

## DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN AN URBANISED ESTUARY AND POSSIBLE IMPLICATIONS FOR SOURCE APPORTIONMENT

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### ABSTRACT

PAHs in Motions Creek (MC) sediment, an urbanised catchment in Auckland, New Zealand, are concentrated in coarse-to-medium sized fractions and preferentially enriched in low-density material (<2.1 g/ml), with 3% of the sediment mass containing 75% of the total PAHs. Regardless of size and density, sediment fractions exhibited a characteristic 'urban pyrogenic' fingerprint. The low-density material consisted of a mixture of plant detritus and various forms of black carbon (BC). Isolated BC particles (250-500 µm) contained 950 µg/g of PAHs, however, the *n*-alkane, unresolved hydrocarbons (UCM) and hopane compositions were inconsistent with those of the bulk sediment. Despite the enrichment of PAHs in >63 µm size fractions (larger than typical pyrogenic source particles) and a pronounced UCM, diagnostic PAH ratios indicated no significant contribution of petrogenic PAHs to the total PAH loading of MC sediment. A discussion of the possible implications for source apportionment of PAHs is presented

### RÉSUMÉ

Les hydrocarbures aromatiques polycycliques (PAHs) dans les sédiments de Motions Creek (MC), un bassin versant urbain d'Auckland (Nouvelle-Zélande), sont concentrées dans des sédiments grossiers ou de taille moyenne, enrichis de préférence de matériau à basse densité (<2.1 g/ml) ; 3 % de la masse de sédiments contient 75 % des HAP. Quel que soit la taille ou la densité, les fractions de sédiments ont montré une empreinte 'pyrogénique urbaine' caractéristique. Le matériau à basse densité consistait d'un mélange de débris de plantes et de formes différentes de noir animal (*black carbon*, ou BC). Des particules isolées de BC (250-500 µm) contenaient 950 µg/g de HAP. Les *n*-alcanes, les UCM et les compositions de hopane ne correspondaient pas à ceux du sédiment total. Malgré l'enrichissement de HAP de fractions de >63 µm (plus grandes que les particules pyrogéniques de source typiques) et un fort taux de UCM, les proportions diagnostiques de HAP indiquaient aucun apport important de HAP pétrogéniques à la concentration totale de HAP dans le sédiment de MC. Nous concluons par une discussion des implications éventuelles pour l'attribution des sources de PAHs.

### 1. INTRODUCTION

PAHs are one of the most important classes of anthropogenic organic contaminants and they are ubiquitous in the aquatic environment. A major route of PAHs into the aquatic environment is via urban runoff, where they are largely associated with particulate matter (ca. 95%; Mackenzie and Hunter, 1979). For example, it was calculated that one storm discharged 4.1 tonnes of total aromatics into the Los Angeles River (Eganhouse and Kaplan, 1981). In addition, Hoffman et al. (1984) calculated that urban runoff contributed 71% of the high molecular weight PAHs discharged into Narragansett Harbour.

Urban streets act as repositories for particulate matter, and are therefore important sources of PAHs. Direct sources include, particulate automobile exhaust, lubricating oil residue, tyre wear particles and abraded bitumen particles (Rogge et al., 1993). Anthropogenic PAHs are generally classified as sources derived from unburnt petroleum (*petrogenic*), and those derived from the combustion of fossil fuels and biomass (*pyrogenic*).

PAHs are associated with the processing, transportation and combustion of fossil fuels. Accordingly, increased fossil fuel consumption that accompanies urban growth is

expected to result in increased emissions of PAHs, particularly from the transport sector. This poses a considerable challenge for the environmental sustainability of many rapidly expanding urban centres where aquatic ecosystems are already under considerable strain. New Zealand's largest city, Auckland, has projected population growth of 50% over the next 20 years. This will result in a large increase in traffic and roading infrastructure, which, in turn, will lead to higher PAH loads discharged into the aquatic environment via runoff.

