
43°
42°
Detroit
Lake St.Clair
Windsor
Wheatley
Wh
Monroe
Toledo
Sandusky
Lorain
Cleveland
Erie
Dunkirk
Port Colborne
Buffalo
BI
951
945
953
946
1021
84
961
962
955
966
971
358
967
357
1012
973
974
969
23
935
932
Zones of hydrocarbon exploitation
● 23 Stations
SCALE
0 20 40 60 80 km
0 10 20 30 40 50 mi
N
NE
E
SE
S
SW
W
NW
LAKE ERIE

Section 5.1), may still be affected by combustion produced PAH delivered from Detroit. The somewhat increased importance of car soots over fire soots at this site (Fig. 4.2.5c) also supports this suggestion. Further, station 951 may not be significantly affected by the gas field due to its relatively remote position with respect to the major hydrocarbon reservoirs and the exploitation zone (Fig. 5.2.3, 5.2.4). The latter might have resulted in somewhat reduced importance of petroleum derived compounds at this site. Finally, station 932, although located within the zone of hydrocarbon production, might in addition be affected by combustion-produced PAH originating at Buffalo. These compounds are probably transported through the atmosphere since, as it was previously shown (see Section 5.1; Fig. 5.1.11), the pattern of water circulation in the Eastern Basin prevents any penetration of pollution upstream.

Intensity of degradation (the North Zone): The processes of decomposition are generally very important within the North Zone being most intensive at station 946. Most stations within this zone are shifted left in Figure 5.2.3. This displacement is caused by their low position on PC 1 for molecular composition representing relative abundance of higher and lower molecular weight compounds (Fig. 4.2.5a). In the mixing curves for concentration ratios, these stations are shifted far away from all primary and secondary sources and their mixing arrays. This is especially true for station 946 and 967 (Fig. 4.1.2-4.2.3). The importance of decomposition processes within this zone can possibly be attributed to the increased presence of oil in sediments and very low rates of sedimentation (Fig. 5.1.6). Station 946, in addition, occupies the extreme position on PC

2 for molecular composition assumed to represent weathering processes resulting in unbalanced relative contribution of BeP and BaP (Fig. 4.2.5b). Furthermore, the ratio Py/Per for this site demonstrates the lowest value in the lake indicating ongoing diagenetic processes (Fig. 4.2.1). The importance of different processes at this site can possibly be attributed to the lowest in the lake sedimentation rates (Fig. 5.1.6) and consequently greatest exposure of the assemblage to transformations by different processes.

A single station within this cluster (Wh) does not seem to be affected by processes of PAH decomposition. In Figure 5.2.3 this station is placed together with major sources due to overall predominance of lower molecular weight compounds in the assemblage (Fig. 4.2.5a). Moreover, this site plots directly on the mixing curves for molecular composition (Fig. 4.2.2, 4.2.3). It seems possible that the weathering processes are again masked here by continuous supply of lower molecular weight compounds from the nearby community. However, the station at Wheatley appears to be strongly affected by the process represented by PC2 for molecular composition (Fig. 4.2.5b) and previously found important at site 946.

In conclusion, the North Zone is characterized by an increased influence of petroleum-related sources which can possibly be attributed to seepage of crude hydrocarbons from reservoirs underlying the area and/or seepage and spills of petroleum products resulting from gas production operations in the northern part of the lake. Somewhat decreased contribution of petroleum at a few stations might be attributed to their relative position with respect to the sites of fluvial influx, hydrocarbon reservoirs and production areas. Atmospheric transport of city-produced compounds might also reduce the influence of petroleum-related sources in some areas. Decomposition (possibly biodegradation) processes, assumingly enhanced by the presence of hydrocarbons in sediments and low sedimentation rates, are very important within this zone. Only a single station at Wheatley does not seem to be subjected to this process. However, this site, together with station 946, is strongly affected by another process resulting in reduced BaP/BeP ratios.

Thus, combustion related sources seem to generally dominate on the lake scale. Their contribution is the greatest at Buffalo. On the contrary, the signal of the Detroit River is characterized by importance of petroleum. At Cleveland petroleum-derived PAH are found in traces. The highest contribution of petroleum-related sources is observed in the northern part of the lake where extensive hydrocarbon fields exist and are currently being exploited. Processes of weathering obliterating the PAH assemblage in sediments seem to be very active across the lake. These processes appear to be enhanced at sites where hydrocarbons can be detected in sediments. Low sedimentation rates also seem to result in greater alteration of the PAH assemblage due to weathering. In addition, the distance from the areas of PAH production appears to be an important factor forming the assemblage. Hence, at sites located close to the production areas (human communities), processes of decomposition seem to be masked by a constant supply of less stable compounds to the sediments.

5.2.3 MOLECULAR VS. ISOTOPIC

The fact that two different data sets were used in a number of similar analyses, suggests a convenient opportunity to compare the relative usefulness of molecular and isotopic data in identification of major PAH sources. It is well known (*e.g.*, Neff, 1979; Wakeham *et al.*, 1980) and was clearly shown in the current study that natural processes of decomposition can significantly alter the molecular composition of a PAH assemblage after its release into environment. The latter, in turn, may reduce the usefulness of these data in certain analyses designed to identify the original PAH sources. Conversely, the isotopic composition was shown to little change due to the same processes (*e.g.*, O'Malley, 1994). Thus, it is natural to expect that isotopic data might sometimes provide more help in the source identification procedure. Two analyses in this study clearly demonstrated that studies of the isotopic composition of a PAH assemblage can greatly supplement conventional consideration of their molecular signature.

A comparative analysis of graphs with mixing curves generated for molecular and isotopic ratios shows that only the latter can provide a reliable estimate of the relative importance of petroleum and different combustion sources in the formation of PAH assemblage. The cloud of samples on the graphs with mixing curves generated from molecular data is shifted away from the curves and prominent end members. This makes identification and quantification of the relative importance of different end members almost impossible. Conversely, the curves generated using both molecular and isotopic signatures and plotted for isotopic ratios show that almost all samples plot within the range of statistical variation of the end members and/or within their mixing arrays. Consequently, only these plots allowed the relative contribution of prominent primary and secondary sources to be quantitatively estimated in the present study.

Further, a comparison of the results of principal components analysis for both molecular and isotopic composition enables the relative usefulness of both data sets to be quantified. As it was shown in the previous discussion, the first two components in the principal components analysis for molecular composition account for the alteration of the PAH assemblage by weathering processes. These two components represent as much as 76.5% of total variance in samples. Thus, only the third component in analysis for molecular composition is responsible for the actual relative contribution of different combustion and petroleum sources. This component explains only 11.4% of total variability. On the contrary, in isotopic composition, the first component explains the relative contribution of the two primary sources. This component takes as much as 66.4% of total variability. A simple calculation brings one to conclude that the isotopic data in this procedure was 5.8 times as useful as the molecular.

The above examples demonstrate that identification of PAH isotopic composition should be considered as a technique highly supplementary to the conventional molecular analysis. A similar conclusion was made by O'Malley (1994), who studied the sources of polycyclic aromatic hydrocarbons in two areas of eastern Canada.

