OCCURRENCE OF BIPHENYL AND DIPHENYL ETHER IN THE ST. CLAIR RIVER: SEDIMENT CONTAMINATION BY HEAT TRANSFER FLUIDS

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NWRI Contribution No. 89-47

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December 1989

MANAGEMENT PERSPECTIVE

Biphenyl, 4-ethyl biphenyl, diphenyl ether and several related synthetic organic compounds were all identified in extracts from sediments in the St. Clair River. Concentrations were highest along the Canadian shore, downstream from the industrialized area, likely indicating a Canadian source. The ratio of biphenyl to diphenyl ether and the identities of some of the other organics strongly suggested that the sediments were contaminated by heat exchanger fluids.

Both biphenyl and diphenyl ether have previously been observed in environmental samples but their occurrence has not previously been associated with heat exchanger fluids. The actual source in Sarnia is not obvious. Heat transfer fluids are apparently not manufactured in Sarnia so it is not likely that they are discharged as manufacturing wastes. They are normally used in closed systems, operating at elevated temperatures and pressures, and it has been supposed that there was little possibility for release during use. It may be that operations involving heat exchangers are not as 'closed' as previously thought.

Heat exchanger fluids are toxic and their release, particularly as a non-aqueous phase, could have impacts on the biota of receiving waters. However, their impact may not be limited to toxicity to aquatic biota. A major point of concern is the possibility of these compounds becoming chlorinated during or after release. Some effluents are treated with chlorine prior to discharge. Should diphenyl ether be present in these effluents, it would be chlorinated. Whitby Harbour is believed to have been contaminated by polychlorinated diphenyl ethers (PCDEs) containing from 2 to 8 chlorines from such a source. If surface water containing diphenyl ether is used for drinking water, there is also the possibility that PCDEs could be formed during the chlorine disinfection process. There may therefore be some potential for human exposure in areas where drinking water is removed from surface waters downstream from industrialized areas.

PERSPECTIVE-GESTION

Le biphényle, le 4-éthyl-biphényle, l'éther diphénylique et plusieurs autres composés organiques synthétiques apparentés ont tous été identifiés dans des extraits de sédiments prélevés dans la rivière Ste-Claire. Les concentrations les plus élevées ont été observées le long de la rive canadienne, en aval de la zone industrialisée, ce qui indique que la source se trouve probablement au Canada. Le rapport biphényle/éther diphénylique et l'identité de certaines des autres substances organiques semblent fortement indiquer que les sédiments ont été contaminés par des fluides caloporteurs.

Le biphényle et l'éther diphénylique ont déjà été décelés dans des échantillons environnementaux, mais c'est la première fois que leur présence est associée à des fluides caloporteurs. La source réelle à Sarnia n'est pas évidente. Comme on ne fabrique pas, semble-t-il, des fluides caloporteurs à Sarnia, il est peu probable que ces substances constituent des déchets de fabrication. Les fluides caloporteurs sont normalement utilisés dans des systèmes hermétiques, à des températures et à des pressions élevées, et on suppose que les risques de rejet pendant l'utilisation ne sont guère élevés. Il est possible que les systèmes utilisant des caloporteurs ne soient pas aussi "hermétiques" qu'on ne le croyait.

RÉSUMÉ

Le biphényle, le 4-éthyl-biphényle, l'éther diphénylique et plusieurs autres composés aromatiques apparentés ont tous été identifiés dans des extraits de sédiments prélevés dans la rivière Ste-Claire. La concentration des plus importants de ces composés variait de non décelable à 490 µg/g (dans le cas de l'éther diphénylique) et de non décelable à 150 µg/g (dans le cas du biphényle). Ce sont les eaux en aval des zones industrialisées qui présentaient les concentrations les plus élevées. Le rapport biphényle/éther diphénylique et l'identité de certaines des autres substances organiques semblent fortement indiquer que les sédiments ont été contaminés par des fluides caloporteurs. La présence de fluides caloporteurs dans les sédiments en aval de la zone où ils sont utilisés mais non fabriqués indique que ces fluides, bien qu'ils soient utilisés dans des systèmes hermétiques, risquent dans une certaine mesure d'être rejetés dans l'environnement. On examine plusieurs points relatifs à la nature toxique de ces produits.

Les fluides caloporteurs sont toxiques, et leur rejet, plus particulièrement sous forme d'une phase non aqueuse, pourrait avoir un effet sur le biote des eaux réceptrices. Toutefois, il se peut que la toxicité pour le biote aquatique ne soit pas le seul effet de ces composés. La chloration possible de ces composés pendant et après leur rejet est une importante source d'inquiétude, car certains effluents sont traités avec du chlore avant d'être rejetés. Tous les éthers diphényliques présents dans ces effluents seraient alors chlorés. Les eaux du port de Whitby auraient été contaminées, croit-on, par des éthers diphényliques polychlorés (PCDE) renfermant de 2 à 8 atomes de chlore, qui provenaient de cette source. Si des eaux de surface contenant de l'éther diphénylique sont utilisées comme eau de boisson, alors il peut également avoir formation de PCDE durant le procédé de désinfection au chlore. En conséquence, les humains risquent dans une certaine mesure d'être exposés, dans les régions où l'eau destinée à la consommation est constituée d'eaux de surface captées en aval des zones industrialisées.

ABSTRACT

Biphenyl, 4-ethyl biphenyl, diphenyl ether and several related aromatics were all identified in extracts from sediments in the St. Clair River. Concentrations of the most prominent of these compounds ranged from non-detectable to 490 ug/g (diphenyl ether) and to 150 ug/g (biphenyl). Concentrations were highest downstream from an industrialized area. The ratio of biphenyl to diphenyl ether and the identities of some of the other organics strongly suggested that the sediments were contaminated by heat exchanger fluids. The presence of heat exchanger fluids in sediments downstream from an area where they are used but not manufactured indicates that, although they are used in closed systems, there is some potential for release into the environment. Several toxicological concerns are discussed.

INTRODUCTION

Much of our knowledge of environmental pollution by synthetic organic compounds is based on research conducted on organochlorines and other compounds responsive to an electron capture detector. While this focus is understandable since many organochlorines are persistent and can bioaccumulate, there are many industrial chemicals produced in much greater amounts than organochlorines which may go undetected because they are not responsive to electron capture detectors or are not present on

lists of 'priority' or 'target' compounds used in routine monitoring programs. It is of interest therefore, to examine environmental samples, particularly those from industrialized areas, for the presence of previously undetected compounds and to identify the sources of these compounds where possible.

In the Great Lakes system, the St. Clair River forms the connecting channel between Lakes Huron and St. Clair. An extensive petrochemical industrial complex is located along the Canadian shores of this river near the city of Sarnia, Ontario. In 1985, in response to the discovery of pools of non-aqueous material on the bottom of the St. Clair River near Sarnia, a multi-agency investigation into the nature, sources and extent of contamination in this section of the river was carried out. The pools were found to contain a variety of chlorinated organic compounds including tetrachloroethene, tetra-, penta-, and hexachloroethanes, chlorobutenes, chlorohexadienes, chloro styrenes and octachloronaphthalene (1). This complex composition suggested that the source of these pools was not a simple spill of tetrachloroethene as was originally thought.

During the course of the investigation, sediments on the Canadian side of the river downstream from Sarnia were observed to contain an estimated 4 metric tons of brown tarry material (2). An examination of the the depth distribution of this tarry material and of several of the major chlorinated constituents of the non-aqueous puddles revealed that they did not correlate. Thus the tarry material did not appear to be related to the chlorinated

solvent pollution. In an effort to identify the nature and source of this tar, Nagy et al. (3) analysed for non-chlorinated organics and found a variety of aliphatic hydrocarbons (HCs) and polycyclic aromatic hydrocarbons (PAHs) at high concentrations in the sediments on the Canadian side of the river. The absence of odd-carbon preference in the HCs, the presence of several alkylated PAHs, and the overall distribution of these compounds suggested the refineries and petrochemical plants downstream from Sarnia as probable sources.