The Auckland Regional Council monitors a total of 27 estuarine sites in the Auckland area (ARC, 2002), with the majority of the sites (i.e. 20) containing less than 1 µg/g and five sites containing between 1 and 2 µg/g. In contrast, Meola Creek and Motions Creek estuaries contain ca. 6 and 11 µg/g, respectively, and a major concern is whether these represent a future scenario for Auckland's other estuaries. Therefore we need to understand how sediment PAHs relate to input sources and how much of the PAH load in urban runoff actually accumulates in sediments.

The importance of transport, fate and source apportionment of PAHs have long been recognised, and have been the focus of much research since the late 1970's. On a global scale, the PAH fingerprint of aquatic sediments from urbanised centres are all remarkably similar and typical of

high temperature pyrolysis, (McCready et al., 2000; Zakaria et al. 2000, and ref therein). Despite the global urban-pyrolytic distribution of PAHs, a number of studies have implicated other sources such as asphalt particles and sump oil as major sources of PAHs (Wakeham et al. 1980; Mackenzie and Hunter, 1979).

Pyrogenic source particles are expected to be very small, since exhaust particles are sub-micron (Hildemann et al., 1991) and PAHs are associated with <3 µm atmospheric fallout particles (Pierce and Katz, 1975). This implies that pyrogenic PAHs should be concentrated in the fine fraction (e.g. <63 µm), however, this is contrary to recent studies showing an enrichment of pyrogenic PAHs in medium-to-coarse particles (i.e. >125 µm; Wang et al., 2001; Rockne et al., 2002). Therefore, *are fine combustion-derived particulates still the major source of PAHs in these sediments?*

Previous research at NIWA (unpublished results) has shown that Motions Creek (MC) estuarine sediments show an enrichment of PAHs in >125 µm size fractions. Therefore the main aim of this research was to use a combination of size and density fractionation to isolate the major contaminated particles, and, using different molecular markers, attempt to reconcile this material with potential source materials (e.g. car tyres, sump oil, bitumen, coal tar etc) and environmental source matrices (road dust, atmospheric settling particles).

## 2. GEOGRAPHICAL SETTING

The city of Auckland is situated in the upper part of the North Island and is New Zealand's largest city, with a population of 1.08 million. Much of Auckland city, including the central business district and ports, border the Waitemata Harbour. Motions Creek (MC) is spring feed and runs a very short distance (ca. 2 km) before discharging into Waitemata Harbour. The Motions catchment is ca. 463 ha and includes a section of Auckland's busiest motorway.

## 3. EXPERIMENTAL SECTION

### 3.1 Sample Collection

Surficial (0-20 mm) estuarine samples were collected from the estuarine region of Motions Creek (MC-1) and wet sieved into 63 µm, 63-125 µm, 125-250 µm, 250-500 µm, 500-1000µm and >1000µm size fractions. Sediments were density separated using 2.15 g/ml solution of sodium polytungstate in 50 ml centrifuge tubes. The floated material was collected, washed and freeze-dried. For comparison, another sample was collected ca. 1 km upstream in a non-tidal, fresh water region of the creek (MC-2). This sample was freeze-dried and analysed as bulk sediment only. A sample representing motorway runoff was collected near a gutter drain – this sample is herein referred to as *road dust*. Source materials analysed included car tyre particles, bitumen, used oil, diesel soot, charcoal, coal and coal tar

pitch. Although not collected as part of the study, previous PAH data from atmospheric fallout particles collected in the Auckland area were re-analysed. These particles were originally collected in gravitational traps set ca. 1 m from a residential roadside.