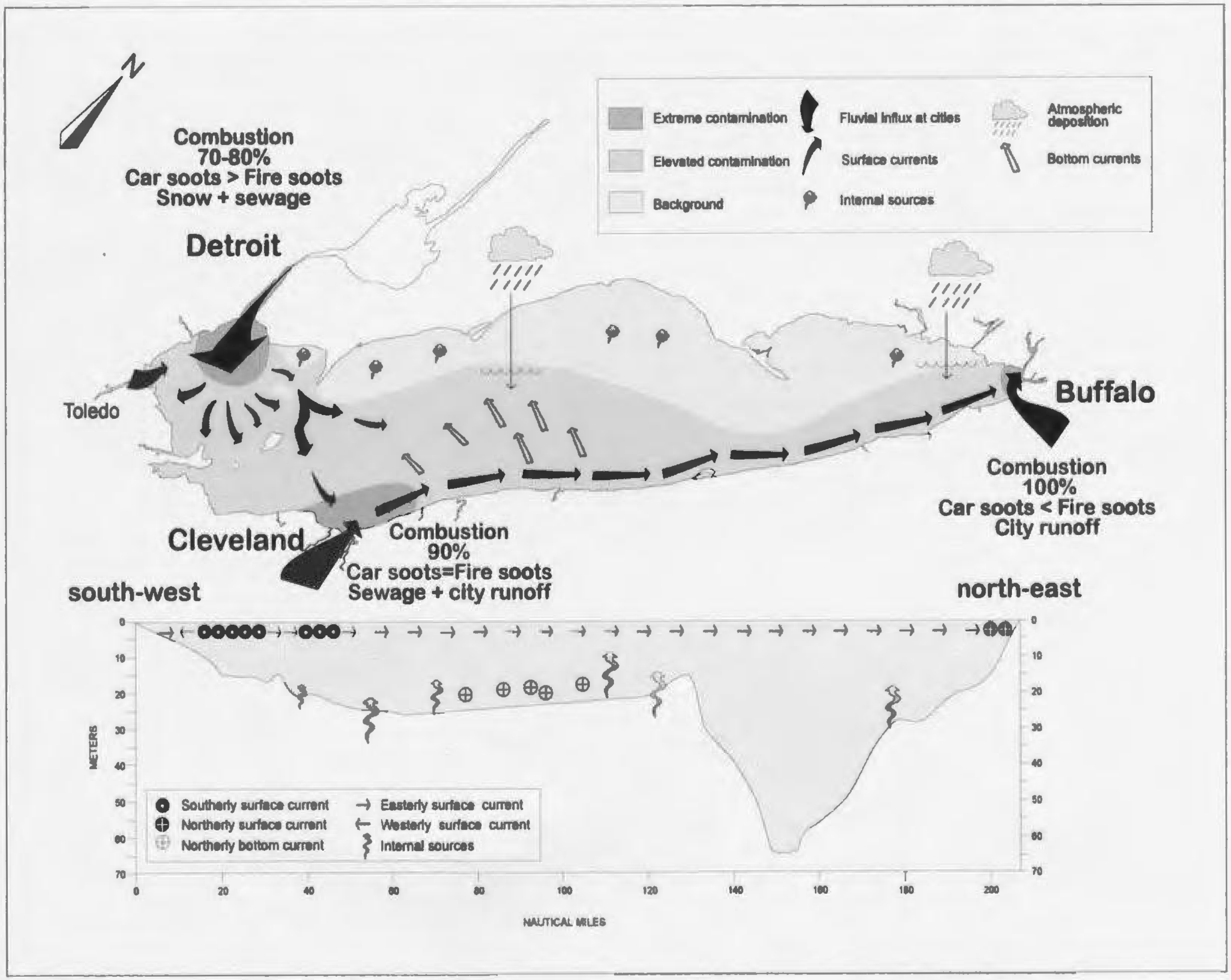
5.3 A MODEL OF SOURCES, PATHWAYS, TRANSPORT AND DEPOSITION OF PAH IN LAKE ERIE

The spatial distribution of sediments with similar molecular and isotopic signatures of PAH was considered in the first study and a mechanism that might create and maintain this distribution scheme was suggested. Another, more detailed study, was based on the comparison of molecular and isotopic composition of PAH in samples with characteristic signatures of major primary and secondary sources. This research allowed an insight into sources and processes participating in the formation of the PAH assemblage in sediments of different parts of the lake. The two studies can be summarized to create a general model of sources, pathways, transport and deposition of PAH in the lake (Fig. 5.3.1).

The major pollution signal is brought to the lake by the Detroit River and injected into the northern part of the Western Basin (Fig. 5.3.1). This signal is generally represented by combustion produced PAH in which car emissions slightly dominate. However, petroleum products seem to be also abundant in the river waters and thus significantly contribute to the PAH assemblage introduced with its flow. Most PAH seem to initially enter the river with snow melt and/or its disposal. The city sewage may also serve as an important pathway of these compounds into the fluvial and further lacustrine environment.

Upon entering the lake, the flow of the Detroit River is distributed by the surface currents veering in different directions and contaminating the whole basin (Fig. 5.3.1). An additional signal, characterized mostly by combustion derived compounds, might

Figure 5.3.1 **Descriptive model of sources, pathways, transport and deposition of PAH in Lake Erie.**


N
Combustion
70-80%
Car soots > Fire soots
Snow + sewage
Detroit
Toledo
Extreme contamination
Elevated contamination
Background
Fluvial influx at cities
Surface currents
Internal sources
Atmospheric deposition
Bottom currents
Buffalo
Combustion
100%
Car soots < Fire soots
City runoff
Cleveland
Combustion
90%
Car soots=Fire soots
Sewage + city runoff
south-west
north-east
METERS
0
10
20
30
40
50
60
70
Southerly surface current
Northerly surface current
Northerly bottom current
Easterly surface current
Westerly surface current
Internal sources
0
20
40
60
80
100
120
140
160
180
200
NAUTICAL MILES

originate from the Maumee River at Toledo and the Raisin River at Monroe. In addition, some diagenetic processes may contribute to the PAH assemblage in the southeastern part of the basin.

Although the major pollution introduced by the Detroit River is distributed and deposited within the Western Basin, the major flow laden with contaminated sediment particles leaves the western part of the lake to enter the Central Basin (Fig. 5.3.1). On exiting the Peele Passage, the flow splits into two parts. The northern branch contaminates sediments of the central part of the lake, while the southern branch reaches the Ohio shore and turns east to become a part of a strong easterly directed drift following along the shore.

At Cleveland, the flow bearing the residual pollution signal is joined by contaminated outflow of the Cuyahoga River (Fig. 5.3.1). The compounds introduced here are predominantly of combustion origin with slight traces of oil. The PAH originating from both car emissions and fire places are further brought into the river with direct city runoff and may partially emanate from storm sewers. The polluted particles are further transported and deposited along the southern shore towards the Niagara River outlet. This contamination can also be partly distributed towards the central part of the lake by existing here compensatory bottom currents and temporary circulation patterns.

Further east, a strong pollution signal is introduced by the Buffalo River at Buffalo (Fig. 5.3.1). The river flow contains only combustion-produced PAH originating from both car emissions and fire places, the latter possibly predominant. This pollutants are conveyed into the river through direct city runoff. However, due to strong hydraulic currents existing at this reach, the contaminated flow of the Buffalo River is entirely diverted into the Niagara River and out of the lake. Therefore, no significant sediment contamination is caused by this flow in other portions of the Eastern Basin.

The above described pattern leaves the northern part of the Central and Eastern Basins relatively unpolluted (Fig. 5.3.1). The background levels of contamination found here can possibly be attributed to seepage of hydrocarbons from the underlying reservoirs and/or spills and leaks of petroleum products during production operations. The processes of atmospheric deposition do not seem very important in the formation of PAH assemblage in sediments. However, traces of city-derived airborne pollutants can be found in remote regions of the Central and Eastern Basins.

Finally, processes of natural weathering altering the PAH assemblage have been found important. These processes seem especially active in the northern areas, where hydrocarbons might be present in sediments. Hence, deferential degradation of the assemblage formed by the above mechanisms accounts for the observed molecular and isotopic compositions of PAH in sediments.

6. CONCLUSIONS

The major conclusions that emerge from the study described above can be summarized as follows:

Three prominent zones characterized by similar molecular and isotopic composition of compounds can be identified in the lake. The PAH fluvially introduced at major cities, are further transported and redistributed by surface and bottom circulation. The latter creates a specific pattern of distribution of differentially contaminated sediments. This pattern, superimposed on some background level of contamination, seems to be responsible for the three-cluster structure observed in the lake.

A subtle interplay between different combustion and petroleum sources and ongoing processes of natural degradation seems to be responsible for the observed within-zone variability in molecular and isotopic composition. Produced mostly from urban centers, combustion-derived PAH appear to dominate in the contaminated zones while the background zone shows high contribution of petroleum-type sources to the formation of PAH assemblage. The latter might result from seepage of hydrocarbons known to underlie this area and/or leaks and seeps from production operations. This zone is also marked by intensive degradation of less stable compounds.

Finally, identification of the isotopic composition of PAH in sediment samples was again shown a technique highly supplementary to the more conventional studies of their molecular composition. Its application is especially important when the identification of original PAH sources is the objective.

In conclusion, it is essential to emphasize that the presented scheme of spatial distribution is very general, and is subject to the limitations imposed by spatial resolution of the sampling program. More detailed coverage for the Central and especially Eastern Basins would be necessary to affirm the patterns suggested for these areas. Additional samples from sites close to the mouths of different tributaries would probably allow the major sources and pathways of PAH to the lacustrine sediments to be further clarified. Finally, more information on molecular and isotopic signatures of different primary and secondary sources that could possibly contribute to the PAH inventory of lake sediments will be required for a more detailed PAH source apportionment of Lake Erie.

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8. APPENDICES

Appendix A1. Total PAH concentrations (ng/g) and concentrations of 16 parental PAH (**a**) with respective standard deviations (**b**) for 23 sediment samples from Lake Erie, Great Lakes.

a)

Station	**TPAH**	**Ae**	**Fl**	**Pa**	**A**	**Fa**	**Py**	**BA**	**Chy**	**BbF**	**BkF**	**BeP**	**BaP**	**Per**	**Ip**	**DBA**	**BP**
974	2137	1.0	36.0	122.5	37.5	162.0	188.5	192.0	109.5	222.0	82.0	184.5	150.0	206.5	160.5	45.0	237.5
973	1669	0.0	43.7	197.0	69.0	217.0	230.5	147.0	115.0	115.0	45.5	89.0	84.5	134.0	65.0	17.5	99.5
1012	1503	1.8	17.0	107.0	31.3	114.0	129.5	118.5	96.5	157.5	67.3	133.3	122.5	61.8	112.3	15.8	217.0
969	2000	3.3	30.1	127.9	35.9	160.4	177.0	173.9	106.2	196.2	69.9	167.4	127.9	322.5	112.0	18.3	170.9
971	5304	0.0	50.8	343.3	107.0	400.3	464.8	534.3	318.8	580.3	216.3	448.5	427.8	180.5	359.5	72.8	799.3
357	2590	8.7	32.4	169.1	49.7	193.5	203.5	257.1	139.2	248.9	102.4	217.1	177.5	212.1	173.5	30.0	375.8
358	2310	7.5	27.0	141.5	45.5	181.0	210.5	182.0	172.0	248.0	104.5	196.5	199.5	136.5	185.5	41.0	231.5
967	1109	0.0	7.0	38.2	11.5	73.5	61.9	90.9	64.6	131.9	47.3	101.9	82.7	96.9	89.0	21.3	190.3
966	2037	0.0	17.5	117.0	39.0	168.0	188.5	204.5	121.5	214.5	82.0	168.0	176.5	125.0	150.0	26.5	238.5
Wh	364	0.8	9.3	71.6	22.0	45.3	33.1	42.3	24.6	15.6	2.8	19.6	9.6	14.0	11.4	6.5	35.6
962	1308	0.0	4.8	59.8	15.5	116.5	110.5	112.3	71.5	149.3	60.3	113.8	83.8	100.3	126.0	20.5	163.8
961	3107	0.0	26.0	146.0	42.5	259.5	234.0	217.5	163.0	378.0	173.0	292.5	185.5	166.0	225.5	55.5	542.0
84	2511	0.0	13.4	100.5	30.5	177.2	237.3	234.3	169.9	367.6	99.5	231.3	172.9	101.2	186.7	27.6	361.2
955	4709	0.0	51.8	299.3	134.3	428.3	399.8	359.3	309.0	438.0	234.0	321.0	399.0	288.8	378.0	77.3	591.8
953	2810	0.8	23.3	136.1	46.1	225.0	188.3	186.4	124.9	349.1	130.1	244.9	164.6	181.5	233.6	33.8	541.1
951	1036	0.0	8.3	60.8	17.5	94.8	80.8	102.5	70.8	121.8	38.3	111.5	60.0	46.8	85.8	13.3	123.0
1021	485	0.0	1.3	16.8	3.5	52.5	52.8	52.8	29.3	49.0	14.0	36.5	29.8	67.8	28.3	8.0	42.5
946	224	0.3	1.9	5.9	2.3	5.7	8.4	25.1	10.4	10.8	1.9	24.2	5.1	99.9	6.8	2.9	12.2
945	308	0.0	0.6	10.3	3.5	23.5	21.6	28.6	18.5	35.2	12.9	32.1	17.6	33.8	22.7	3.9	43.4
23	869	0.2	6.5	63.7	15.0	85.0	73.9	81.8	61.0	98.2	37.1	84.0	63.3	44.3	56.3	9.3	89.2
935	1583	1.0	12.5	103.5	38.0	134.8	132.8	133.0	103.5	168.3	73.0	134.3	122.5	87.0	113.5	36.3	189.5
932	271	0.0	45.0	5.9	2.1	14.8	14.2	13.0	9.2	18.3	7.1	14.4	10.6	79.6	13.3	2.9	20.5
Bf	4979	48.0	126.8	523.5	171.8	630.8	521.3	343.5	525.8	441.0	190.5	288.8	343.5	129.0	296.3	56.3	342.0