In addition to the above chemicals, several aromatic compounds not usually associated with petroleum pollution were identified in the sediments by gas chromatography/mass spectrometry (GC/MS). This paper documents the identity and distribution of these compounds and discusses potential sources to the river.

MATERIALS AND METHODS

Sampling

The sediment extracts used in this study were the same ones used by Nagy et al. (3) in their study of hydrocarbon distribution and were aliquots of the raw extracts used by Oliver and Pugsley (2) to examine the distribution of chlorinated compounds. The original sediment samples were collected in the fall of 1985 along transects extending offshore from 20 sites along the river (Fig 1.). Five of the sites were located along the U. S. shore and 15 sites along the more industrialized Canadian shore. For each transect, samples were obtained at distances of 10, 25 and 100 m

from shore, designated as A, B, and C, respectively. At sites where a benthos corer could penetrate the sediment, shallow cores were obtained. At other sites, samples were collected with a Shipek grab sampler. Loose gravelly sands low in silt-clay (0 - 20%) were recovered at all sites except for 8 and 14 where the clay-rich glacial sediment substrate was exposed (4).

After sieving to remove material greater than 2mm in size, samples were homogenized and subsampled. At sites 15B and 16A, core length was long enough to permit subdivision. The core from site 15B was divided into three segments, of depths 0-3 cm, 3-6 cm and 6-9 cm from the sediment surface while the one from site 16A was sub-divided into five segments corresponding to depths of 0-3 cm, 3-8 cm, 8-13 cm, 13-18 cm and 18-24 cm from the sediment surface.

Analysis

Sediments were soxhlet extracted sequentially with an acetone/hexane (1:1) mixture followed by benzene. After the extracts were combined and washed with aqueous base to separate the acids for separate analysis, the base/neutral fraction was concentrated by evaporation and an aliquot subjected to fractionation by column chromatography following a modification of the method of Samoiloff et al. (5). The column contained 10 g fired silica gel added as a slurry in hexane. The hexane was drained until it reached the top of the bed, then the sample was added to the column which was again drained to the top of the bed. Four

fractions were then collected by sequential elution with the following solvents;

fraction 1	80 ml hexane
fraction 2	85 ml dichloromethane/hexane (20:80)
fraction 3	85 ml dichloromethane/hexane (60/40)
fraction 4	50 ml dichloromethane followed by 50 ml methanol

Prior to elution with one of the above solvent mixtures, the flask that had contained the sample was rinsed with an aliquot of that solvent and added to the column. Eluates were concentrated for analysis by evaporation at room temperature under vacuum. The compounds discussed in this paper were all found in fractions 1 and 2.

Identification of the compounds of interest was accomplished by GC/MS on a Riber-Nermag R1010 mass spectrometer and a Carlo-Erba 4160 gas chromatograph. On-column injections were made onto a 30 m, DB-5 fused silica column. After an initial hold of 2 min. at 70 °C, the oven temperature was programmed at 4 degrees per minute to 285 °C where it was held for 10 min. The MS was operated in electron impact mode with an ionization potential of 70 ev, a filament current of 200 mA and a source temperature of 170 °C. At least one sample from each transect and all segments from the two cores were examined by GC/MS.

For each sample, quantitative analyses were performed on fractions 1 and 2 using gas chromatography with flame ionization detectors (GC/FID) against an external standard containing

biphenyl, 4-ethyl biphenyl and diphenyl ether which were used as received from Aldrich Chemical Co., Ltd. Since the FID response factors for these three compounds differed by less than 5%, an average response factor was calculated and used to estimate concentrations of diethyl biphenyl which was not commercially avaliable. Analyses were performed using a splitless injection technique on a Perkin-Elmer Sigma 2000 gas chromatograph equipped with a 30 m, DB-5 fused silica capillary column. Following an initial hold of 2 min. at 70 °C, the oven temperature was increased at 4°C/min to 280°C where it was held for 15 min. Injector and detector temperatures were both 280°C. Authentic samples of various Dowtherm heat transfer fluids were generously supplied by Dow Chemical Co., Ltd.

RESULTS AND DISCUSSION

The total ion current chromatograms for fractions 1 and 2 of a sample containing all the compounds of interest are presented in Figure 2. For the purposes of discussion, all the prominent peaks of these chromatograms are numbered. The identities of the compounds responsible for most of the numbered peaks have been determined by computerized searches of mass spectral libraries or, in some cases, interpretation of the mass spectra and are listed in Table 1. As noted in Table 1, many of these compounds are HCs and PAHs which have been the subject of a previous

publication (3); they will not be discussed further here. Five of the remaining compounds were identified as aromatics probably arising from anthropogenic sources. These included two diethyl benzenes (2 & 3), biphenyl (8), diphenyl ether (24), an ethyl biphenyl isomer (25). The computerized data base search failed to identify several other compounds, including compounds 27 and 28. These two compounds had essentially identical mass spectra suggesting that they were isomers of the same chemical composition. They were tentatively identified as diethyl biphenyls based on a comparison of their mass spectra with that of biphenyl and of the 4-ethyl biphenyl.

The mass spectra of biphenyl, 4-ethyl biphenyl and compound 27 are presented in Figure 3. The mass spectrum of biphenyl is relatively simple with only one intense cluster around the molecular ion at m/e 154 which is also the base peak. In the mass spectrum of 4-ethyl biphenyl, the base peak is found at m/e 167, the result of a loss of $\cdot CH_3$ from the molecular ion at m/e 182. The base peak in the mass spectrum of compound 27 (m/e 195) is related to the apparent molecular ion by a similar loss of 15 mass units. In addition, several of the more important features found in the mass spectrum of 4-ethyl biphenyl, including peaks at m/e 77, 152, 165, 166, 167 and 168 are also present in the mass spectrum of 27. Finally, the spectrum of 27 contains an ion at m/e 181, 1 mass unit below the molecular ion of 4-ethyl biphenyl, suggesting that 27 can be converted to a structure similar to 4-ethyl biphenyl by loss of a neutral fragment of mass 29, presumably

$\cdot CH_2CH_3$. Based on these spectral features, we suggest that compounds 27 and 28 are isomers of diethyl biphenyl.

To examine the distribution of these compounds, the concentrations of biphenyl, diphenyl ether and 4-ethyl biphenyl in all samples were determined by quantitative analysis and the concentration of compound 27 was estimated using an average response factor as follows. As shown in Table 2, the response factors of the flame ionization detector for biphenyl, diphenyl ether and 4-ethyl biphenyl were very similar. Assuming that the other simple aromatics would have similar response factors, the average response factor calculated in Table 2 was used to estimate the concentration of compound 27. The results of these analyses are presented in Table 3. Biphenyl and diphenyl ether were the most widely distributed with detectable levels for at least one site on each transect. The concentration of diphenyl ether ranged from nondetectable levels to 490 ug/g while biphenyl varied from nondetectable to 149 ug/g. The distribution of these two compounds by transect is presented in Figure 1. Levels along the five transects on the U. S. side (transects 1,5,7,11 and 20) and all Canadian transects upstream from transect 12 were from two to three orders of magnitude less than concentrations observed downstream from transect 12 on the Canadian side. For these downstream transects, the samples taken 10m offshore were, with one exception, higher than the corresponding samples taken 25 m offshore. Concentrations observed 100m offshore were comparable to levels along the U. S. and upstream Canadian transects. These

results indicate significant biphenyl and diphenyl ether contamination of the nearshore area along the Canadian shore, downstream from transect 12. Concentrations observed for 4-ethylbiphenyl and estimated for diethylbiphenyl were considerably lower with maxima of 5.0 and 5.2 ug/g respectively. Although the results are not as clear as for biphenyl and diphenyl ether, the distribution of these compounds also indicates higher levels along the Canadian side of the river downstream from the industrialized area.