### 3.2 Sample extraction and analysis

Standard procedures were used for PAH analysis. Briefly, weighed samples of dry sediment/source materials were spiked with a mixture of 7 deuterated surrogates (d<sub>8</sub>-naphthalene, d<sub>10</sub>-acenaphthene, d<sub>10</sub>-phenanthrene, d<sub>10</sub>-fluoranthene, d<sub>10</sub>-pyrene, d<sub>12</sub>-benz[a]anthracene and d<sub>12</sub>-perylene). Samples were extracted with dichloromethane using accelerated solvent extraction (Dionex ASE-200). Extracts were cleaned-up by passing through a silica column (4g), then exchanged into heptane with *p*-terphenyl-d<sub>14</sub> added as the internal standard. Samples were analysed using selected ion monitoring (SIM) on a HP 5890/5972 GCMS. All concentrations are based on dry-weight extracted, and included the following 24 PAHs (abbreviations in parentheses): naphthalene (NAPH); 2-methylnaphthalene (2M-NAPH); -methylnaphthalene (1M-NAPH); biphenyl (Biphen); 2,6-dimethylnaphthalene (2,6DM-NAPH); acenaphthylene (ACTHY); acenaphthene (ACE); 2,3,5-trimethylnaphthalene (235TM-NAPH); fluorene (FL); phenanthrene (PHE); anthracene (ANT); 1-methylphenanthrene (1M-PHE); fluoranthene (FLTH); pyrene (PYR); benz[a]anthracene (BaA); chrysene (CHRY); benzo[b]fluoranthene (BbF); benzo[k]-fluoranthene (BkF); benzo[e]pyrene (BeP); benzo-[a]pyrene (BaP); perylene (PER); indeno[1,2,3-*c,d*]pyrene (InP); dibenz[*a,h*]anthracene (DBA); benzo[*g,h,i*]perylene (BghiP).

Full-scan acquisitions and extracted ion chromatograms at *m/z* 85 and *m/z* 191 provided qualitative information regarding UCM, *n*-alkanes and hopanes, respectively. Alkyl homologue distributions (AHD) of phenanthrene were based on integration of peak area from extracted ion chromatograms at *m/z* 178, 192, 206 and 220 for C<sub>0</sub>, C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> methylated phenanthrenes, respectively.

## 4. RESULTS AND DISCUSSION

### 4.1 Distribution of PAHs in MC estuarine sediments

#### 4.1.1 Size fraction

Table 1 shows the sediment characteristics of surface Motions Creek sediment. The concentration of PAHs ranged between 4.1 in the <63 µm fraction up to 109 µg/g in the 250-500 µm fraction.

Wang et al. (2001) similarly found that >250 µm fractions from three sites in the Boston harbour contained between 4-7 times higher PAH concentrations than the <62 µm fraction. Rockne et al. (2002) have reported 4-fold higher PAH concentrations in the <500 µm fraction for two intertidal creeks in New York/New Jersey Harbour. Despite a

Table 1: PAHs in size-fractionated MC estuarine sediment

Grain size (µm)	% of sediment mass	ΣPAH µg/g	% of composite <sup>a</sup> ΣPAH
<63	56.0	4.1	17.4
63-125	16.5	15.4	19.2
125-250	25.3	25.2	48.0
250-500	1.6	108.7	13.2
500-1000	0.4	70.2	2.1
>1000	0.3	5.4	0.1
composite <sup>a</sup>		13.3	

<sup>a</sup> mass weighted average of all grain size fractions

lower concentration, the 125-250 µm fraction of MC sediment contributes the largest proportion of total sediment PAHs at 48% (25% of sediment mass). In contrast, the <63 µm fraction contributes only 17% while comprising 56% of the sediment mass.

#### 4.1.2 Density separation

Amorphous carbon (e.g. soot carbon) has a density of up to 1.8-2.1 g/ml, therefore sediments were separated using a 2.15 g/ml sodium polytungstate solution. Table 2 shows that with the exception of the >1000 µm fraction, the light material contained between 10-200 times higher PAH concentrations than the equivalent heavy size fraction, with a maximum concentration of 720 µg/g (125-250 µm fraction). The light fractions have a higher organic carbon (OC) content (21.8-37.4%) than the corresponding heavy fractions (0.34-3.7%). The enrichment in the light fractions is still evident after normalising to OC but is far less pronounced. For example, in the 125-250 µm fraction light fraction enrichment decreases from a factor of 200 (dry weight basis) to just 3.6 for OC normalised PAH concentrations.

