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Stable Carbon Isotopic Apportionment of Individual Polycyclic Aromatic Hydrocarbons in St. John's Harbour, Newfoundland

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Much interest has recently focused on the quantitative apportionment of multiple sources of toxic and carcinogenic compounds in natural aquatic systems. Apportionment studies of polycyclic aromatic hydrocarbons (PAH) are of great interest because, in addition to their suspected toxic and carcinogenic properties, they also have a wide range of potential natural and anthropogenic sources. This paper presents the results of a study where the primary source inputs of PAH to sediments of St. John's Harbour are quantitatively assessed using a combination of molecular abundance and carbon isotope measurements of individual (4- and 5-ring) PAH. Mass balance calculations using a two-component mixing model show that approximately 50–80% of the PAH input to the Harbour sediments is of combustion origin, likely dominated by vehicular emissions carried by surface runoff from the city of St. John's. Direct petroleum-related contribution, possibly dominated by crankcase oil, accounts for the remaining 20–50% of the total PAH input.

Introduction

The toxic and carcinogenic characteristics of polycyclic aromatic hydrocarbons (*1*), a group of compounds that consist of two or more fused benzene rings, have led to increased interest in tracing the origin of these compounds in depositional environments such as sediments. Present approaches to elucidating or apportioning primary source inputs of PAH to aquatic environments have largely relied on the molecular fingerprint or the relative abundance of individual PAH or groups of PAH believed to characterize

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a wide variety of natural and anthropogenic sources (*2–7*). However, because of the molecular similarities of a variety of PAH sources and the susceptibility of molecular distributions to changes as a result of physical, chemical, and biological weathering in natural environments, source apportionment based solely on the molecular fingerprint has remained largely qualitative. The possibility of combining the molecular approach with compound-specific carbon isotope ($^{13}C/^{12}C$) signatures to enable a more quantitative assessment of PAH sources in natural sedimentary environments has been recently investigated (*8, 9*). For example, O'Malley et al. (*8*) have already demonstrated that, in contrast to the molecular distribution, the carbon isotopic signature of individual 4- and 5-ring PAH is quantitatively retained during weathering (volatilization, photolysis, microbial degradation). Also, it was shown that distinct isotopic signatures are produced by primary petroleum and combustion-related PAH sources (*9*). In this paper, the results of two-component mixing calculations for St. John's Harbour surface sediments are presented to demonstrate the quantitative utility of a combined molecular and isotopic source apportionment technique for PAH.

Experimental Section

Study Site Description. The city of St. John's, Newfoundland (Figure 1), is concentrated on the north side of the Harbour, consisting solely of small commercial and residential properties. The potential primary PAH sources identified in the immediate vicinity of the Harbour include fireplace and heating stove wood combustion, domestic heating furnaces, vehicle exhaust emissions, petroleum spillage, crankcase oil, and road-building materials including asphalt. Sediments and organic matter are deposited in the Harbour primarily through raw sewage and storm sewer inputs, snow dumping, urban runoff, and riverine inputs (Figure 1) as well as by direct discharges (e.g., from shipping) and from wet and dry aerial deposition. Contributions of primary PAH sources, which refer to the original site or process of formation of the compounds (e.g., wood burning, fossil fuel burning, crude oil), are considered in the present apportionment calculations. Indirect PAH sources (such as sewage, snow dumping, urban runoff, and riverine inputs) are only intermediate reservoirs that receive PAH contributions from the primary sources. Hence the latter are not considered as primary sources.

Sampling. Surface sediment samples (upper 2 cm) were collected using a solvent-washed Van Veen grab sampler. Sediments were obtained from the deep portion of the Harbour and close to input sources such as sewage outfalls (Figure 1) and landfill leachate plumes. Although the sedimentation rate was not determined, the sediments are expected to be relatively recent (<10 years) due to the significant inputs of sediment and organic matter from raw sewage, storm sewer runoff, and snow dumping.