The concentrations of the above organics in the sediment cores from sites 15b and 16a are presented in Table 4. All four compounds of interest were found throughout the cores but their distributions differed (Fig. 4). Concentrations of both phenyl ether and biphenyl decreased with depth, particularly at site 16a, whereas concentrations of diethyl biphenyl in both cores and 4-ethyl biphenyl at site 16a increased with depth. Since Oliver and Pugsley (3) and Rukavina (4) noted that the tarry substances in the cores were present in the lower segments, the distributions observed for phenyl ether and biphenyl suggest that they are not related to tar content and likely have a different source. The distribution of tar more closely corresponds to the distribution of hydrocarbons reported (3) for these cores (Fig. 4) which were suggested to be petroleum-related.

Both biphenyl and diphenyl ether have previously been observed in environmental samples but the actual source of these compounds has not been identified. Diphenyl ether was observed in a European

lake water (6) and in seawater, lake water, snow and biota from various points in Nova Scotia, Canada (7). Hites & Lopez-Avila (8) reported the presence of both biphenyl and diphenyl ether in samples of water and sediment from a small river and estuary system receiving effluents from a specialty chemicals plant. The distribution shown in Figure 1 seems to clearly indicate non-natural sources since concentrations downstream from the industrialized area are orders of magnitude above those in other areas of the river.

Neither biphenyl or diphenyl ether is among the products produced at any of the petrochemical plants in the area so it was considered unlikely that the entered the river as manufacturing waste. Therefore, the possibility that these compounds could have entered the river as a result of industrial use of formulations containing them was investigated. Although diphenyl ether has a number of commercial applications including use in soaps, perfumes, industrial solvents, thermosetting resins, flame retardants, dye carriers and flavourings, the major use by far is as a component of heat transfer fluids. Dowtherm A, one of the oldest and most widely used heat transfer fluids (9) is an eutectic mixture of 73.5% diphenyl ether and 26.5% biphenyl. A chemically identical product is marketed by the Monsanto Company as Therminol VP-1.

In view of the commercial importance of the diphenyl ether/biphenyl eutectic, the sediment data were examined to determine the ratio of diphenyl ether to biphenyl. The relationship between the concentrations of biphenyl and diphenyl

ether in the sediments from transects 12 to 19 is examined in Figure 5. For comparison purposes, a line representing the composition of the eutectic is also shown. The observed ratios were in reasonable agreement with the composition of the eutectic, particularly in the samples containing the highest concentrations. The close correspondence between the ratio of the two compounds and the eutectic composition and the known commercial use of the eutectic strongly suggest that these compounds entered the river as heat transfer fluids.

The identity of the other compounds identified provide further support for the suggestion that sediments in this industrialized area are contaminated by heat transfer fluids. Ethyl biphenyls are a major component of the heat transfer fluid Dowtherm-LF while Dowtherm J consists of a mixture of diethyl benzenes. In Figure 6, total ion current chromatograms of these three heat transfer fluids are presented with the numbered peaks corresponding to the same compound in Figure 2. A comparison of the diethyl benzene and ethyl biphenyls in these figures reveals strong similarities in isomeric composition between the authentic heat transfer fluids and the sediment sample.

Although the results in Figure 1 seem to clearly indicate at least one source of these chemicals along the Canadian shore downstream from transect 12, the route by which these compounds entered the river is not obvious. Since heat transfer fluids are apparently not manufactured in Sarnia, it is not likely that they are discharged as manufacturing wastes. Heat transfer fluids are

normally used in closed systems, operating at elevated temperatures and pressures. For example, the application range of Dowtherm A is 15 to 400 °C and its pressure range is from atmospheric to 152.5 psig (10). The upper limits of the operating ranges of Dowtherm J and LF are somewhat lower, 315 and 343 °C respectively (11, 12). Since these upper temperature limits are all about the same as the flash points for these products, leaks from heat transfer systems could pose a safety hazard and are usually avoided and corrected during normal industrial operations. In addition, heat transfer fluids are not inexpensive and the largest manufacturer, Dow Chemical, accepts used Dowtherm from customers and reprocesses this material for credit (13). Therefore there is considerable economic incentive to industry to prevent leaks of these compounds and to recycle used material.

The fact that the compounds are found in the river sediment near industrial effluent discharges does not imply that they must have entered the river in these effluents. For one thing, there is uncertainty as to the source of the river sediments with which the chemicals are associated. A study of the size distribution of the sediment along the Canadian industrial reach, found that its gravel content was too high to be explained by bedload transport from Lake Huron or by local erosion of the underlying glacial sediment (4). It was suggested that the anomalous texture might be the result of fill used to extend the shoreline. There is evidence in aerial photographs that extensive alteration of the shoreline by fill took place between 1955 and 1973, and the

sediments themselves show large variations in particle size and thickness more consistent with introduced fill than with natural, sorted river sediment. For example, as shown in Figure 7, the silt/clay content of the 25m offshore sediments for the Canadian sites varied from greater than 90% to less than 1%. The most highly contaminated sediments had very low silt/clay content. Conversely, the sites with exposed glacial clay had very low concentrations, although levels in the exposed clay at station 14a were higher than those in exposed clay upstream from transect 12. If fill is an important part of the non-clay component of the river sediment, the possibility that it was contaminated and contributed directly to the chemical loading to the river cannot be excluded.

Alternatively, it may be that operations involving heat exchangers are not as 'closed' as previously thought. The substances under discussion are all sparingly soluble in water (10 to 20 mg/l at ambient temperatures) and are denser than water. If they were released as nonaqueous fluids, the coarse sediments could have acted as a sponge and trapped them as they were transported along the bottom. If they entered flowing systems as an emulsion, or formed one as a result of strong mixing, they could possibly be transported considerable distances downstream. The effect would be an extremely heterogeneous distribution with local pockets of high concentration. Evidently some sort of transport has occurred since measurable levels were found in eroding glacial clay at transect 14.

The route by which these contaminants entered the system

likely influences both the nature and extent of their environmental impact. In view of the apparent immobility of the fill used in the shoreline modifications, if they entered the system as contaminants in that fill, their impact would likely be restricted to the benthic community in the immediate area. However if they entered the system in the effluent discharges, their impact could be more widespread, particularly if they were discharged as a separate non-aqueous phase.

Toxicity data on heat transfer fluids from the manufacturer indicate a low order of systemic toxicity (10, 12). The reported LD_{50} values for oral administration to rats are 1.4 gm/kg for Dowtherm LF and 2-4 gm/kg for Dowtherm A. Published values on the toxicity of heat transfer fluids to aquatic species are rare and there appears to be no data on the effect of these substances on benthic biota. The acute toxicity of diphenyl ether to sheepshead minnow (Cyprindon variegatus) has been reported to be 2.4 mg/l and the NOEL to be 1.0 mg/l (14). These values are several orders of magnitude above the concentrations observed by Addison (7) who found from 3 to 179 ng/l in Nova Scotian waters. However, the sites sampled by Addison were not near petrochemical industries and likely do not represent ambient levels in areas likely to be polluted by heat transfer chemicals. In addition, these toxicity tests were conducted on dissolved material. The possibility that these chemicals could enter aquatic systems as a nonaqueous phase seems not to have been investigated. Laboratory tests of acute toxicity of dissolved material may not be appropriate if aquatic

organisms are exposed to nonaqueous phase dispersions or high concentrations in sediments.

The impact of these heat transfer substances may not be limited to toxicity to biota in the receiving waters. Another point of concern is the possibility of these compounds becoming chlorinated during or after release. Some effluents are treated with chlorine prior to discharge. Should diphenyl ether be present in these effluents, it would be chlorinated. Contamination of Whitby Harbour on Lake Ontario by polychlorinated diphenyl ethers (PCDEs) containing from 2 to 8 chlorines has been attributed to such a source (15). If surface water containing diphenyl ether is used for drinking water, there is also the possibility that PCDEs could be formed during the chlorine disinfection process. PCDEs are of concern because they are toxic and can bioaccumulate. Accumulation and depuration patterns of PCDEs in fish resembled those observed for PCBs with a similar number of chlorine atoms per molecule (16). The PCDEs were somewhat more persistent in fish than the corresponding PCBs.