Table 2. PAHs in size- and density-fractionated MC estuarine sediment.

Grain size (µm)	% Contribution to total sediment mass		ΣPAH µg/g	
	Light	Heavy	Light	Heavy
<63	1.0	55.0	101	1.7
63-125	0.31	16.1	511	3.6
125-250	0.65	24.6	720	3.6
250-500	0.37	1.2	333	6.2
500-1000	0.30	0.09	46	4.8
>1000	0.25	0.04	2.6	11.4
Composite <sup>a</sup>	2.9	97.1	300	2.6

<sup>a</sup> mass weighted average of all grain size fractions

Figure 1 illustrates the size and density distribution of PAHs in MC sediment. Noteworthy features include: (1) for the total sediment, the light fraction constitutes 3% of the total MC sediment; (2) the light 125-250 µm fraction contribute the largest proportion of PAHs (ca. 42%) but represents only 0.62% of the total sediment mass. Comparable enrichments of PAHs in low-density fractions of sediments have been previously reported (Prah and Carpenter 1983, Ghosh et al., 2000 and Rockne et al., 2002). Because the majority of the PAHs are associated with a readily separable, low-density fraction, this may prove useful for sediment remediation (Rockne et al., 2002) and also have implications for contaminant/sediment dispersion models, which use a mineral density of 2.6 g/ml.

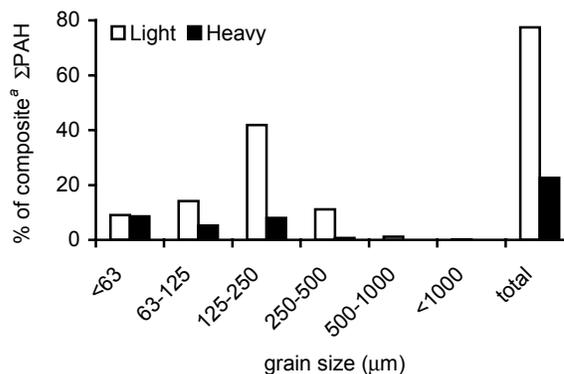


Figure 1. Percentage distribution of PAHs in density and particle-size separated MC sediment (<sup>a</sup> size and density, mass-weighted average composite ΣPAH = 11.1 µg/g)

#### 4.2 Black carbon (BC) particles in low-density fractions

Microscopic investigation of the 250-500µm fraction of MC sediment revealed a heterogeneous mixtures comprised of organic detritus, various black carbon form and a colourless inorganic material. Treatment of the light material with HF removed 60% of the mass, leaving only detritus and BC particles. A crude separation of the particle type was achieved by a 'swirling-settling-decanting' method using a solution density of 1.2 g/ml. Manual separation was used to further 'purify' the detrital material.

Plant and BC enriched particles had the same PAH profile as the bulk sediment (Figure 2), indicating that this low-density material contributes significantly to the total PAH load of the sediment. Predictably, the concentration of PAHs was highest in the BC particulate fraction, with a total 950 µg/g, compared to the plant material with 66 µg/g. Similar high PAH concentrations (300-3800 µg/g) have been reported for BC particles from Milwaukee Harbour sediment (Ghosh et al., 2000).