Various primary combustion sources (domestic fireplaces and chimneys, wood stoves, car mufflers, and domestic furnaces) were sampled by scraping approximately 5 g of soot material with a solvent-washed spatula onto precleaned aluminum foil. The material was then transferred to precleaned brown glass vials. Diesel-powered
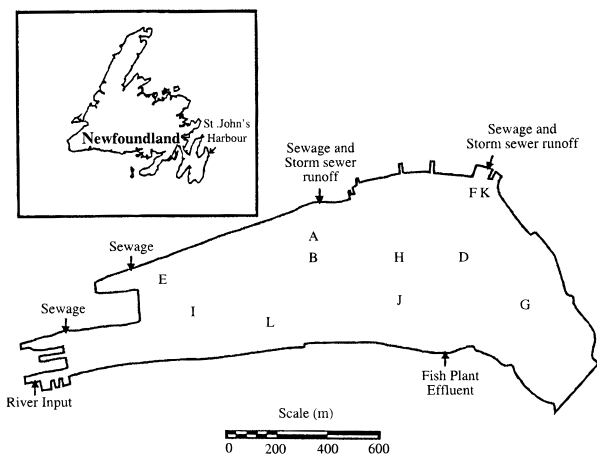
FIGURE 1. Study area and location of sampling sites, raw sewage, and riverine inputs in St. John's Harbour.

cars are not widely used in the city area; therefore most of the mufflers sampled in this study were from gasoline-powered cars.

Individual crankcase oil samples were directly sampled from car engines, and further composite samples were obtained by sampling the waste oil sump of garages in the St. John's area. Other petroleum-related sources (crude oil, No. 2 fuel oil, gasoline, outboard motor effluents, and virgin crankcase oils) identified as potential PAH sources were also sampled and analyzed. All sediment, combustion, and petroleum samples were stored at −20 °C until processed.

Sample Preparation and Analysis. Detailed descriptions of sample preparation, PAH extraction, purification, identification and quantification procedures were reported previously (*8*). Briefly, air-dried sediments were Soxhlet extracted in glass-distilled dichloromethane for 24 h. The extracts were then concentrated and purified using Sephadex and silica columns. The aliphatic fraction was initially eluted off the silica column with hexane and the aromatic fraction with 1:1 dichloromethane/hexane. The prominent PAH were separated, identified, and quantified using a gas chromatograph equipped with a flame ionization detector and a 30 m × 0.11 mm i.d., 0.12 μm film thickness CPSil-5 capillary column (Chrompak).

For the gas chromatograph/combustion/isotope ratio mass spectrometer (GC/C/IRMS) analyses, all samples were taken up in appropriate volumes of a solution containing three internal reference compounds (acenaphthalene and C_{21} and C_{25} *n*-alkanes) with known isotopic compositions. The addition of these compounds enabled instrument performance and reliability of background subtraction to be independently assessed in complex sample matrices. Although an external CO_2 reference gas was used to calculate compound-specific $\delta^{13}C$ (see eq 1) values in *all* samples, the known isotopic values of the internal reference compounds aided the careful selection of background points so that the $\delta^{13}C$ values (referred to as δ values for the remainder of the text) of individual PAH sitting on a significant unresolved complex mixture (UCM) could be reliably determined. Due to the significant backgrounds observed in some samples, the automatic background correction procedure occasionally did not simultaneously recover the δ values of the three internal reference compounds. In such cases, manual background correction was performed. This was undertaken in two stages. The

first stage entailed manual selection of new background points between the first two reference compounds (17−50 min) and then fitting a new polynomial background trace (45/44 and 46/44) until the δ values of these two compounds were as close as possible to their predetermined values. The δ values of the compounds of interest adjacent to and between these two internal standards were then reported. Samples peak δ values in the second portion of the chromatogram (portion containing the second and third internal reference compounds, 40−70 min) were obtained using the same procedure described above except that the latter two standards were used to verify the validity of the background trace.

$$\delta^{13}C\text{‰ (per mil)} = 1000[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1] \quad (1)$$