Several authors have reported a relationship between the presence of PCDEs in the environment and proximity to industrial sources. Jaffe et al. (17) reported that fish in industrialized areas of the Saginaw Bay, Michigan, watershed contained detectable PCDEs but fish from rural parts of that watershed and other non-industrialized areas did not. PCDEs were also detected in the tissue and eggs of birds from a number of sites in the United States (18) and in marine organisms and suspended sediment from an

estuarine ecosystem receiving industrial discharges (19).

It is evident from our results that heat transfer fluids are present in aquatic sediments downstream from an industrial area where they are used but not manufactured. This suggests that despite the fact that they are used in closed systems, there is some potential for release into the environment. Further studies in other industrial areas, particularly those with petrochemical plants, to determine the generality of these observations appear warranted. If it is found that pollution of aquatic systems by heat transfer fluids is common, studies of their environmental impact under conditions realistically approximating actual routes of exposure should be conducted.

REFERENCES

(1) Carey, J. H.; Hart, J. H. Water Poll. Res. J. Canada 1986, 21, 309-322.

(2) Oliver, B. G.; Pugsley, C. W. Water Poll. Res. J. Canada 1986, 21, 369-379.

(3) Nagy, E.; Carey, J. H.; Hart, J. H. Water Poll. Res. J. Canada, 1986, 21, 390-397.

(4) Rukavina, N. Water Poll. Res. J. Canada 1986, 21, 295-302.

(5) Samoiloff, M. R.; Bell, J.; Birkholz, D. A.; Webster, G. B. R.; Arnott, E. G.; Pulak, R.; Madrid, A. Environ. Sci. Technol. 1983, 17, 329-334.

(6) Grob, K.; Grob, G. J. Chromatog. 1974, 90, 303-313.

(7) Addison, R. F. Marine Pollution Bulletin 1977, 8, 237-240.

(8) Hites, R. A.; Lopez-Avila, V. in Contaminants and Sediments, Vol. 1, R. A. Baker (ed), Ann Arbor Science Publishers: Ann Arbor, MI, 1981; Chapter 3, pp 53-66 .

(9) Minton, P. E.; Plants, C. A. Heat Exchanger Technology (Nonwater Media). In **Encyclopedia of Chemical Technology**, R. E. Kirk and D. F. Othmer (eds.), 3rd ed. Vol. 12. John Wiley & Sons, Toronto, 1980.

(10) Dow Chemical. Dowtherm A Heat Transfer Fluid. product brochure No. 176-1337-85. 1985. Dow Chemical Company Inc., Midland, Michigan.

(11) Dow Chemical. Dowtherm J Heat Transfer Fluid. product brochure No. 176-1240-85. 1985. Dow Chemical Company Inc., Midland, Michigan.

(12) Dow Chemical. Dowtherm A Heat Transfer Fluid. product brochure No. 176-1338-85R. 1985. Dow Chemical Company Inc., Midland, Michigan.

(13) Dow Chemical. Health, Environmental and Safety Considerations in High Temperature Heat Transfer Fluid Systems. publication no. 176-1336-83. 1983. Dow Chemical Company Inc., Midland, Michigan.

(14) Heitmuller, P. T.; Hollister, T. A.; Parrish, P. R. Bull. Environ. Contam. Toxicol. 1981, 27, 596-604.

(15) Coburn, J. A.; M. Comba. unpublished observations

(16) Zitko, V.; Carson, W. G. Chemosphere 1977, 6, 293-301.

(17) Jaffe, R.; Stemmler, E. A.; Eitzer, B. D.; Hites, R. A. J. Great Lakes Res. 1985, 11, 156-162.

(18) Stafford, J. Chemosphere 1983, 12, 1487-1495.

(19) Lake, J. L.; Rogerson, P. F.; Norwood, C. B. Environ. Sci. Technol. 1981, 15, 549-553.

Table 1. Compounds present in the total ion current chromatograms for the fractionated extract from site 13B

Peak #	GC/MS*	Identity	Remarks
1.	91/106	ethylbenzene, C_8H_{10}, 106	+
2.	105/134	diethylbenzene, $C_{10}H_{14}$, 134	+
3.	105/134	diethylbenzene, $C_{10}H_{14}$, 134	+
4.	128/128	naphthalene, $C_{10}H_8$, 128	#
5.	142/142	2-methylnaphthalene, $C_{11}H_{10}$, 142	#
6.	142/142	1-methylnaphthalene, $C_{11}H_{10}$, 142	#
7.	104/158	unidentified	
8.	154/154	biphenyl, $C_{12}H_{10}$, 154	+
9.	141/156	dimethylnaphthalene, $C_{12}H_{12}$, 156	#
10.	152/152	acenaphthalene, $C_{12}H_8$, 152	tent.
11.	153/154	unidentified	
12.	205/221	unidentified	
13.	166/166	fluorene, $C_{13}H_{10}$, 166	#
14.	142/282	hexachlorobenzene, C_6Cl_6, 282	
15.	178/178	phenanthrene, $C_{14}H_{10}$, 178	#
16.	178/178	anthracene, $C_{14}H_{10}$, 178	
17.	202/202	pyrene , $C_{16}H_{10}$, 202	#
18.	57/317	sat. hydrocarbon,	#
19.	57/343	sat. hydrocarbon,	#
20.	57/352	sat. hydrocarbon,	#
21.	191/368	unidentified	
22.	71/291	sat. hydrocarbon,	#
23.	85/408	sat. hydrocarbon,	
24.	170/170	diphenyl ether, $C_{12}H_{10}O$, 170	+
25.	167/182	4-ethylbiphenyl, $C_{14}H_{14}$, 182	+
26.	205/220	2,6-di-t-butyl-p-cresol,	tent.
27.	195/210	diethylbiphenyl, $C_{16}H_{18}$, 210	tent.,+
28.	195/210	diethylbiphenyl, $C_{16}H_{18}$, 210	tent.,+
29.	207	unidentified	
30.	235/235	unidentified	
31.	235/235	unidentified	
32.	263/263	unidentified	
33.	263/263	unidentified	
34.	175/368	unidentified	

\+ discussed here
\# discussed by Nagy et al. (1986)
* base peak (m/e)/highest significant mass (m/e)

Table 2. Response factors for a variety of aromatic compounds on a flame ionization detector.

Compound	Area	wt. injected (ng)	wt. inj./area (ng/unit area)
diphenyl ether	140990	16.6	1.18×10^{-4}
4-ethyl biphenyl	79681	8.4	1.05×10^{-4}
3,3'-dimethyl biphenyl	139790	13.5	0.97×10^{-4}
4,4'-dimethyl biphenyl	341010	35.2	1.03×10^{-4}
biphenyl	394270	40.9	1.04×10^{-4}
o-xylene	352300	44.8	1.27×10^{-4}
		average	1.09×10^{-4}

Table 3. Concentrations of four aromatic compounds in sediments from the St. Clair River.

	biphenyl	phenyl ether	4-ethyl biphenyl	diethyl biphenyl
Site 1a				
1b	0.2	0.8		0.5
1c				
Site 2a				
2b				
2c	0.5	0.9		0.7
Site 3a				
3b	0.2	0.3	0.1	0.1
3c	0.2	0.4		
Site 4a	0.5	1.0		
4b				
4c	0.1	0.3		
Site 5a	0.2	0.7		0.4
5b				
5c				
Site 6a				
6b	0.8	2.4		1.5
6c	0.1	0.2		
Site 7a				
7b	0.3	1.1		0.6
7c	0.2	0.4		
Site 8a				
8b	0.3	0.4	0.1	
8c	0.3	0.4	0.1	
Site 9a	0.1	0.1		
9b				
9c	0.2	0.3	0.1	
Site 10a	1.6	1.1	0.3	1.0
10b	0.3	0.4		
10c	0.4	0.6	0.1	
Site 11a				
11b				
11c	0.3	1.0		0.5
Site 12a	14.	47.		
12b	0.3	0.7		
12c		0.2		
Site 13a	149.	490.	2.5	1.5
13b	0.4	6.1	4.9	3.4
13c				
Site 14a	3.8	12.	0.2	0.2
14b	11.	15.	0.6	0.6
14c				
Site 15a	37.	76.		0.3
15b	7.3	44.	0.3	0.6
15c	0.4	0.4		
Site 16a	9.9	30.	0.6	1.5
16b	1.0	2.4		
16c				
Site 17a	4.2	14.		0.5
17b	0.8	2.2		
17c	0.6	1.2		
Site 18a	40.	124.		0.3
18b	23.	62.		
18c	0.5	2.4		
Site 19a	14.	29.		0.1
19b	2.0	5.8		0.9
19c	0.5	1.3		
Site 20a	0.3	0.6		
20b	0.5	1.9		1.1
20c	0.3	0.4		