Although the relative mass of BC particles and plant detritus could not be determined, we believe that the majority of the PAHs in the light fraction are associated with the BC

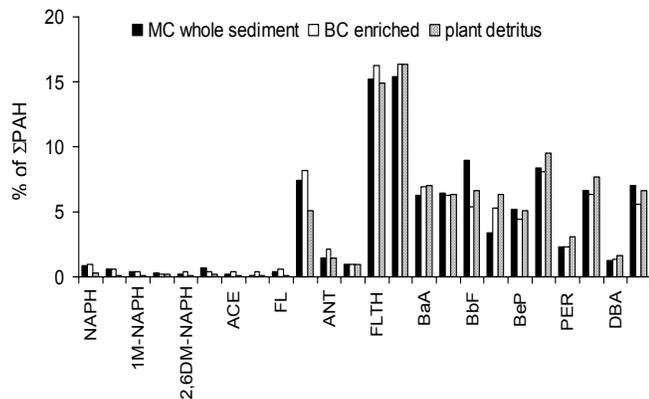


Figure 2. Percentage distribution of PAHs in whole MC sediment, BC enriched and plant detritus fractions (x-axis displays every alternate PAH; see analytical section for abbreviations)

particles, and that most of the 66 µg/g of PAHs in the detrital fraction are due to non-separated BC particles. Conversely, Rockne et al. (2002) concluded PAHs in Pile Creek (NYHarbour) were preferential sorbed to detrital plant debris because of no correlation with soot carbon content. Photomicrographs of Pile Creek sediment showed an abundance of 100-250 µm black particles (estimated from scale). Because these are too large to be soot particles, they must represent an alternative BC form (i.e. coal, charcoal, bitumen, coal tar etc), which is not measured by the Gustafsson soot method. Hence, the non-correlation with soot carbon does not necessarily imply PAH enrichment in plant detritus. Furthermore, it is difficult to reconcile the very high levels of PAHs onto what was initially uncontaminated plant material, in the presence of BC particles. Especially considering that partitioning coefficients for most forms of BC (Jonker and Koelmans, 2002; Bucheli and Gustafsson, 2000; Brandt and De Groot, 2001; Mahjoub et al., 2000; Walters and Luthy et al., 1984) are much higher than those determined for wood (Trapp et al., 2001).

#### 4.3 PAH Profiles of MC estuarine sediment

Regardless of grain size and density, the MC sediment fraction exhibited remarkably similar profiles for the 24 analysed PAHs (Figure 2). In accord with the vast majority of sediments from industrialised/urbanised catchments, the PAH profiles indicates that pyrogenic sources are the major input of PAHs. Representative distributions of PAHs are shown in Figure 2.

#### 4.4 Preliminary source identification analyses

##### 4.4.1 Polycyclic aromatic hydrocarbons

Table 3 summarises the PAH totals of the various source materials and environmental matrices analysed. It is worth noting that the concentration of PAHs in MC sediments is higher than that of road dust and comparable to atmospheric fallout particles. Because these materials are

Table 3. Total PAH of various samples/source materials

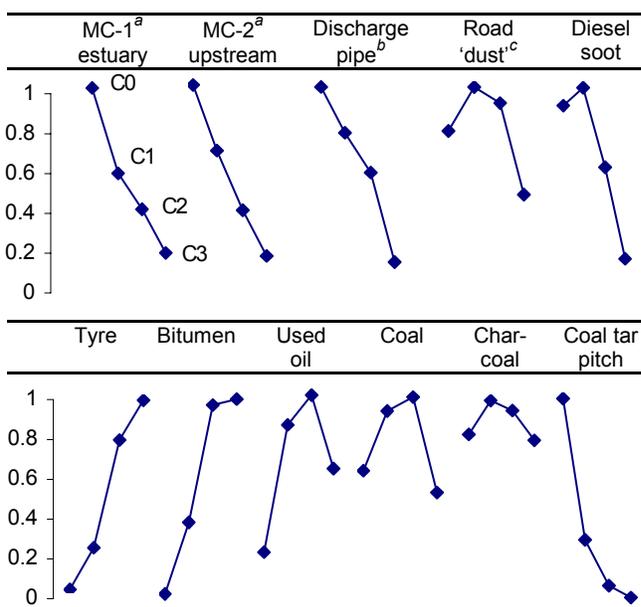
Sample	ΣPAH <sup>a</sup> (µg/g)	Sample	ΣPAH (µg/g)
Tyre	21-95	Road 'dust'	3-4
Bitumen	11-19	Atmospheric fallout	12-27
Used oil	51.5	Discharge pipe	3-7
Charcoal	22.8	MC-1	12-17
Coal	4.6	MC-2	23-26
Pitch	72200	MC-BC <sup>b</sup>	954
		MC-detritus <sup>b</sup>	65.8