The external CO_2 reference gas was calibrated relative to PDB (Pee Dee Belemnite) using primary standards NBS 22-graphite and NBS 19-TS limestone. On the basis of results obtained by Abrajano (unpublished data) using standard phenanthrene solutions which showed no degradation in precision in peak sizes down to 1 nmol of carbon, all standards and samples were diluted so that a 1 μL injection contained between 5 and 10 nmol of carbon of the compounds of interest. Multiple compound-specific isotope measurements on a standard mixture of PAH were performed with a precision (2σ) of between 0.25‰ and 0.39‰ and an accuracy that ranged between 0.01‰ and 0.57‰. GC/C/IRMS measurements on a range of field samples were performed with a precision of better than 0.30‰ for well-separated 3-, 4-, and 5-ring compounds while precisions of up to 0.85‰ were recorded for some high molecular weight coeluting isomers. Details covering the determination of the precision and accuracy have been reported (*8*).

Results and Discussion

PAH concentrations relative to percent total organic carbon (TOC) in the Harbour sediments were significantly elevated compared to those determined in nonurbanized embayments around Newfoundland including some in close proximity to St. John's Harbour (e.g., Conception Bay, Figure 2). The observed levels were also consistent with concentrations identified in other similarly contaminated Harbour sites (*10−14*). The dominance of 3-, 4-, and 5-ring parental PAH (i.e., compounds containing carbon and hydrogen only) in the molecular fingerprint together with the presence of alkylated PAH and a significant UCM were indicative of PAH inputs from both combustion and petroleum origin. However, the presence of low concentrations of retene and perylene in the sediments also suggested minor contributions of diagenetically derived compounds (*15*). Therefore, using the molecular fingerprint alone, PAH contributions from combustion, petroleum-related, and diagenic sources were identified in these Harbour sediments. The unweighted mean δ values of the individual 3-, 4-, and 5-ring PAH in the sediments ranged between −26.3‰ and −24.6‰ while the sample to sample variation was less than 0.3‰. The most distinctive feature in the overall range of δ values was the significantly enriched 3-ring PAH (phenanthrene and anthracene) compared to the 4- and 5-ring compounds (Figure 3).

On the basis of total PAH abundance in the primary sources investigated, wood burning and vehicular emissions
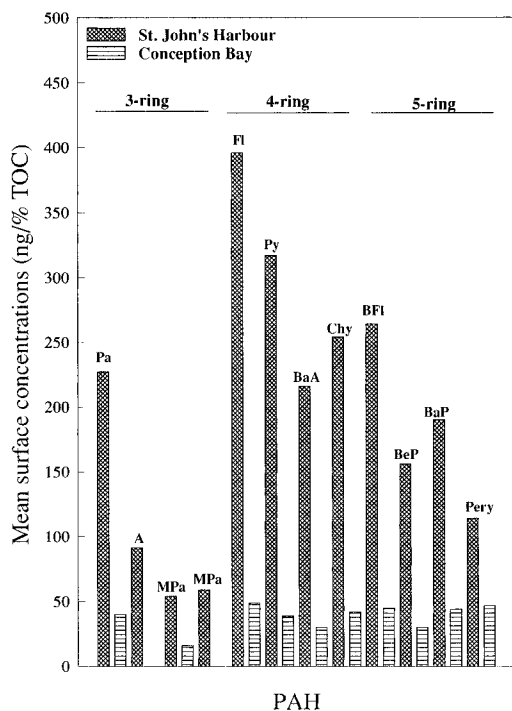
FIGURE 2. Mean surface sediment concentrations (ng/% total organic carbon) of the 3-ring parental and methylated compounds and 4- and 5-ring parental PAH in St. John's Harbour (TOC = 11% ± 3%) and Conception Bay (TOC = 1% ± 0.2%), Newfoundland: Pa = phenanthrene, A = anthracene, MPa = methylphenanthrene, Fl = fluoranthene, Py = pyrene, BaA = benz[a]anthracene, Chy = chrysene, BFl = benzofluoranthenes, BeP = benzo[e]pyrene, BaP = benzo[a]pyrene, and Pery = perylene. The isomers of MPa are distinguished by having methyl groups at the 2 and 3 and the 1 and 9 carbon positions.
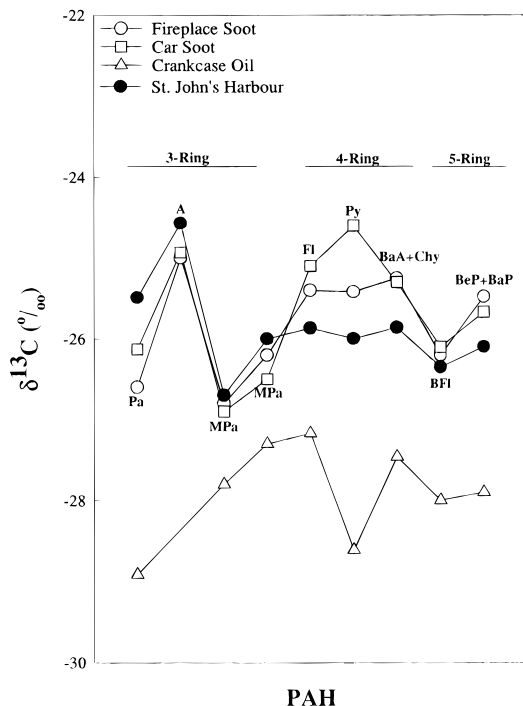