Appendix A1. (cont.)

b)

Station	Ae	Fl	Pa	A	Fa	Py	BA	Chy	BbF	BkF	BeP	BaP	Per	Ip	DBA	BP
974	0.32	1.45	0.71	1.73	1.80	4.17	1.03	11.67	12.48	10.36	9.40	12.37	8.03	14.39	0.74	10.08
973	0.00	1.13	6.58	3.04	5.13	7.18	1.91	4.14	4.38	0.42	7.42	4.60	32.28	0.46	0.57	8.52
1012	0.84	2.58	9.65	4.83	6.88	6.74	6.63	7.70	11.32	9.66	11.81	8.47	3.87	5.86	4.42	30.53
969	0.91	0.33	1.32	1.19	1.01	3.95	8.02	4.48	1.69	2.79	1.88	1.93	4.14	0.41	3.14	0.16
971	0.00	5.11	23.12	6.08	16.02	18.00	90.37	15.50	47.43	12.09	36.42	36.59	10.20	29.24	14.65	148.95
357	0.32	1.71	8.64	1.42	15.41	13.78	36.37	11.26	28.92	14.86	10.76	7.83	2.71	2.40	4.89	51.09
358	1.52	0.95	0.81	2.33	0.67	0.81	2.02	6.36	7.00	4.03	7.92	11.35	5.41	3.64	5.87	21.07
967	0.00	0.18	0.98	0.65	1.36	1.19	1.33	4.25	1.84	1.18	1.90	0.64	1.67	2.20	1.19	8.27
966	0.00	0.78	11.53	0.53	6.72	13.12	15.45	4.56	1.73	7.81	5.48	9.19	7.99	6.86	0.67	10.71
Wh	0.21	0.33	7.82	1.64	3.73	4.19	5.83	5.11	2.45	0.56	5.80	1.04	1.61	1.06	1.27	3.08
962	0.00	0.43	5.30	2.13	8.06	8.53	6.71	6.70	12.60	2.50	5.96	3.84	1.70	2.59	3.23	13.02
961	0.00	1.10	4.03	3.82	6.97	0.14	2.44	1.34	53.32	24.64	32.46	9.40	26.38	23.55	5.16	106.17
84	0.00	2.32	12.24	14.78	49.40	61.10	63.49	55.84	86.50	24.22	58.88	42.13	24.29	52.45	6.50	63.43
955	0.00	4.03	32.56	6.05	53.93	0.16	10.61	6.68	6.05	15.59	8.06	11.56	5.99	21.64	10.39	117.10
953	0.13	0.64	7.03	1.35	21.48	7.00	9.12	1.99	31.74	2.28	11.19	9.28	6.42	28.51	1.22	15.22
951	0.00	0.16	4.84	2.49	1.71	4.33	7.94	1.73	9.56	2.49	14.07	4.03	5.53	5.82	2.28	0.80
1021	0.00	0.00	1.54	0.34	3.71	4.61	6.98	3.62	1.56	3.84	8.31	4.24	0.21	7.16	2.37	8.66
946	0.03	0.17	0.49	0.15	0.35	0.49	8.18	0.79	0.81	0.22	3.63	1.31	10.96	0.97	0.53	1.74
945	0.00	0.01	0.19	0.36	0.47	0.01	5.49	1.04	1.33	0.56	1.57	0.66	1.57	3.51	0.63	0.19
23	0.04	0.46	4.53	0.25	7.87	6.84	11.14	1.28	11.01	2.75	5.58	3.60	2.88	3.19	1.07	11.51
935	0.81	0.49	7.44	0.02	11.97	4.14	4.81	10.87	22.95	0.11	12.14	9.46	6.72	20.22	4.30	1.40
932	0.00	0.04	0.09	0.11	0.23	0.33	3.07	0.28	0.64	0.82	0.81	0.00	6.84	1.52	1.56	0.81
Bf	14.55	18.61	31.93	3.02	62.53	11.24	1.17	46.78	14.53	6.63	12.73	15.49	7.69	13.74	0.00	19.20

Appendix A2. Isotopic composition ($\delta^{13}C$, ‰) of 15 parental PAH in 23 sediment samples from Lake Erie, Great Lakes.

Station	Ae	Fl	Pa	A	Fa	Py	BA	Chy	BbF	BkF	BeP	BaP	Per	Ip/DBA	BP
974	-	-	-26.0	-	-26.1	-26.2	-24.4	-24.4	-25.5	-25.0	-26.2	-25.2	-27.3	-27.6	-28.4
973	-	-24.1	-26.4	-26.1	-26.3	-26.2	-25.2	-25.5	-	-	-	-	-27.5	-	-
1012	-	-24.7	-26.2	-	-26.8	-26.3	-24.2	-24.8	-	-	-26.5	-26.6	-	-	-
969	-28.2	-26.2	-26.7	-26.3	-25.9	-25.7	-24.9	-26.3	-25.7	-26.5	-27.2	-27.8	-29.7	-	-
971	-	-	-27.1	-27.5	-26.4	-26.4	-24.6	-25.1	-25.8	-26.3	-26.7	-26.7	-27.7	-	-
357	-27.8	-25.3	-26.8	-26.6	-26.5	-26.6	-25.0	-26.1	-24.9	-26.1	-26.8	-27.0	-28.6	-27.9	-29.3
358	-	-23.8	-25.7	-25.5	-25.8	-25.8	-25.9	-26.3	-26.4	-27.0	-27.2	-27.1	-28.5	-26.3	-27.8
967	-	-	-28.4	-	-26.9	-27.4	-23.3	-25.1	-25.7	-26.1	-26.3	-26.1	-28.6	-24.8	-23.9
966	-	-26.3	-26.9	-26.6	-26.2	-26.3	-25.5	-27.2	-27.4	-	-29.8	-28.8	-	-	-
Wh	-	-	-28.4	-	-26.5	-26.7	-	-	-	-	-	-	-	-	-
962	-	-	-26.6	-	-25.4	-24.9	-22.9	-24.3	-25.3	-25.7	-26.3	-25.9	-28.6	-25.3	-25.2
961	-	-	-26.2	-27.0	-26.1	-24.9	-24.9	-25.7	-25.2	-26.9	-26.5	-27.0	-29.4	-	-
84	-	-	-27.2	-27.9	-25.6	-25.1	-22.9	-24.8	-25.4	-25.5	-26.2	-25.3	-27.2	-25.2	-24.9
955	-	-	-25.7	-25.7	-25.0	-25.0	-25.3	-25.2	-24.3	-26.1	-25.6	-25.1	-27.5	-24.8	-29.1
953	-	-25.2	-25.9	-26.8	-26.3	-28.5	-25.5	-26.4	-26.2	-	-26.8	-	-29.4	-	-
951	-	-	-29.2	-	-27.5	-25.2	-22.8	-24.9	-25.6	-	-27.7	-27.6	-30.0	-28.6	-
1021	-	-	-	-	-27.8	-26.0	-	-22.1	-24.2	-	-	-	-29.1	-	-
946	-	-26.4	-26.5	-	-28.7	-26.0	-24.1	-25.8	-24.9	-	-27.9	-27.7	-28.2	-30.6	-31.2
945	-	-	-	-	-27.4	-25.1	-	-27.2	-	-27.2	-	-	-	-	-
23	-24.4	-	-25.9	-26.1	-25.6	-24.5	-25.0	-25.5	-24.6	-25.8	-26.2	-25.1	-27.2	-25.9	-24.8
935	-	-	-26.5	-	-25.0	-24.9	-24.3	-25.8	-24.9	-25.8	-25.3	-24.2	-27.4	-24.2	-27.4
932	-	-	-	-	-25.6	-24.4	-24.1	-26.4	-	-	-	-	-30.0	-	-
Bf	-	-24.5	-24.4	-23.9	-24.3	-23.9	-23.1	-23.1	-23.7	-23.9	-23.7	-23.7	-26.2	-22.4	-