Table 4. Concentrations of four aromatic compounds in sediment cores from the St. Clair River (ug/g).

	depth	biphenyl	phenyl ether	4–ethyl biphenyl	diethyl biphenyl
Site 15b	0–3 cm	7.3	24.5	0.3	0.6
	3–6 cm	8.0	27.5	0.2	1.2
	6–9 cm	3.4	13.3		1.5
Site 16a	0–3 cm	9.9	29.8	0.6	1.5
	3–8 cm	2.9	8.7	1.0	0.9
	8–13 cm	3.2	6.4	2.0	2.9
	13–18 cm	3.9	5.8	1.3	3.4
	18–24 cm	5.2	5.3	2.0	5.2

FIGURES

Figure 1. Distribution of biphenyl and diphenyl ether at sites on 20 transects along the St. Clair River.

Figure 2. Total ion current chromatograms for the fractionated extract from site 13B: (a) fraction 1; (b) fraction 2.

Figure 3. Electron impact mass spectra of (a) biphenyl, (b) 4-ethyl biphenyl and (c) compound 27.

Figure 4. Distributions of phenyl ether ( ) and diethyl biphenyl ( ) in a core from site 16a. Also shown for comparison purposes is the hydrocarbon distribution of Nagy et al. (1986) ( ) and the distribution of tarry substances reported in ref. (3).

Figure 5. Relationship between biphenyl and diphenyl ether concentrations (ug/g dry weight) at sites on the Canadian side of the river, downstream from transect 12.

Figure 6. Total ion current gas chromatograms of three heat transfer fluids with the components labelled according to their designation in Figure 1. (a) Dowtherm J, (b) Dowtherm A, (c) Dowtherm LF

Figure 7. Sediment composition at nearshore sites along the Canadian side of the river. (- - -) silt-clay content %, (----) biphenyl concentration ug/g, (-- - --) diphenyl ether ug/g.

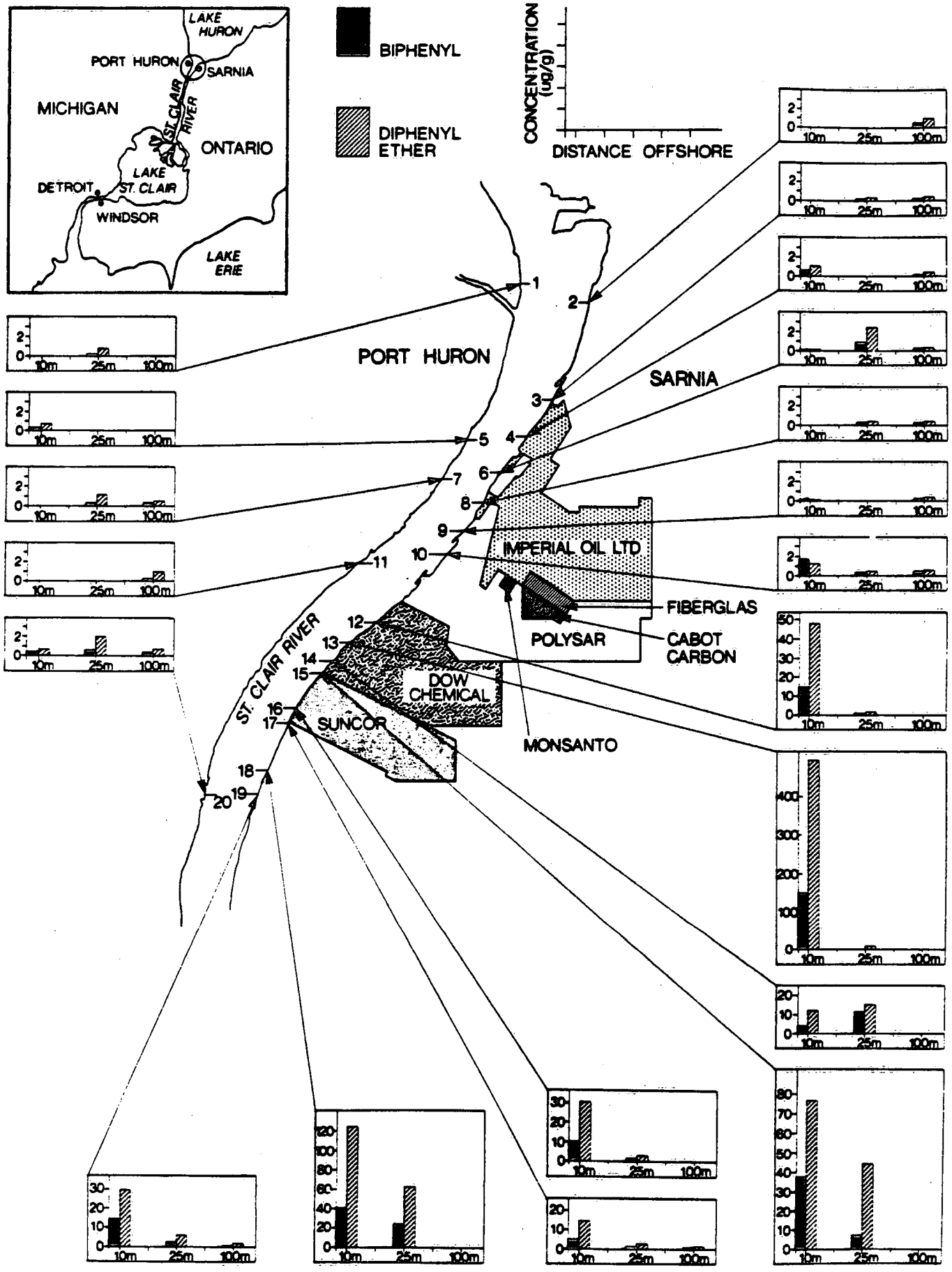
LAKE HURON
PORT HURON
SARNIA
MICHIGAN
ST. CLAIR RIVER
ONTARIO
LAKE ST. CLAIR
DETROIT
WINDSOR
LAKE ERIE
BIPHENYL
DIPHENYL ETHER
CONCENTRATION (ug/g)
DISTANCE OFFSHORE
PORT HURON
SARNIA
IMPERIAL OIL LTD
FIBERGLAS
POLYSAR
CABOT CARBON
DOW CHEMICAL
SUNCOR
MONSANTO
ST. CLAIR RIVER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
10m
25m
100m