FIGURE 3. Isotopic compositions of the 3-ring parental and methylated PAH and the 4- and 5-ring parental PAH in the surface sediments of St. John's Harbour with the three prominent primary sources.

(combustion) and crankcase oil (petroleum-related) were identified as the dominant PAH input sources to the Harbour sediments (Table 1). The molecular fingerprints

TABLE 1

Mean Concentration[a] of Prominent PAH in the Primary Sources

PAH	crankcase oil	fire soot	car soot
3-ring			
naphthalene	4.45	BDL[b]	0.68
methylnaphthalene	6.84	BDL	0.99
methylnaphthalene[c]	4.41	BDL	0.59
dimethylnaphthalene	2.89	BDL	0.30
trimethylnaphthalene	2.24	BDL	0.17
fluorene	5.27	BDL	BDL
phenanthrene	5.14	2.86	1.65
anthracene	0.57	0.85	0.92
methylphenanthrene[c]	4.22	1.46	0.87
methylphenanthrene	2.64	1.58	0.53
4-ring			
fluoranthene	3.05	5.50	1.79
pyrene	4.06	5.77	1.98
benz[a]anthracene	0.99	3.63	1.20
chrysene	1.58	5.27	1.49
5-ring			
benzofluoranthenes	1.97	2.89	2.09
benzo[a]pyrene	1.89	1.37	1.99
benzo[e]pyrene	0.46	1.04	2.70

[a] In μg/g of sample material. [b] BDL = below detection limit of 0.02 μg/μL. [c] Isomers of methylnaphthalene and methylphenanthrene.