Appendix A3. **Normalized (to their total sum) concentrations of seven 4-, 5-ring PAH in samples and prominent primary and secondary sources utilized in the source identification procedure.**

Stations	Fa	Py	BaA	Chy	BFl	BeP	BaP
974	0.126	0.146	0.149	0.085	0.236	0.143	0.116
973	0.208	0.221	0.141	0.110	0.154	0.085	0.081
1012	0.121	0.138	0.126	0.103	0.239	0.142	0.130
969	0.136	0.150	0.148	0.090	0.226	0.142	0.109
971	0.118	0.137	0.158	0.094	0.235	0.132	0.126
357	0.126	0.132	0.167	0.090	0.228	0.141	0.115
358	0.121	0.141	0.122	0.115	0.236	0.132	0.134
967	0.112	0.095	0.139	0.099	0.274	0.156	0.126
966	0.127	0.142	0.155	0.092	0.224	0.127	0.133
Wh	0.235	0.172	0.219	0.128	0.095	0.102	0.050
962	0.142	0.135	0.137	0.087	0.256	0.139	0.102
961	0.136	0.123	0.114	0.086	0.290	0.154	0.097
84	0.105	0.140	0.139	0.101	0.276	0.137	0.102
955	0.148	0.138	0.124	0.107	0.233	0.111	0.138
953	0.139	0.117	0.116	0.077	0.297	0.152	0.102
951	0.139	0.119	0.151	0.104	0.235	0.164	0.088
1021	0.166	0.167	0.167	0.092	0.199	0.115	0.094
946	0.062	0.092	0.274	0.113	0.138	0.265	0.056
945	0.124	0.114	0.151	0.097	0.253	0.169	0.093
23	0.146	0.126	0.140	0.104	0.232	0.144	0.108
935	0.134	0.132	0.133	0.103	0.241	0.134	0.122
932	0.146	0.140	0.128	0.091	0.250	0.141	0.104
Bf	0.192	0.159	0.105	0.160	0.192	0.088	0.105
***Primary Sources*[1]**							
Car Soot	0.187	0.170	0.087	0.109	0.178	0.132	0.137
Fire Soot	0.199	0.169	0.114	0.189	0.169	0.088	0.071
Crankcase Oil	0.225	0.292	0.069	0.111	0.136	0.130	0.036
***Secondary sources*[1]**							
Sewage	0.242	0.182	0.110	0.135	0.145	0.086	0.099
Snow	0.249	0.211	0.112	0.164	0.150	0.063	0.051
Road Sweeps	0.201	0.164	0.099	0.144	0.149	0.111	0.132
Atmosphere (total)[2]	0.272	0.193	0.049	0.092	0.237	0.089	0.068

[1] After O’Malley, 1994;

[2] After Eisenrich and Strachan, 1992

Appendix A4. Isotopic signatures (δ^{13}C, ‰) for samples and primary and secondary sources (Stark *et al.*, 1995) employed in the source apportionment procedure. Isotopic compositions for BA/Chy, BbF/BkF, and BeP/BaP represent averages weighted according to the relative abundance of compounds. Standard deviations for sources are given in parentheses.

Stations	Pa	Fa	Py	BA/Chy	BbF/BkF	BeP/BaP	Per
974	-26.00	-26.10	-26.20	-24.40	-25.36	-25.75	-27.30
973	-26.40	-26.30	-26.20	-25.33	-	-	-27.50
1012	-26.20	-26.80	-26.30	-24.47	-	-26.55	-
969	-26.65	-25.90	-25.65	-25.43	-25.91	-27.46	-29.70
971	-27.10	-26.40	-26.40	-24.79	-25.94	-26.70	-27.70
357	-26.80	-26.50	-26.63	-25.39	-25.25	-26.89	-28.55
358	-25.70	-25.80	-25.80	-26.09	-26.58	-27.15	-28.50
967	-28.40	-26.85	-27.40	-24.05	-25.81	-26.21	-28.60
966	-26.90	-26.20	-26.30	-26.13	-27.40	-29.29	-
Wh	-28.40	-26.50	-26.70	-	-	-	-
962	-26.60	-25.40	-24.90	-23.44	-25.42	-26.13	-28.60
961	-26.20	-26.10	-24.90	-25.24	-25.73	-26.69	-29.40
84	-27.15	-25.60	-24.05	-23.70	-25.42	-25.82	-27.20
955	-25.70	-25.00	-25.00	-25.25	-24.93	-25.32	-27.50
953	-25.90	-26.30	-28.50	-25.86	-26.20	-26.80	-29.40
951	-29.20	-27.50	-25.20	-23.66	-25.60	-27.66	-30.00
1021	-	-27.80	-26.00	-22.10	-24.20	-	-29.10
946	-26.50	-28.65	-26.00	-24.60	-24.90	-27.87	-28.20
945	-	-27.40	-25.10	-27.20	-27.20	-	-
23	-25.90	-25.60	-24.50	-25.21	-24.93	-25.73	-27.20
935	-26.50	-25.00	-24.90	-24.95	-25.17	-24.78	-27.40
932	-	-25.55	-24.40	-25.06	-	-	-29.95
Bf	-24.40	-24.30	-23.90	-23.10	-23.76	-23.70	-26.20
Primary Sources							
Car Soot	-24.90 (0.62)	-26.10 (0.13)	-23.20 (0.83)	-24.42 (0.78)	-25.20 (0.80)	-24.70 (0.63)	-
Fire Soot	-25.30 (0.47)	-26.20 (0.17)	-25.70 (0.27)	-24.35 (0.10)	-25.40 (0.33)	-23.93 (0.37)	-
Crankcase Oil	-29.10 (0.28)	-28.40 (0.33)	-28.60 (0.37)	-27.90 (0.30)	-28.60 (0.50)	-27.40 (0.53)	-
Secondary sources							
Road Sweeps	-23.0 (0.17)	-23.60 (0.20)	-23.60 (0.20)	-22.04 (0.23)	-23.00 (0.17)	-22.47 (0.30)	-

Appendix A5. Characteristic PAH ratios and other criteria commonly used in the sources identification procedure.

Σ 4,5-ring PAH	Predominance of parental 4,5-ring PAH is indicative of combustion[1].
Unresolved Complex Mixture (UCM)	Biodegraded petroleum[1]
Acenaphthene (Ae)	Combustion-specific PAH[2]
Fluoranthene/Pyrene (Fa/Py)	Fa/Py ratios greater than unity are associated with combustion sources and predominance of Py is commonly associated with petroleum sources[2].
Benzo(b)fluoranthene/Benzo(e)Pyrene BbF/BeP	BeP is associated with high petroleum inputs[2].
Benzo(a)pyrene/Benzo(e)pyrene BaP/BeP	Predominance of BaP is characteristics of combustion sources[2].
Perylene (Per)	Per chiefly originates from diagenesis[1].
Pyrene/Perylene (Py/Per)	Py/Per ratio greater than unity is indicative of anthropogenic sources of PAH assemblage[1].

[1] After O'Malley, 1994
[2] After Yunker and MacDonald, 1995

Appendix A6. The two-component mass balance model employed in the source identification procedure. (After O'Malley, 1994.)

The relative contribution from combustion and petroleum-related sources to a sample can be estimated using a two component mass balance model:

$$\delta^{13}C = \sum_{k=1}^{n} \delta^{13}C_A{}^k f_A{}^k$$

$$\text{where} \sum_{k=1}^{n} f_A{}^k = 1$$

A = Compound of interest

k = Sources of interest

f = fractional contribution of A from k

To solve this equation uniquely, only two major contributors should be considered at a time. For example, "Car soots" and "fire soots" can be combined into a "combustion source", while all petroleum-related sources can be considered as a "petroleum source". Then to calculate the relative contribution from each source to formation of, for instance Fa, one should solve the equation using $\delta^{13}C$ values for Fa in sample and both end-members:

$$\delta^{13}C_{(\text{Fa samp})} = \delta^{13}C_{(\text{Fa comb})}\,(f) + \delta^{13}C_{(\text{Fa pet})}\,(1-f)$$

$$f = [\delta^{13}C_{(\text{Fa samp})} - \delta^{13}C_{(\text{Fa pet})}]/[\delta^{13}C_{(\text{Fa comb})} - \delta^{13}C_{(\text{Fa pet})}] * 100\%$$

Appendix A7. The hyperbolic equation for generation of mixing curves for ratio-ratio plots.

The relative contribution from two major primary sources or end-members to a sample can be assessed using both molecular and isotopic ratios included in a two component mixing equation suggested by Vollmer, 1976, developed by Longmuir *et al.*, 1978, and applied for the apportionment of PAH sources by O'Malley, 1994 and O'Malley *et al.*, 1996. The mixing equation is a hyperbola of the form:

$$Ax + Bxy + Cy + D = 0,$$

where A, B, C, and D are the coefficients:

$$A = a_2b_1y_2 - a_1b_2y_1$$

$$B = a_1b_2 - a_2b_1$$

$$C = a_2b_1x_1 - a_1b_2x_1$$

$$D = a_1b_2x_2y_1 - a_2b_1x_1y_2$$

and x, y are general variables along the abscissa and ordinate respectively reprezenting coordinates of the end-member i.