FIG. 1

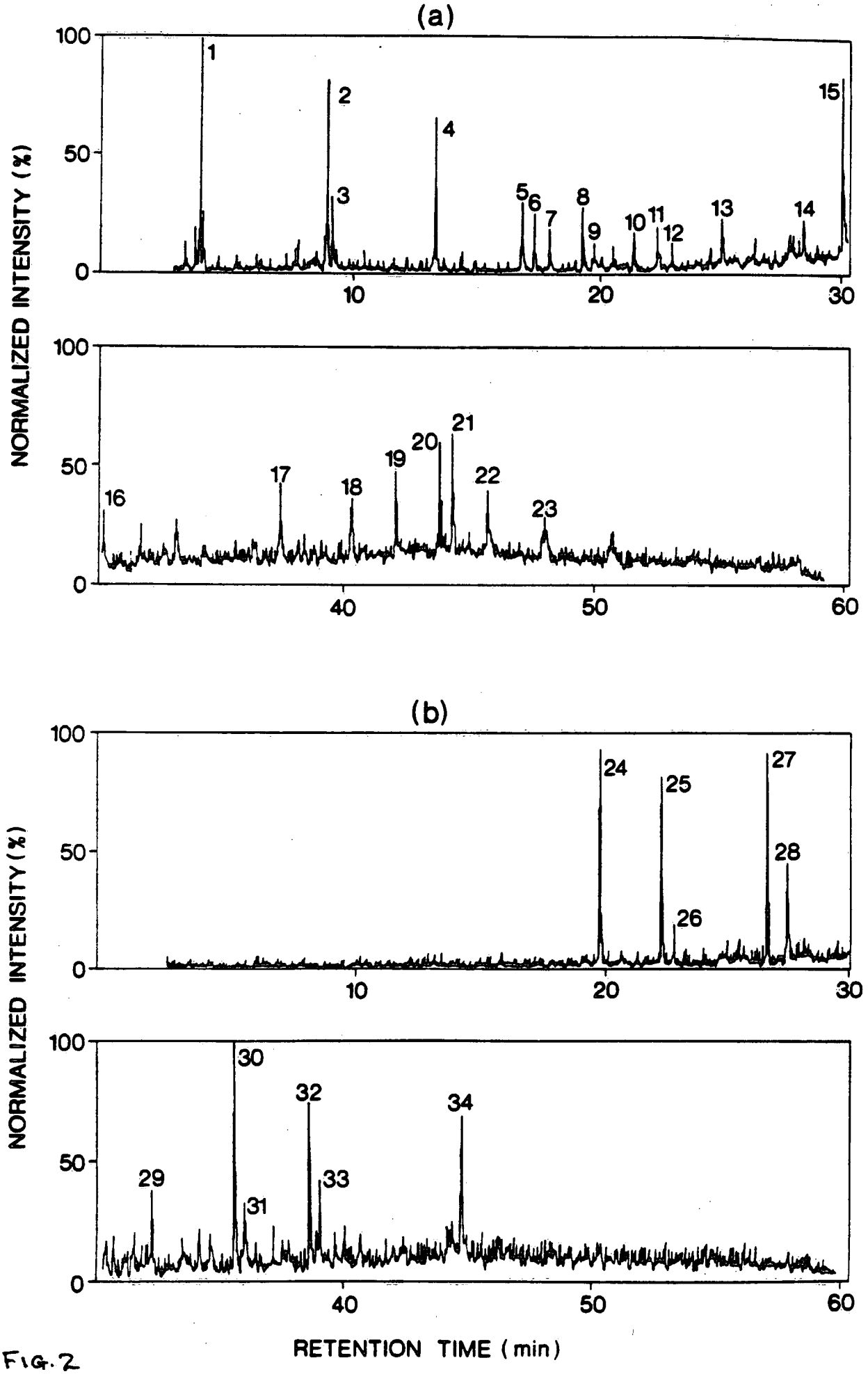
(a)
100
50
0
NORMALIZED INTENSITY (%)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
10
20
30
100
50
0
16
17
18
19
20
21
22
23
40
50
60
(b)
100
50
0
NORMALIZED INTENSITY (%)
24
25
26
27
28
10
20
30
100
50
0
29
30
31
32
33
34
40
50
60
RETENTION TIME (min)

FIG. 2

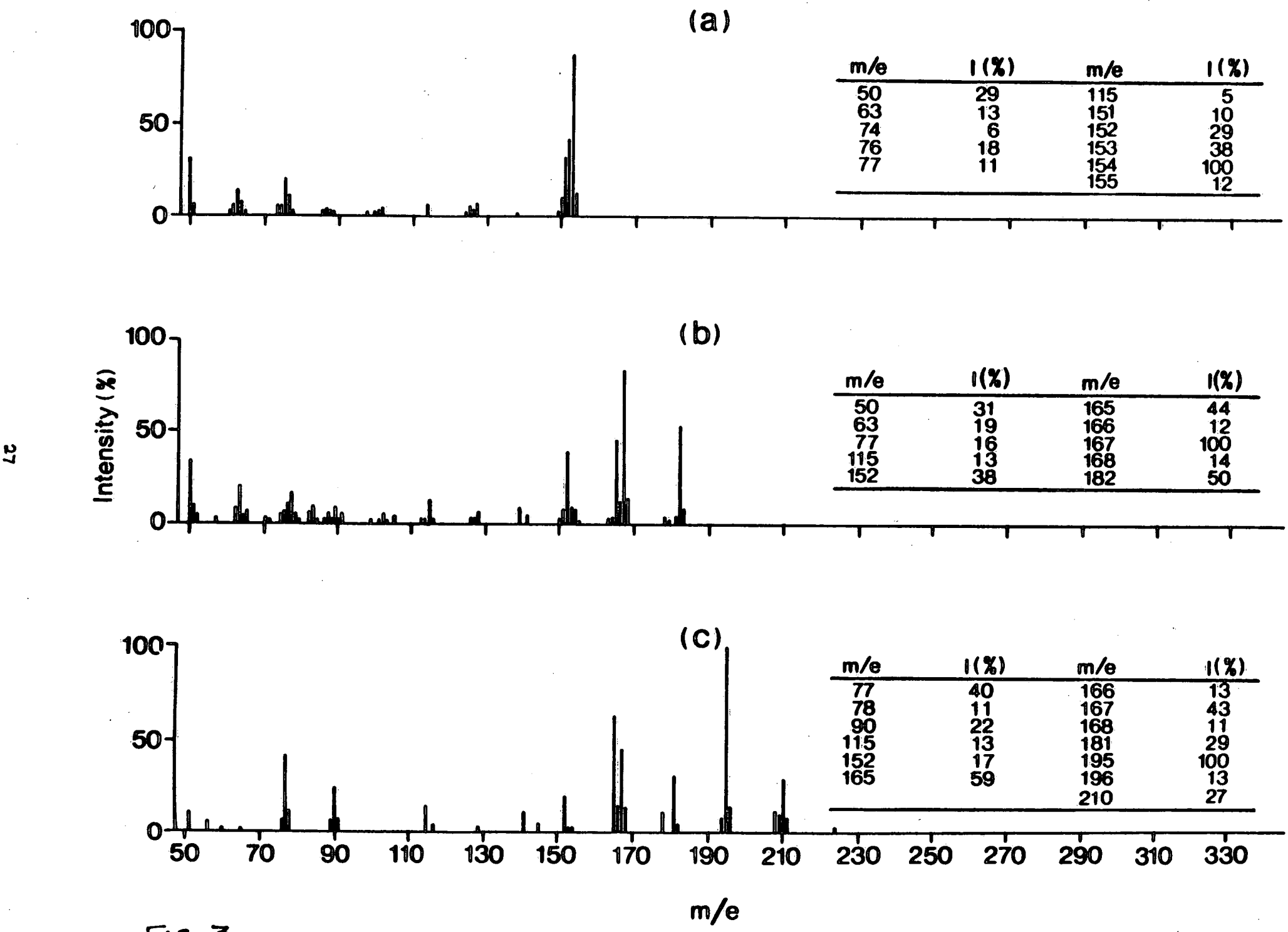
(a)
100
50
0
m/e | I(%) | m/e | I(%)
50 29 115 5
63 13 151 10
74 6 152 29
76 18 153 38
77 11 154 100
155 12
(b)
100
50
0
Intensity (%)
m/e | I(%) | m/e | I(%)
50 31 165 44
63 19 166 12
77 16 167 100
115 13 168 14
152 38 182 50
(c)
100
50
0
m/e | I(%) | m/e | I(%)
77 40 166 13
78 11 167 43
90 22 168 11
115 13 181 29
152 17 195 100
165 59 196 13
210 27
50 70 90 110 130 150 170 190 210 230 250 270 290 310 330
m/e