of these sources were consistent with previously reported wood-burning, vehicular emissions, and crakcase oil fingerprints (16−21). As expected (16−19), wood burning and vehicle muffler soot samples were dominated by 3-, 4-, and 5-ring parental PAH with generally lower concentrations of 2-ring parental and methylated compounds (Table 1). In contrast, the molecular fingerprint of crankcase oil samples consisted of elevated concentrations of 2- and 3-ring parental and methylated PAH with lower concentrations of 4- and 5-ring species (20, 21). The corresponding unweighted mean δ values of these PAH sources are shown in Figure 3, where combustion and petroleum-related sources are clearly separated. PAH from the combustion reactions (wood burning and vehicular emissions) were generally more enriched in ^{13}C compared to the corresponding compounds isolated from crankcase oil. In spite of the differences in the combustion processes and the nature of the precursor materials, the compound to compound δ value variations within the fire and car soot samples (n = 11 and 12, respectively) were comparable (Figure 3). Car soots were, however, consistently characterized by ^{13}C-enriched pyrene compared to wood-burning sources. PAH isolated from crankcase oil samples (n = 16) were substantially more depleted in ^{13}C and were characterized by phenanthrene and pyrene significantly depleted in ^{13}C. Unlike the results for combustion sources, phenanthrene in the crankcase oil was more depleted in ^{13}C than its methylated derivatives and pyrene was more ^{13}C depleted than fluoranthene. In the past, PAH in crankcase oils have been mainly attributed to the incomplete combustion of gasoline hydrocarbons (19, 20). Since the muffler PAH are also derived from the incomplete combustion of gasoline, the reason for the presence of ^{13}C-depleted PAH in the crankcase oils is unknown but it may suggest that they are derived from a source other than gasoline combustion. Although anthracene was present in the crankcase oils investigated, concentrations were insufficient for the determination of its isotopic composition.
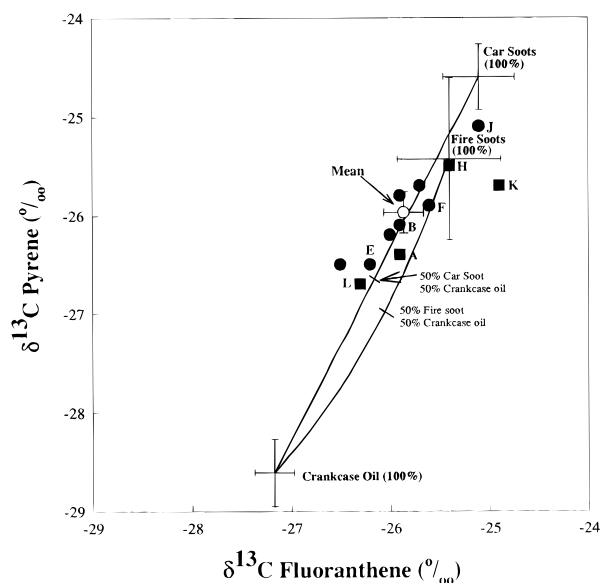
FIGURE 4. Fluoranthene (Fl) and pyrene (Py) δ values of the individual sediment samples from St. John's Harbour plotted on the mixing curves generated by mixing the $\delta^{13}C$ and the mean normalized concentrations of these compounds in the prominent primary sources. Sediment sites plotting on or close to the crankcase oil/car soot curves are represented by the round solid symbols while the square solid symbols distinguish sites plotting closer to the crankcase oil/fire soot curves. The hollow circle represents the unweighted mean δ Fl and Py values of all the sediment sites investigated. Error bars represent the sample to sample variations (1σ) observed for these compounds in the source and sediment samples, and letter notations represent some of the sample site locations in the Harbour.
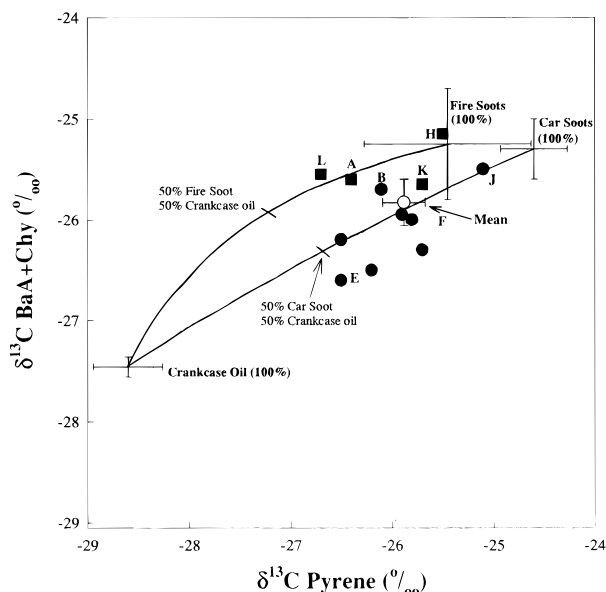

FIGURE 5. Pyrene (Py) and unweighted mean benz[a]anthracene + chrysene (BaA + Chy) δ values of the individual sediment samples from St. John's Harbour plotted on the mixing curves generated by mixing the $\delta^{13}C$ and the mean normalized concentrations of these PAH in the prominent primary sources.