The curvature of hyperbola is controlled by the B coefficient and can be estimated by calculating r:

$$r = a_1b_2/a_2b_1$$

Suppose one wants to calculate the coefficients for compounds, X, Y, Z, and W with X/Y ratio on the x axis and Z/W ratio on the y axis, and car soots and crankcase oil representing combustion and petroleum end-members respectively. Then the above parameters are assigned as follows:

Appendix A7. (cont.)

x_1, = X_1/Y_1 ratio of concentrations of X and Y in car soot;

x_2, = X_2/Y_2 ratio of concentrations of X and Y in crankcase oil;

y_1, = Z_1/W_1 ratio of concentrations of Z and W in car soot;

y_2, = Z_2/W_2 ratio of concentrations of Z and W in crankcase oil

a_1, = concentration of compound W in car soot;

a_2, = concentration of compound W in crankcase oil;

b_1, = concentration of compound Y in car soot;

b_2, = concentration of compound Y in crankcase oil;

For simular calculations employing the isotopic composition and concentration of two individual compounds (X and Y), the parameters are as follows:

x_1, = isotopic composition of compound X in car soot;

x_2, = isotopic composition of compound X in crankcase oil

y_1, = isotopic composition of compound Y in car soot;

y_2, = isotopic composition of compound Y in crankcase oil

a_1, = concentration of compound Y in car soot;

a_2, = concentration of compound Y in crankcase oil;

b_1, = concentration of compound X in car soot;

b_2, = concentration of compound X in crankcase oil;

Appendix A8. Correlation matrix for concentrations of 16 parental PAH identified in sediment samples from Lake Erie (n=23).

	Ae	**Fl**	**Pa**	**A**	**Fa**	**Py**	**BA**	**Chy**
Ae	1.0000 P<0.0000	-	-	-	-	-	-	-
Fl	0.8100 P<0.0000	1.0000 P<0.0000	-	-	-	-	-	-
Pa	0.7193 P<0.0001	0.8938 P<0.0000	1.0000 P<0.0000	-	-	-	-	-
A	0.6594 P<0.0006	0.8725 P<0.0000	0.9818 P<0.0000	1.0000 P<0.0000	-	-	-	-
Fa	0.6742 P<0.0004	0.8606 P<0.0000	0.9787 P<0.0000	0.9741 P<0.0000	1.0000 P<0.0000	-	-	-
Py	0.5593 P<0.0055	0.8039 P<0.0000	0.9573 P<0.0000	0.9467 P<0.0000	0.9730 P<0.0000	1.0000 P<0.0000	-	-
BA	0.3362 P<0.1167	0.6243 P<0.0015	0.8430 P<0.0000	0.8259 P<0.0000	0.8616 P<0.0000	0.9389 P<0.0000	1.0000 P<0.0000	-
Chy	0.7335 P<0.0001	0.8622 P<0.0000	0.9707 P<0.0000	0.9571 P<0.0000	0.9815 P<0.0000	0.9611 P<0.0000	0.8497 P<0.0000	1.0000 P<0.0000
BbF	0.3394 P<0.1131	0.5886 P<0.0031	0.7952 P<0.0000	0.7799 P<0.0000	0.8611 P<0.0000	0.9141 P<0.0000	0.9492 P<0.0000	0.8467 P<0.0000
BkF	0.3633 P<0.0884	0.6326 P<0.0012	0.8263 P<0.0000	0.8419 P<0.0000	0.8967 P<0.0000	0.9172 P<0.0000	0.9211 P<0.0000	0.8660 P<0.0000
BeP	0.2814 P<0.1933	0.5493 P<0.0066	0.7718 P<0.0000	0.7527 P<0.0000	0.8295 P<0.0000	0.8941 P<0.0000	0.9605 P<0.0000	0.8085 P<0.0000
BaP	0.3987 P<0.0595	0.6710 P<0.0005	0.8691 P<0.0000	0.8812 P<0.0000	0.9032 P<0.0000	0.9502 P<0.0000	0.9666 P<0.0000	0.8990 P<0.0000
Per	0.0822 P<0.7091	0.4028 P<0.0567	0.4618 P<0.0265	0.4933 P<0.0168	0.5134 P<0.0122	0.5634 P<0.0051	0.6043 P<0.0023	0.4356 P<0.0377
Ip	0.3406 P<0.1117	0.6046 P<0.0022	0.8083 P<0.0000	0.8254 P<0.0000	0.8779 P<0.0000	0.9114 P<0.0000	0.9341 P<0.0000	0.8551 P<0.0000
DBA	0.2987 P<0.1662	0.5935 P<0.0028	0.7831 P<0.0000	0.8077 P<0.0000	0.8453 P<0.0000	0.8798 P<0.0000	0.8972 P<0.0000	0.8173 P<0.0000
Bp	0.1139 P<0.6050	4165 P<0.0480	0.6528 P<0.0007	06521 P<0.0007	0.7272 P<0.0001	0.7882 P<0.0000	0.8956 P<0.0000	0.6830 P<0.0003

Appendix A8. (cont.)

	BbF	BkF	BeP	BaP	Per	Ip	DBA	Bp
BbF	1.0000 P<0.0000	-	-	-	-	-	-	-
BkF	0.9644 P<0.0000	1.0000 P<0.0000	-	-	-	-	-	-
BeP	0.9889 P<0.0000	0.9615 P<0.0000	1.0000 P<0.0000	-	-	-	-	-
BaP	0.9452 P<0.0000	0.9637 P<0.0000	0.9454 P<0.0000	1.0000 P<0.0000	-	-	-	-
Per	0.5829 P<0.0035	0.6238 P<0.0000	0.6236 P<0.0015	0.6035 P<0.0023	1.0000 P<0.0000	-	-	-
Ip	0.9708 P<0.0000	0.9870 P<0.0000	0.9660 P<0.0000	0.9716 P<0.0000	0.6253 P<0.0014	1.0000 P<0.0000	-	-
DBA	0.9152 P<0.0000	0.9609 P<0.0000	0.9247 P<0.0000	0.9410 P<0.0000	0.6131 P<0.0019	0.9534 P<0.0000	1.0000 P<0.0000	-
Bp	0.9473 P<0.0000	0.9279 P<0.0000	0.9605 P<0.0000	0.8784 P<0.0000	0.5790 P<0.0038	0.9310 P<0.0000	0.8806 P<0.0000	1.0000 P<0.0000

Appendix A9. Correlation matrix for $\delta^{13}C$ values of 15 parental PAH identified in sediment samples from Lake Erie, Great Lakes.

	Ae	Fl	Pa	A	Fa	Py	BA	Chy	BbF	BkF
Ae	1.0000 N=4 P<0.0000	-	-	-	-	-	-	-	-	-
Fl	1.0000 N=2 P<0.0000	1.0000 N=9 P<0.0000	-	-	-	-	-	-	-	-
Pa	0.5514 N=4 P<0.4486	0.5563 N=9 P<0.1198	1.0000 N=20 P<0.0000	-	-	-	-	-	-	-
A	0.7422 N=3 P<0.4676	0.5152 N=7 P<0.2367	0.8859 N=12 P<0.0001	1.0000 N=12 P<0.0000	-	-	-	-	-	-
Fa	0.6255 N=4 P<0.3745	0.4738 N=9 P<0.1976	0.5559 N=20 P<0.0109	0.7095 N=12 P<0.0098	1.0000 N=23 P<0.0000	-	-	-	-	-
Py	0.7187 N=4 P<0.2813	0.1527 N=9 P<0.6949	0.3172 N=20 P<0.1730	0.4222 N=12 P<0.1715	0.4496 N=23 P<0.0314	1.0000 N=23 P<0.0000	-	-	-	-
BA	-0.2600 N=4 P<0.7400	-0.0636 N=9 P<0.8708	-0.3901 N=19 P<0.0987	0.0176 N=12 P<0.9567	-0.0305 N=20 P<0.8985	0.3466 N=20 P<0.1343	1.0000 N=20 0.0000	-	-	-
Chy	0.4147 N=4 P<0.5853	0.4412 N=9 P<0.2345	0.1557 N=19 P<0.5244	0.4203 N=12 P<0.1737	0.0387 N=22 P<0.8643	0.1823 N=22 P<0.4167	0.6873 N=20 P<0.0008	1.0000 N=22 0.0000	-	-
BbF	0.7519 N=4 P<0.2481	0.1916 N=7 P<0.6807	0.3887 N=17 P<0.1231	0.4674 N=11 P<0.1472	0.1616 N=18 P<0.5218	0.5371 N=18 P<0.0215	0.3475 N=17 0.1717	0.6743 N=18 P<0.0021	1.0000 N=18 0.0000	-
BkF	0.8350 N=4 P<0.1650	0.1072 N=4 P<0.8928	0.4201 N=13 P<0.1529	0.5025 N=9 P<0.1680	0.6519 N=14 P<0.0115	0.3125 N=14 P<0.2766	0.6313 N=13 0.0207	0.8861 N=14 0.0000	0.6437 N=13 P<0.0176	1.0000 N=14 0.0000

Appendix A9. (cont.)