FIG. 3

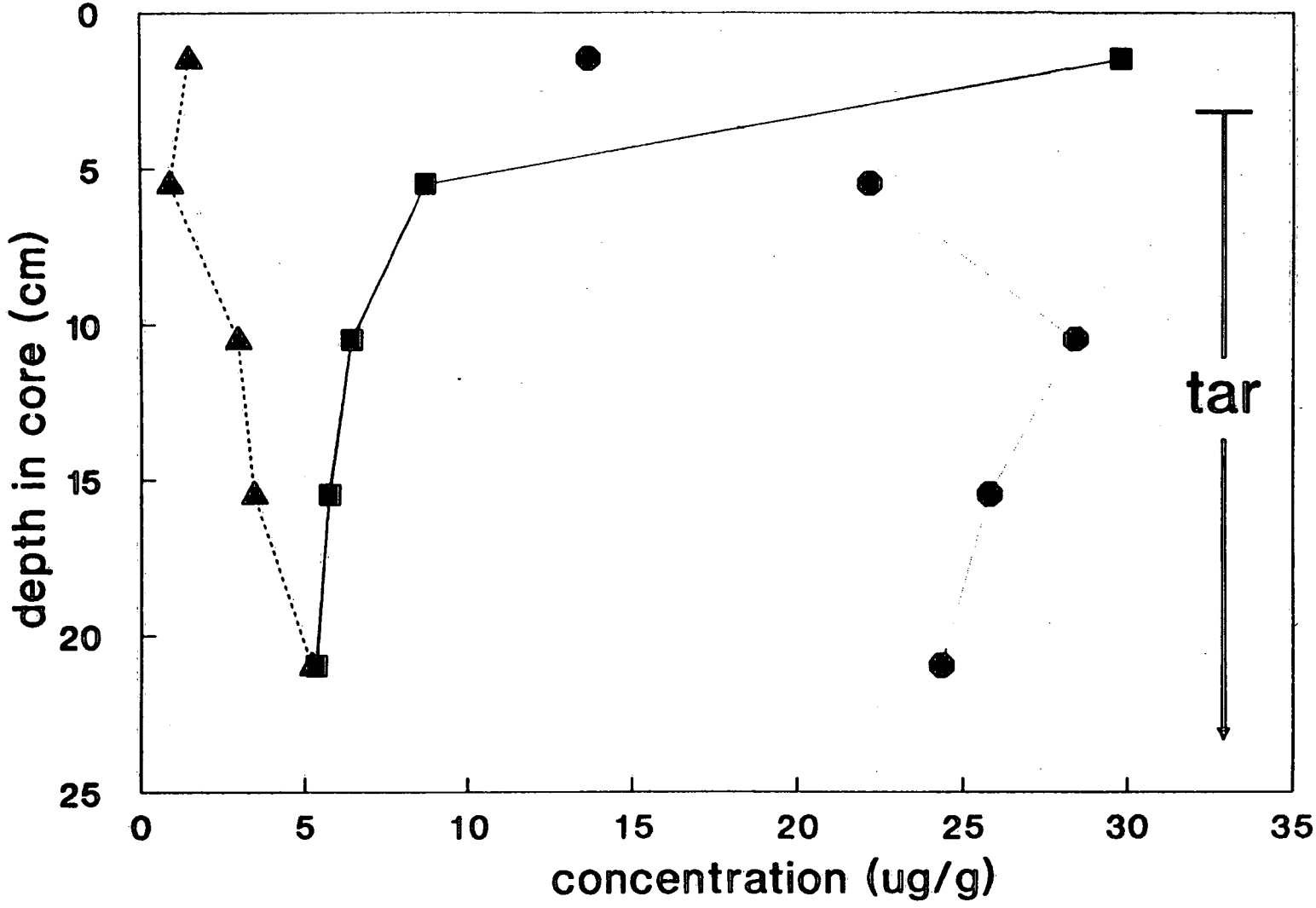
depth in core (cm)
0
5
10
15
20
25
0
5
10
15
20
25
30
35
concentration (ug/g)
tar

Fig. 4

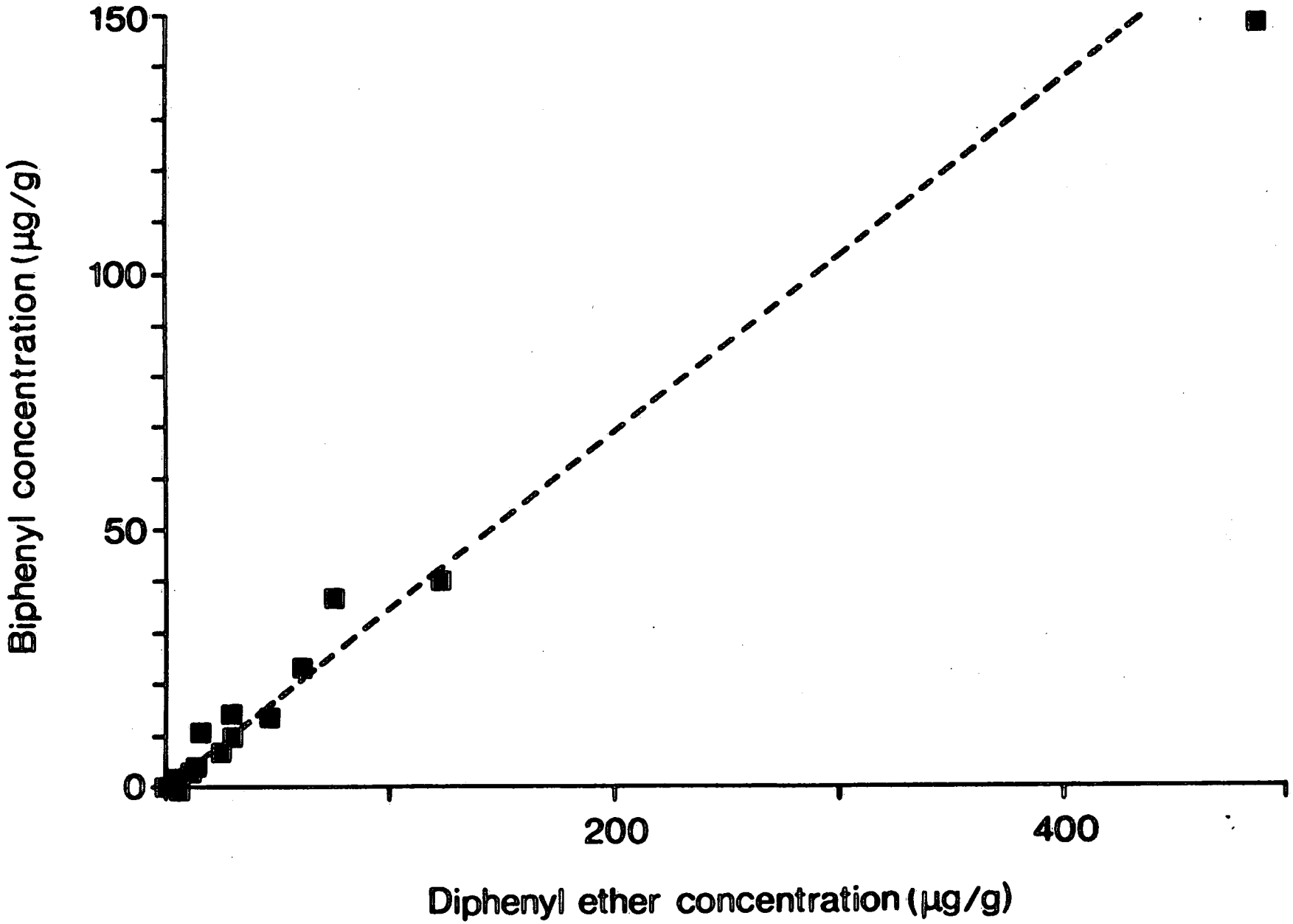
150
100
50
0
200
400
Biphenyl concentration (µg/g)
Diphenyl ether concentration (µg/g)