Comparison of the PAH δ values in the sediments and in the three primary sources indicated that the 4- and 5-ring compounds have carbon isotopic compositions bracketed by those of the three primary sources (Figure 3). Appropriately, a mixture of these three sources would explain the isotopic signature of the PAH in the sediment. The 3-ring PAH in the sediments, unlike the 4- and 5-ring compounds, are, however, enriched in ^{13}C relative to all
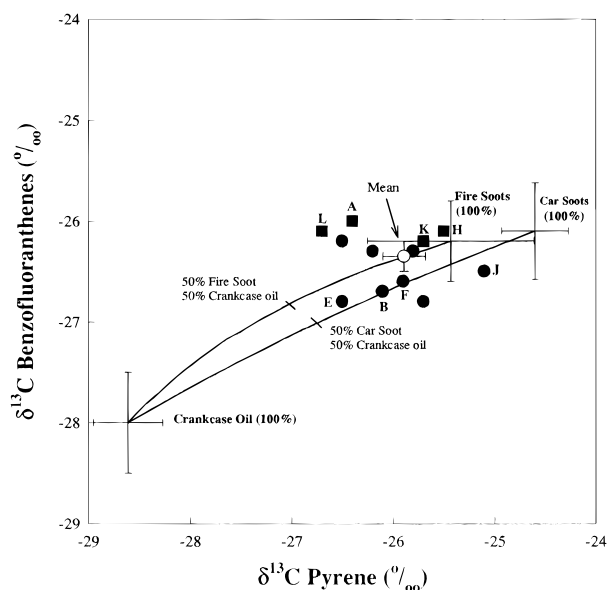

FIGURE 6. Pyrene (Py) and the benzofluoranthene (BFl) δ values of the individual sediment samples from St. John's Harbour plotted on the mixing curves generated by mixing the $\delta^{13}C$ and the mean normalized concentrations of these PAH in the prominent primary sources.

sources. This was consistently observed in most of the sediment samples investigated and would indicate that processes other than mixing (e.g., weathering) or sources in addition to the three identified may have influenced the isotopic compositions of these 3-ring compounds. However, subsequent discussions will focus on the 4- and 5-ring PAH where further quantification of sources appears warranted since they were shown to be more stable in the environment (8).

A more quantitative approach to apportionment of sources of PAH in sediments can be undertaken with the use of *both* the molecular abundance and isotopic composition of the individual compounds. To demonstrate the potential of this approach, we employed a two-component Langmuir mixing equation, which is described in detail in (22). The use of this mixing equation assumes that there is no *significant* preferential loss or gain of one compound over another prior to deposition. To eliminate concentration effects from the primary sources considered, the mean concentrations of the individual 4- and 5-ring PAH were initially normalized to the total 4- and 5-ring PAH content of their respective sources. Mixing curves were then generated by mixing the δ values and the normalized concentrations of various combinations of the 4- and 5-ring PAH isolated from the primary sources investigated. Separate mixing curves were defined for the fire soot/crankcase oil and car soot/crankcase oil end-member pairs, and examples of these curves are shown in Figures 4—6, along with the unweighted mean and individual δ values of the PAH isolated from the individual sediment samples. The mixing curves resulting from the Langmuir equation are hyperbolic, with curvature dependent on the relative concentrations of the individual PAH in the respective sources. If the concentrations of the individual PAH are the same in both sources, then the mixing curves will follow a straight line. Different concentrations will cause the mixing curves to move up (concave, Figure 5) or down (convex). The error bars represent the sample to sample variation in isotopic values