	Ae	Fl	Pa	A	Fa	Py	BA	Chy	BbF	BkF
BeP	0.7129 N=4 P<0.2871	0.5923 N=8 P<0.1218	0.4730 N=18 P<0.0474	0.4930 N=11 P<0.1234	0.6373 N=18 P<0.0044	0.4241 N=18 P<0.0794	0.3386 N=18 P<0.1693	0.7283 N=18 0.0006	0.7987 N=17 0.0001	0.8160 N=13 P<0.0007
BaP	0.8770 N=4 P<0.1230	0.6128 N=7 P<0.1435	0.4600 N=17 P<0.0632	0.4448 N=10 P<0.1977	0.6829 N=17 P<0.0025	0.5291 N=17 P<0.0290	0.3262 N=17 P<0.2014	0.6850 N=17 P<0.0024	0.7196 N=16 0.0017	0.7979 N=13 0.0011
Per	0.9217 N=4 P<0.0783	0.4775 N=7 P<0.2786	0.5323 N=17 P<0.0278	0.3892 N=11 P<0.2368	0.4394 N=19 P<0.0598	0.2578 N=19 P<0.2866	0.0690 N=18 P<0.7856	0.3241 N=19 P<0.1758	0.4897 N=17 P<0.0460	0.7811 N=13 0.0016
Ip/DBA	0.2168 N=3 P<0.8609	0.7358 N=4 P<0.2642	0.3948 N=12 P<0.2041	0.5971 N=6 P<0.2108	0.8906 N=12 P<0.0001	0.4605 N=12 P<0.1319	0.1470 N=12 P<0.6485	0.4752 N=12 P<0.1184	0.3653 N=12 P<0.2430	0.4680 N=10 P<0.1726
Bp	0.4076 N=3 P<0.7327	0.9878 N=3 P<0.0996	-0.4771 N=10 P<0.1632	-0.4954 N=5 P<0.3961	0.4225 N=10 P<0.2238	0.1372 N=10 P<0.7055	0.5087 N=10 P<0.1332	0.4325 N=10 P<0.2119	-0.2605 N=10 P<0.4673	0.1406 N=9 P<0.7182

	BeP	BaP	Per	Ip/DBA	Bp
BeP	1.0000 N=18 0.0000	-	-	-	-
BaP	0.9177 N=17 P<0.0000	1.0000 N=17 0.0000	-	-	-
Per	0.7337 N=16 0.0012	0.8465 N=15 P<0.0001	1.0000 N=19 0.0000	-	-
Ip/DBA	0.8823 N=12 0.0001	0.8309 N=12 0.0008	0.5971 N=6 P<0.2108	1.0000 N=12 0.0000	-
Bp	0.4215 N=10 P<0.2251	0.4272 N=10 0.2182	-0.4954 N=5 P<0.3961	0.4225 N=10 P<0.2238	1.0000 N=10 0.0000

Appendix B1. The output of a principal components analysis performed on the concentrations of seven compounds (Ae, Fl, Fa, BbF, Per, DBA, BP) selected for the analysis of spatial distribution pattern: **a)** percentage of total variance explained by principal components; **b)** weights of variables in the three first principal components, variables (1-7) correspond with the seven selected compounds as listed in the caption; **c)** scores of the three first principal components, case numbers (1-23) correspond with the 23 stations as listed in Appendix A1.

a)

```
Tue Dec 24  1996  10:00:31 AM

          Principal Components Analysis
--------------------------------------------------
    Component    Percent of     Cumulative
     Number       Variance      Percentage
        1         67.77364        67.77364
        2         20.20547        87.97911
        3          7.86086        95.83997
        4          1.85944        97.69941
        5          1.40340        99.10281
        6           .58134        99.68415
        7           .31585       100.00000
--------------------------------------------------
```

b)

```
Variable: MOLSPDST.WEIGHTS   (length = 7 7)
----------------------------------------------------------
(1,1)  0.250078     (1,2) -0.678499     (1,3) -0.0151317
(2,1)  0.366322     (2,2) -0.443205     (2,3) -0.184789
(3,1)  0.441186     (3,2) -0.17208      (3,3)  0.0856554
(4,1)  0.43098      (4,2)  0.192722     (4,3)  0.262127
(5,1)  0.302179     (5,2)  0.311627     (5,3) -0.878145
(6,1)  0.424055     (6,2)  0.202348     (6,3)  0.157881
(7,1)  0.389545     (7,2)  0.372021     (7,3)  0.305797
----------------------------------------------------------
```

Appendix B1. (cont.).

c)

```
Tue Dec 24  1996  10:03:48 AM

Variable: MOLSPDST.PCOMP   (length = 23 7)
-----------------------------------------------------------------
( 1,1)  0.721785     ( 1,2)  0.474457     ( 1,3) -0.828452
( 2,1) -0.409935     ( 2,2) -0.571828     ( 2,3) -0.617448
( 3,1) -1.00813      ( 3,2) -0.178239     ( 3,3)  0.542434
( 4,1)  0.421157     ( 4,2)  0.479534     ( 4,3) -2.43035
( 5,1)  4.09667      ( 5,2)  1.62845      ( 5,3)  1.13523
( 6,1)  1.02039      ( 6,2)  0.137214     ( 6,3) -0.720556
( 7,1)  0.531816     ( 7,2) -0.135226     ( 7,3)  0.0247753
( 8,1) -1.18284      ( 8,2)  0.262267     ( 8,3)  0.153907
( 9,1) -0.229972     ( 9,2)  0.330256     ( 9,3)  0.0697396
(10,1) -2.44136      (10,2) -0.681196     (10,3)  0.518943
(11,1) -1.08933      (11,2)  0.228307     (11,3)  0.140138
(12,1)  1.90656      (12,2)  1.26515      (12,3)  0.538783
(13,1)  0.327215     (13,2)  0.71063      (13,3)  0.815986
(14,1)  3.91759      (14,2)  1.50541      (14,3) -0.581327
(15,1)  1.33642      (15,2)  1.12018      (15,3)  0.153508
(16,1) -1.60875      (16,2) -0.190894     (16,3)  0.544767
(17,1) -2.20345      (17,2) -0.227449     (17,3)  0.0527851
(18,1) -2.46802      (18,2) -0.220729     (18,3) -0.485763
(19,1) -2.54742      (19,2) -0.372306     (19,3)  0.369759
(20,1) -1.87043      (20,2) -0.303115     (20,3)  0.459816
(21,1) -0.547018     (21,2)  0.177879     (21,3)  0.430321
(22,1) -1.91078      (22,2) -0.972382     (22,3) -0.520052
(23,1)  5.23785      (23,2) -4.46637      (23,3)  0.233065
-----------------------------------------------------------------
```

Appendix B2. The output of a principal components analysis performed on the isotopic composition of seven compounds (Pa, Fa, Py, Chy, BbF, BeP, Per) selected for the analysis of spatial distribution pattern: **a)** percentage of total variance explained by principal components; **b)** weights of variables in the three first principal components, variables (1-7) correspond with the seven selected compounds as listed in the caption; **c)** scores of the three first principal components, case numbers (1-23) correspond with the 23 stations as listed in Appendix A2.

a)

```
Tue Dec 24  1996  11:15:48 AM

          Principal Components Analysis
-------------------------------------------------
     Component   Percent of     Cumulative
      Number      Variance      Percentage
         1         52.60755       52.60755
         2         20.96221       73.56976
         3         11.49548       85.06524
         4          6.05574       91.12097
         5          5.25220       96.37318
         6          2.89609       99.26927
         7           .73073      100.00000
-------------------------------------------------
```

b)

```
Variable: ISOSPDST.WEIGHTS   (length = 7 7)
---------------------------------------------------------
(1,1)  0.308297    (1,2) -0.483542    (1,3) -0.344978
(2,1)  0.28378     (2,2) -0.584208    (2,3) -0.0471894
(3,1)  0.277838    (3,2) -0.278673    (3,3)  0.848248
(4,1)  0.386327    (4,2)  0.463421    (4,3)  0.0414758
(5,1)  0.451978    (5,2)  0.24255     (5,3)  0.151634
(6,1)  0.463954    (6,2)  0.267083    (6,3) -0.115026
(7,1)  0.422424    (7,2) -0.0480239   (7,3) -0.348275
---------------------------------------------------------
```

Appendix B2. (cont.)

c)

```
Tue Dec 24  1996  11:20:12 AM

Variable: ISOSPDST.PCOMP   (length = 23 7)
-------------------------------------------------------------
( 1,1)  0.996537     ( 1,2)  0.110925     ( 1,3) -1.00869
( 2,1)  0.348163     ( 2,2) -0.0233338    ( 2,3) -0.762703
( 3,1)  0.240042     ( 3,2)  0.576862     ( 3,3) -0.581203
( 4,1) -0.891371     ( 4,2) -0.695668     ( 4,3)  0.3497
( 5,1) -0.13886      ( 5,2)  0.44015      ( 5,3) -0.715835
( 6,1) -0.326841     ( 6,2)  0.31714      ( 6,3) -0.582255
( 7,1) -0.603481     ( 7,2) -1.43823      ( 7,3) -0.582554
( 8,1) -1.09542      ( 8,2)  1.70282      ( 8,3) -0.80147
( 9,1) -3.67784      ( 9,2) -1.56637      ( 9,3)  0.0492222
(10,1) -2.5835       (10,2)  0.0415966    (10,3) -0.0488192
(11,1)  0.992445     (11,2) -0.2383       (11,3)  0.653783
(12,1)  0.164226     (12,2) -0.505612     (12,3)  0.788717
(13,1)  1.10723      (13,2) -0.061929     (13,3)  0.243283
(14,1)  2.27504      (14,2) -0.812571     (14,3)  0.0196458
(15,1) -1.63973      (15,2) -0.193287     (15,3) -2.39548
(16,1) -1.80948      (16,2)  1.77094      (16,3)  1.84204
(17,1)  1.7485       (17,2)  3.70014      (17,3)  0.440511
(18,1) -0.838353     (18,2)  1.17459      (18,3) -0.0752526
(19,1) -2.39711      (19,2) -0.267732     (19,3)  1.18257
(20,1)  1.82209      (20,2) -0.827005     (20,3)  0.409662
(21,1)  1.67716      (21,2) -0.819925     (21,3)  0.176135
(22,1) -0.63609      (22,2) -1.53993      (22,3)  1.32786
(23,1)  5.26665      (23,2) -0.845267     (23,3)  0.0711353
-------------------------------------------------------------
```

Appendix B3. The output of a principal components analysis performed on the normalized concentrations of seven 4- and 5-ring compounds (Fa, Py, Chy, BA, BFl, BeP, BaP) in samples and prominent primary and secondary sources. **a)** percentage of total variance explained by principal components; **b)** weights of variables in the three first principal components, variables (1-7) correspond with the seven selected compounds as listed in the caption; **c)** scores of the three first principal components, case numbers (1-30) correspond with 23 stations and 7 primary and secondary sources as listed in Appendix A3.