Fig. 5

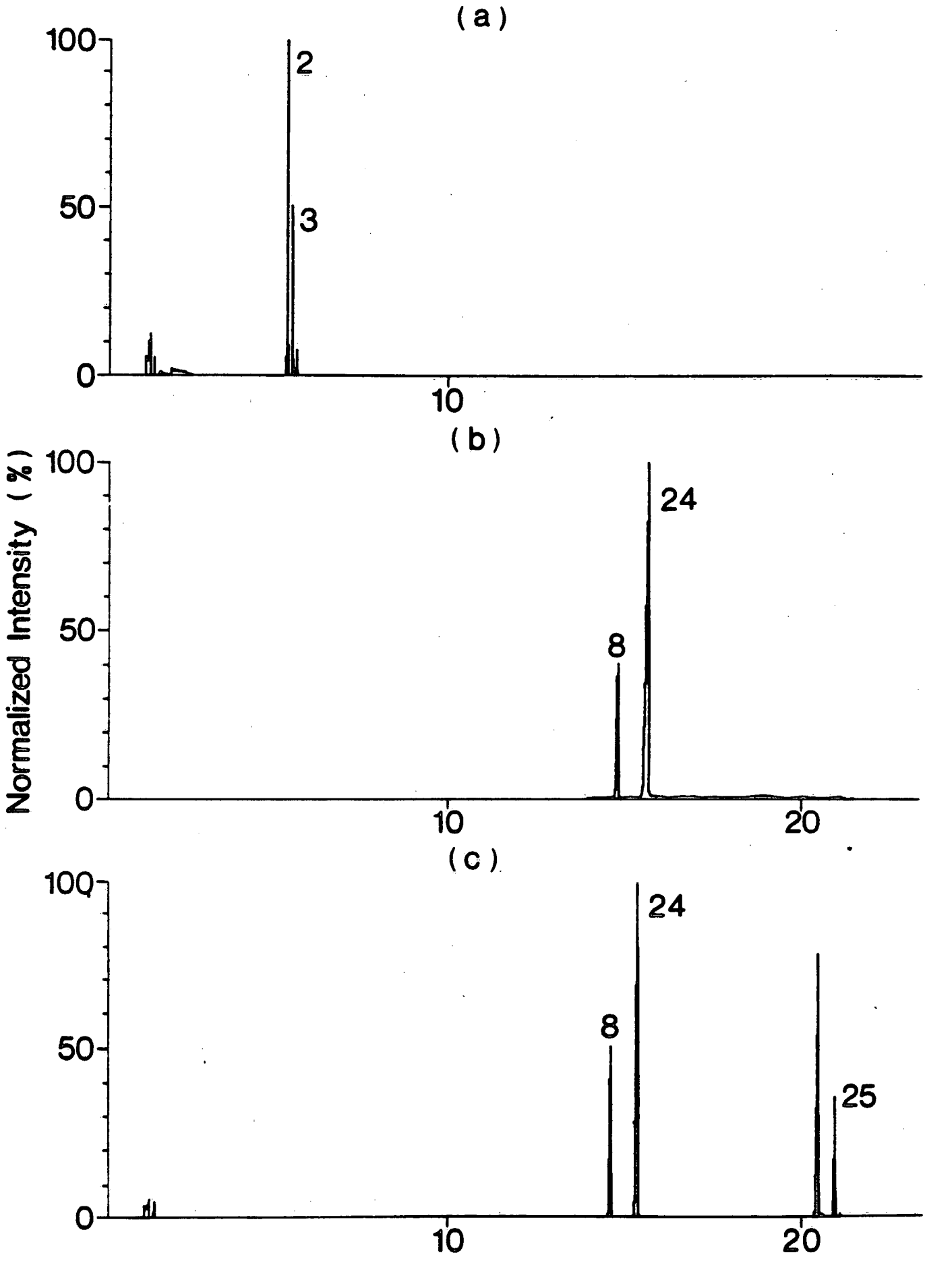
(a)
100
50
0
2
3
10
(b)
100
50
0
24
8
10
20
(c)
100
50
0
24
8
25
10
20
Normalized Intensity (%)
Retention time (min.)

Fig. 6

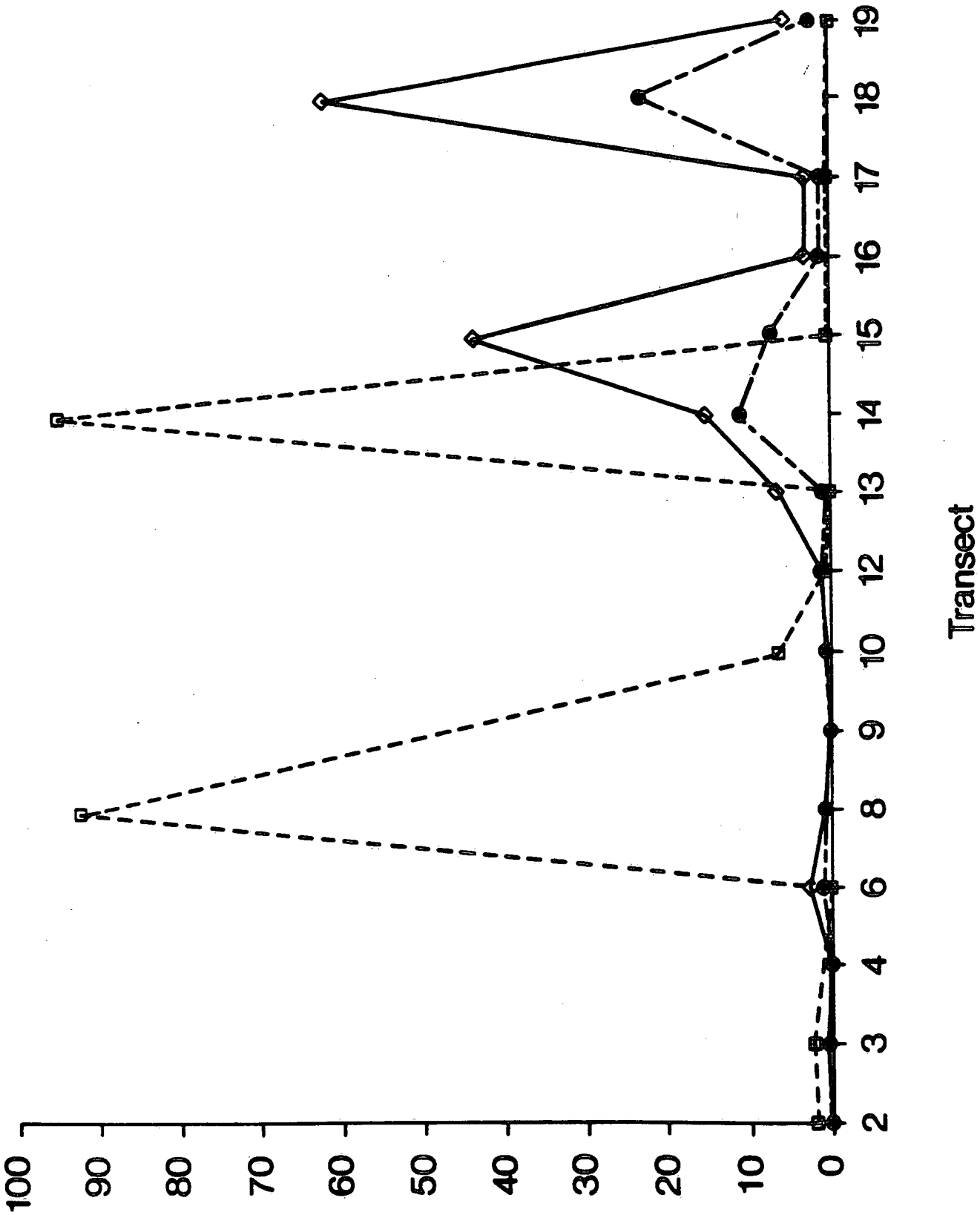
% / Concentration (µg/g)
100
90
80
70
60
50
40
30
20
10
0
2
3
4
6
8
9
10
12
13
14
15
16
17
18
19
Transect

Fig. 7