(1σ) observed for that particular compound during the analysis of the various single and composite source samples. Interestingly, the natural variations in the isotopic values of the PAH in the sediments were generally less than observed for the individual primary source samples, which suggests that an "averaging" of these sources is occurring during deposition in the sediments. Therefore, except in the event of an accidental petroleum spill or large fire, it is unlikely that any one particular source will ever totally dominate PAH input to the sediments. From the various PAH mixing combinations considered, the δ values of the 4- and 5-ring compounds isolated from the sediments generally form distinct mixing patterns between the fire, car soot, and crankcase oil end-members. This quantitatively substantiates earlier assertions that a mixture of these primary sources could explain the range of δ values observed in the sediments. It is notable that the relative positions of the individual sample sites (e.g., B, J, H, and F) on the mixing curves do not significantly change (within experimental error) regardless of the combination of PAH used on the abscissa and ordinate. This is an important criterion which has to be fulfilled if mixing is to be a valid explanation for the observed sample to sample isotopic variations. In general, as indicated by the presence of 3-, 4-, and 5-ring parental PAH in the molecular fingerprint, PAH of combustion origin seem to be dominant contributors to the sediments. This is shown by the bulk of the data points which are concentrated close to the two combustion end-members (Figures 4−6). From the position of the mean values on the mixing curves, the average combustion input is estimated to be approximately between 50 and 80% while the remaining 20−50% of the PAH seem to be derived from crankcase oil contributions. Sites H and J are particularly enriched in combustion-derived PAH, while the maximum input of crankcase oil (approximately 50%) consistently occurred at site E (Figure 5), indicating the heterogenous nature of these sediments, which was not evident from the molecular fingerprints. Also, the relative importance of the two primary combustion sources (fire soot vs car soot) as PAH contributors to the sediments is not evident from the molecular signature, but it is implied by these mixing curves. Although there is not relevance to the geographical position of the sample sites, with the exception of sites A, H, K, and L which plot closer to the fire soot/crankcase oil mixing curve, all the remaining sites tend to be concentrated close to the car soot/crankcase oil mixing curve (Figures 5 and 6). This indicates that a significant portion of the combustion-derived PAH in the Harbour is of car emission origin. This characterization is particularly evident where the mixing curves tend to be well separated (Figure 5). The dominance of car soot PAH compared to fire soots suggests that perhaps a significant portion of wood-burning emissions are being transported away from the sampling area due to wind dispersion, and that car soot inputs may mainly occur as a result of urban road runoff. The importance of crankcase oil inputs to the sediments is indicated by the fact that most of the individual samples were characterized by the presence of a prominent unresolved complex mixture (UCM).

The sample to sample variations around each of the individual PAH in the selected mixing sources were not considered in this two-component mixing approach. Despite this it is evident, from the relative positions of the sediment sampling sites on the mixing curves, that the use of this two-component mixing equation is a valid representation of source mixing in the sediments. If the distribution of the compound-specific δ values in the sediments simply represents statistical variations around one or both combustion sources, why are the observed values almost all depleted in ^{13}C compared to the combustion mean δ values? Furthermore, these values are also shown to be trending toward the ^{13}C-depleted source and not randomly distributed in the mixing diagrams. Clearly, the real statistical variations around each combustion source must be substantially smaller than indicated by the assumed normal distribution based on the analyses of individual fire and car soot sources. As suggested earlier, it is conceivable that a natural averaging of source signatures is taking place prior to sediment deposition, such that extreme isotopic signatures for each source are hardly expressed in the sediments. The observations that (1) the sediments plot on or close to the two mixing curves and (2) the relative proportions contributed by the sources are not affected by the choice of variables (i.e., regardless of the choice of specific PAH) are themselves important evidence in support of the mixing model.

It is apparent from the results presented in this study that the use of compound-specific carbon isotope compositions in combination with the molecular abundance of individual PAH has considerable potential to allow for a more detailed assessment of primary source PAH inputs to sedimentary environments.

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