a)

```
Tue Dec 24  1996  10:28:34 AM

          Principal Components Analysis
---------------------------------------------------
     Component   Percent of     Cumulative
      Number      Variance      Percentage
        1         53.35770       53.35770
        2         23.11028       76.46798
        3         11.43536       87.90334
        4          5.77843       93.68177
        5          4.17612       97.85788
        6          2.14181       99.99970
        7           .00030      100.00000
---------------------------------------------------
```

b)

```
Variable: ML7SRS.WEIGHTS   (length = 7 7)
---------------------------------------------------------
(1,1)  0.486342    (1,2) -0.101066     (1,3) -0.110098
(2,1)  0.453015    (2,2) -0.0423917    (2,3) -0.364327
(3,1) -0.248146    (3,2)  0.629123     (3,3)  0.138469
(4,1)  0.350926    (4,2)  0.19265      (4,3)  0.672157
(5,1) -0.363837    (5,2) -0.465763     (5,3) -0.193662
(6,1) -0.406821    (6,2)  0.346617     (6,3) -0.234028
(7,1) -0.275033    (7,2) -0.466905     (7,3)  0.540279
---------------------------------------------------------
```

Appendix B3. (cont.)

c)

```
Tue Dec 24  1996  10:13:25 AM

Variable: ML7SRS.PCOMP   (length = 30 7)
---------------------------------------------------------------
( 1,1) -1.25688      ( 1,2) -0.225778     ( 1,3) -0.321825
( 2,1)  2.34984      ( 2,2)  0.37778      ( 2,3) -0.554497
( 3,1) -1.16513      ( 3,2) -0.700713     ( 3,3)  0.415915
( 4,1) -0.873601     ( 4,2) -0.0239859    ( 4,3) -0.355927
( 5,1) -1.33422      ( 5,2) -0.25884      ( 5,3)  0.3049
( 6,1) -1.36461      ( 6,2)  0.172624     ( 6,3)  0.0329712
( 7,1) -0.830774     ( 7,2) -0.796681     ( 7,3)  0.8332
( 8,1) -2.23188      ( 8,2) -0.586895     ( 8,3)  0.470051
( 9,1) -1.13237      ( 9,2) -0.416666     ( 9,3)  0.382642
(10,1)  2.35389      (10,2)  2.90151      (10,3)  0.0699133
(11,1) -1.08015      (11,2) -0.399525     (11,3) -0.549618
(12,1) -1.51385      (12,2) -0.820936     (12,3) -0.862725
(13,1) -1.3348       (13,2) -0.414747     (13,3) -0.235729
(14,1) -0.516041     (14,2) -1.11         (14,3)  0.824896
(15,1) -1.75068      (15,2) -1.02531      (15,3) -0.950436
(16,1) -1.14143      (16,2)  0.613399     (16,3) -0.270458
(17,1)  0.147629     (17,2)  0.439071     (17,3) -0.454745
(18,1) -2.92536      (18,2)  5.11584      (18,3) -0.096055
(19,1) -1.666        (19,2)  0.408964     (19,3) -0.38321
(20,1) -0.871796     (20,2) -0.0584912    (20,3)  0.145925
(21,1) -0.973518     (21,2) -0.569496     (21,3)  0.359892
(22,1) -0.890257     (22,2) -0.485277     (22,3) -0.512092
(23,1)  1.85018      (23,2) -0.423541     (23,3)  1.5091
(24,1)  0.63875      (24,2) -1.0643       (24,3)  0.429382
(25,1)  2.86226      (25,2)  0.679539     (25,3)  1.62443
(26,1)  3.83463      (26,2)  0.508305     (26,3) -2.54332
(27,1)  2.64016      (27,2) -0.14906      (27,3)  0.638949
(28,1)  4.10674      (28,2)  0.585476     (28,3)  0.323986
(29,1)  1.59641      (29,2) -0.495401     (29,3)  1.5486
(30,1)  2.47286      (30,2) -1.77687      (30,3) -1.82412
---------------------------------------------------------------
```

Appendix B4. The output of a principal components analysis performed on the isotopic values of seven 4- and 5-ring compounds (Fa, Py, BA/Chy, BbF/BkF, BeP/BaP) in samples and prominent primary and secondary sources. **a)** percentage of total variance explained by principal components; **b)** weights of variables in the three first principal components, variables (1-5) correspond with the five selected compounds as listed in the caption; **c)** scores of the three first principal components, case numbers (1-27) correspond with 23 stations and 4 primary and secondary sources as listed in Appendix A4.

a)

```
Tue Dec 24  1996  10:44:47 AM

          Principal Components Analysis
--------------------------------------------
     Component   Percent of     Cumulative
      Number      Variance      Percentage
        1         66.43407       66.43407
        2         15.95047       82.38454
        3         10.53852       92.92305
        4          4.97558       97.89864
        5          2.10136      100.00000
--------------------------------------------
```

b)

```
Variable: ISOSOURC.WEIGHTS   (length = 5 5)
----------------------------------------------------------
(1,1)  0.412587     (1,2) -0.628282      (1,3)  0.203497
(2,1)  0.41507      (2,2) -0.314259      (2,3) -0.779245
(3,1)  0.443287     (3,2)  0.595639      (3,3) -0.0725632
(4,1)  0.49889      (4,2)  0.368445      (4,3)  1.42818E-3
(5,1)  0.460537     (5,2) -0.126357      (5,3)  0.588302
----------------------------------------------------------
```

Appendix B4. (cont.)

c)

```
Tue Dec 24  1996  10:49:19 AM

Variable: ISOSOURC.PCOMP   (length = 27 5)
-------------------------------------------------------------
( 1,1)  0.30271       ( 1,2)  0.275548      ( 1,3)  0.558032
( 2,1) -0.304508      ( 2,2) -0.210812      ( 2,3)  0.591216
( 3,1) -0.265798      ( 3,2)  0.711325      ( 3,3)  0.191726
( 4,1) -0.551218      ( 4,2) -0.479859      ( 4,3) -0.331055
( 5,1) -0.548823      ( 5,2)  0.198597      ( 5,3)  0.2844
( 6,1) -0.603267      ( 6,2)  0.287322      ( 6,3)  0.366814
( 7,1) -0.996937      ( 7,2) -1.04725       ( 7,3) -0.0693569
( 8,1) -0.491315      ( 8,2)  1.09804       ( 8,3)  0.952239
( 9,1) -2.32706       ( 9,2) -0.821118      ( 9,3) -0.651394
(10,1) -1.50179       (10,2)  0.0436406     (10,3) -0.0874696
(11,1)  1.15936       (11,2)  0.0116086     (11,3) -0.296854
(12,1) -9.01871E-3    (12,2) -0.46725       (12,3) -0.537716
(13,1)  1.04264       (13,2)  0.0173842     (13,3) -0.110557
(14,1)  1.13041       (14,2) -0.905039      (14,3)  0.243486
(15,1) -1.69422       (15,2)  0.0921472     (15,3)  1.59026
(16,1) -0.318243      (16,2)  1.22332       (16,3) -1.06499
(17,1)  0.665231      (17,2)  2.70733       (17,3) -0.477385
(18,1) -1.05674       (18,2)  1.88928       (18,3) -0.817564
(19,1) -2.41198       (19,2) -0.922971      (19,3) -1.23001
(20,1)  0.962491      (20,2) -0.639937      (20,3) -0.32472
(21,1)  1.3145        (21,2) -0.918809      (21,3)  0.371371
(22,1) -0.0286953     (22,2) -0.831984      (22,3) -1.14123
(23,1)  3.4762        (23,2) -0.333511      (23,3)  0.204878
(24,1)  1.64521       (24,2) -0.495439      (24,3) -0.852421
(25,1)  0.966239      (25,2)  0.0704337     (25,3)  0.926397
(26,1) -4.45201       (26,2) -0.387286      (26,3)  1.15159
(27,1)  4.89662       (27,2) -0.164708      (27,3)  0.56031
-------------------------------------------------------------
```

Appendix C1. Weighted scores of the three first principal components extracted from both molecular and isotopic data sets in the analysis of spatial distribution pattern and utilized for further groupping (columns 1-6). The output of the non-hierarchical (K-means) cluster analysis utilized for grouping of the weighted scores (columns 7-9). Three clusters were ordered in the Cluster Analysis Module of Statistica 5.1 (StatSoft, Inc., 1995).

`data file: SPDISTBN.STA [ 23 cases with 9 variables ]`

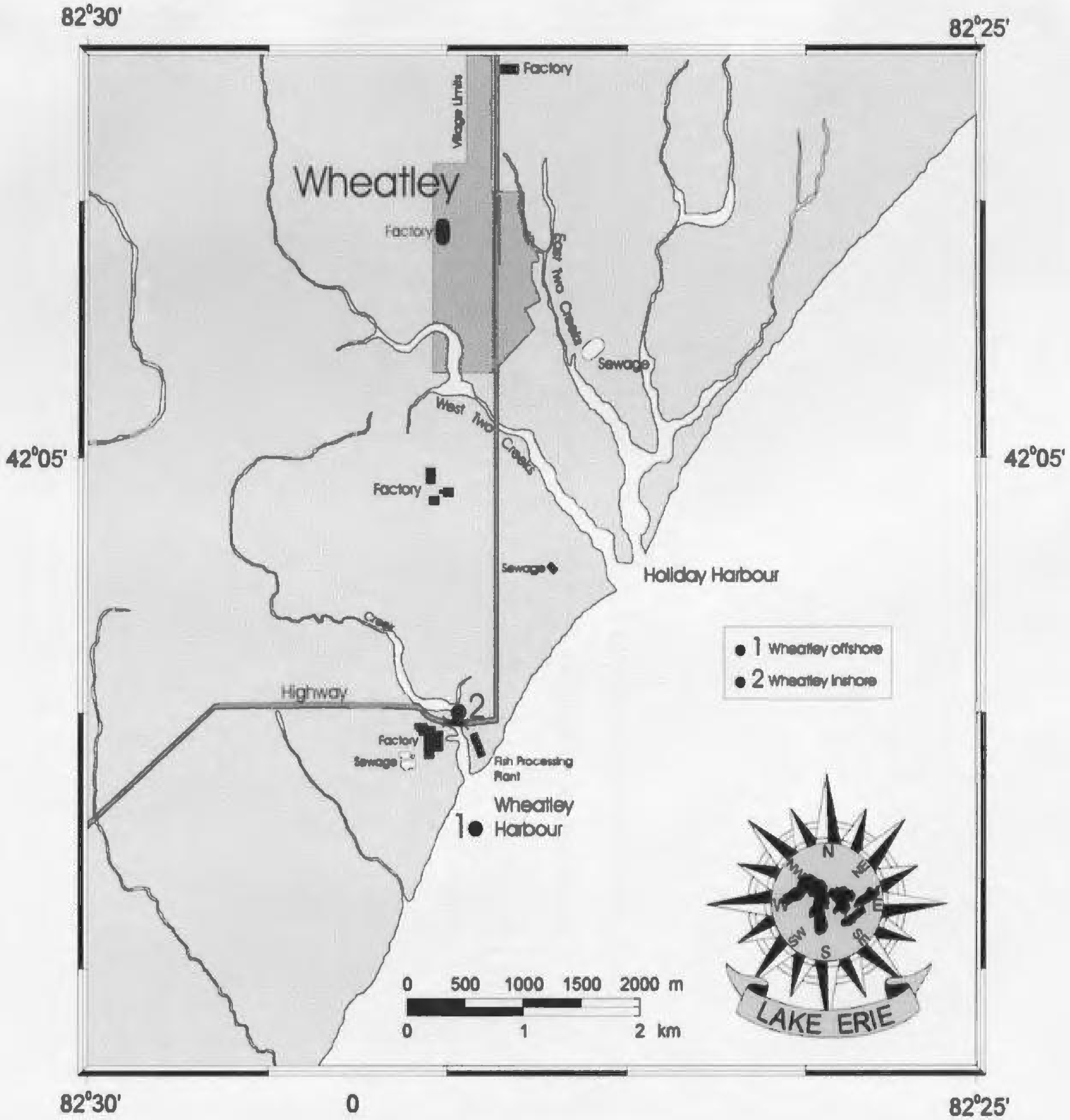
0 CASE NAME	1 PC1_MOL	2 PC2_MOL	3 PC3_MOL	4 PC1_ISO	5 PC2_ISO	6 PC3_ISO	7 CASE_NO	8 CLUSTER	9 DISTANCE
"ST974"	.512	.100	-.066	.618	.028	-.131	1	2	.27
"ST973"	-.291	-.120	-.049	.216	-.006	-.099	2	2	.13
"ST1012"	-.716	-.037	.043	.149	.144	-.076	3	2	.29
"ST969"	.299	.101	-.194	-.553	-.174	.045	4	2	.38
"ST971"	2.909	.342	.091	-.086	.110	-.093	5	1	.70
"ST357"	.724	.029	-.058	-.203	.079	-.076	6	2	.37
"ST358"	.378	-.028	.002	-.374	-.360	-.076	7	2	.35
"ST967"	-.840	.055	.012	-.679	.426	-.104	8	3	.31
"ST966"	-.163	.069	.006	-2.280	-.392	.006	9	3	.67
"Wh"	-1.733	-.143	.042	-1.602	.010	-.006	10	3	.27
"ST962"	-.773	.048	.011	.615	-.060	.085	11	2	.33
"ST961"	1.354	.266	.043	.102	-.126	.103	12	2	.59
"ST84"	.232	.149	.065	.686	-.015	.032	13	2	.21
"ST955"	2.781	.316	-.047	1.411	-.203	.003	14	1	.23
"ST953"	.949	.235	.012	-1.017	-.048	-.311	15	2	.68
"ST951"	-1.142	-.040	.044	-1.122	.443	.239	16	3	.18
"ST1021"	-1.564	-.048	.004	1.084	.925	.057	17	2	.80
"ST946"	-1.752	-.046	-.039	-.520	.294	-.010	18	3	.35
"ST945"	-1.809	-.078	.030	-1.486	-.067	.154	19	3	.27
"ST23"	-1.328	-.064	.037	1.130	-.207	.053	20	2	.64
"ST935"	-.388	.037	.034	1.040	-.205	.023	21	2	.36
"ST932"	-1.357	-.204	-.042	-.394	-.385	.173	22	3	.37
"Bf"	3.719	-.938	.019	3.265	-.211	.009	23	1	.82

Appendix C2. Weighted scores of the three first principal components extracted from both molecular and isotopic data sets in the source apportionment procedure and utilized for further grouping (columns 1-6). The output of the non-hierarchical (K-means) cluster analysis employed for grouping of the weighted scores (columns 7-9). Six clusters were ordered in the Cluster Analysis Module of Statistica 5.1 (StatSoft, Inc., 1995).

data file: SOURCECL.STA [27 cases with 9 variables]

0 CASE NAME	1 PC1_MOL	2 PC2_MOL	3 PC3_MOL	4 PC1_ISO	5 PC2_ISO	6 PC3_ISO	7 CASE_NO	8 CLUSTER	9 DISTANC
"ST974"	.216	.047	.063	-.763	-.059	-.042	1	3	.19
"ST973"	-.218	-.036	.067	1.426	.099	-.072	2	2	.12
"ST1012"	-.190	.122	.022	-.707	-.184	.054	3	3	.07
"ST969"	-.394	-.083	-.037	-.530	-.006	-.046	4	3	.13
"ST971"	-.392	.034	.032	-.810	-.068	.040	5	3	.07
"ST357"	-.431	.049	.041	-.828	.045	.004	6	3	.10
"ST358"	-.713	-.180	-.008	-.504	-.210	.108	7	3	.24
"ST967"	-.351	.189	.108	-1.355	-.154	.061	8	3	.26
"ST966"	-1.664	-.141	-.074	-.687	-.110	.050	9	1	.28
"Wh"	-1.074	.008	-.010	1.429	.763	.009	10	2	.40
"ST962"	.829	.002	-.034	-.656	-.105	-.071	11	4	.13
"ST961"	-.006	-.080	-.061	-.919	-.216	-.112	12	3	.14
"ST84"	.745	.003	-.012	-.810	-.109	-.031	13	4	.19
"ST955"	.808	-.156	.028	-.313	-.292	.107	14	4	.10
"ST953"	-1.211	.016	.180	-1.063	-.270	-.124	15	1	.25
"ST951"	-.228	.210	-.120	-.693	.161	-.035	16	3	.14
"ST1021"	.476	.466	-.054	.090	.115	-.059	17	4	.31
"ST946"	-.756	.325	-.092	-1.776	1.345	-.012	18	1	.58
"ST945"	-1.725	-.159	-.139	-1.011	.108	-.050	19	1	.20
"ST23"	.688	-.110	-.037	-.529	-.015	.019	20	4	.11
"ST935"	.940	-.158	.042	-.591	-.150	.047	21	4	.13
"ST932"	-.021	-.143	-.129	-.540	-.128	-.067	22	3	.16
"Bf"	2.485	-.057	.023	1.123	-.111	.196	23	5	.21
"CAR SOOTS"	1.176	-.085	-.096	.388	-.280	.056	24	4	.34
"FIRE SOOTS"	.691	.012	.105	1.737	.179	.211	25	2	.39
"Crank. Oil"	-3.183	-.067	.130	2.328	.134	-.331	26	6	0.00
"Road SWEEPS"	3.501	-.028	.063	.969	-.130	.201	27	5	.21

Appendix C3. The results of a local-scale study on distribution of PAH contamination in sediments at Wheatley Harbor. Location of sample sites and total concentrations and molecular and isotopic compositions for offshore and inshore samples.


82°30'
82°25'
42°05'
42°05'
82°30'
0
82°25'
Factory
Village Limits
Wheatley
Factory
East Two Creeks
Sewage
West Two Creeks
Factory
Sewage
Holiday Harbour
Creek
Highway
2
Factory
Sewage
Fish Processing Plant
1
Wheatley Harbour
● 1 Wheatley offshore
● 2 Wheatley inshore
N
NE
E
SE
S
SW
W
NW
LAKE ERIE
0 500 1000 1500 2000 m
0 1 2 km

Appendix C3. (cont.)

	Concentrations, ng/g		Isotopic composition ($\delta^{13}C$, ‰)	
	Offshore	**Inshore**	**Offshore**	**Inshore**
TPAH	364	887	N/A	N/A
Ae	0.75	0.75	-	-
Fl	9.25	23.8	-	-
Pa	71.6	97.8	-28.4	-26.9
A	22.0	29.0	-	-
Fa	45.2	158	-26.5	-26.0
Py	33.1	146	-26.7	-25.2
BA	42.2	79.2	-	-
Chy	24.6	110	-	-24.9
BbF	15.6	24.5	-	-
BkF	2.75	28.0	-	-
BeP	19.6	37.5	-	-
BaP	9.63	59.2	-	-
Per	14.0	49.2	-	-
Ip	11.4	13.5	-	-
DBA	6.5	0.0	-	-
BP	35.6	30.5	-	-