<sup>a</sup> ΣPAH = sum of the 24 analysed PAH. <sup>b</sup> BC enriched fraction and isolated plant detritus (refer Section 4.2)

Table 4. Characteristic values of diagnostic PAH ratios

	PHE/ANT	FLTH/ PYR	BaA/ CHRY	MPHE/ PHE
Pyrogenic	<10	>1	>0.9	0.5-1
Petrogenic	>15	<1	≤0.4	2-6

MP = the sum of the mono-methylphenanthrenes



<sup>a</sup> MC-1 = estuarine sediment MC-2 = fresh water streambed sediment. <sup>b</sup> broken discharge pipe near MC-2 location, which contains a lot of particulate matter (presumably from road runoff). <sup>c</sup> road dust refers to particulate debris sample near gutter drain from motorway off-ramp.

Figure 3. The relative distribution of phenanthrene and its mono-, di-, and tri-methylated analogues

'diluted' in stream sediments, there must be either a concentration mechanism (i.e. selective preservation of anthropogenic particles), or alternatively, the streambed

may be contaminated with particulates that are not representative of current urban runoff.

Alkyl homologue distribution (AHD) patterns (Sporstøl et al., 1983; Lake et al., 1979) and a variety of diagnostic PAH ratios are frequently used to distinguish between pyrogenic and petrogenic sources (Table 4; Readman et al., 2002 and ref therein).

The phenanthrene AHD pattern (Figure 3) of MC estuarine sediment is consistent with a pyrogenic source and an almost identical AHD and PAH profile was observed for upstream sediments taken at MC-2. This is consistent with the pyrogenic PAH profile (refer Figure 2) and indicates petrogenic sources do not contribute significantly to the total PAH load of MC sediment. Of the potential source materials examined, the most similar AHD was that of coal tar pitch. Although current inputs are unlikely, historic inputs might be expected on account of the abundance of manufactured gas plants and the use of coal tar products in road construction (Blackburn et al., undated). However, it is not known whether 'historic' particles would be present in surface sediments (0-20mm).

In contrast to pitch, the other pyrogenic source materials contained significant quantities of methyl analogues. Similar AHDs have been observed for automobile exhaust emissions (Jensen and Hites, 1983) and wood soot (Lake et al., 1979).

The road dust sample showed an intermediate phenanthrene AHD, reflecting both pyrogenic and petrogenic inputs. Therefore, road runoff (as sampled) alone cannot adequately account for the pyrogenic PAH composition of MC sediments. In contrast to road dust, material collected from a broken discharge pipe (near MC-2 sampling site), exhibited a strongly pyrogenic AHD similar to that of MC sediment. The reasons for the differences between these two matrices are not apparent, but warrant further investigation.

Because degradation and/or re-partitioning may result in significant post-depositional changes on 2 and 3-ring PAH compounds (McCready et al., 2000), BaA/CHRY ratios are often useful (refer Table 4). The BaA/CHRY ratios in Figure 4a are consistent with the pyrogenic/petrogenic differentiation indicated by PHE AHD patterns. The mixed input of petrogenic sources for road dust/debris and atmospheric fallout particles is confirmed by BaA/CHRY ratios of 0.46 and 0.58, respectively. As mentioned for the AHD, we have no explanation for the pyrogenic nature of the discharge pipe material (BaA/CHRY = 0.9). BC enriched particles and plant detritus had almost identical ratios to that of the bulk MC sediments.

A 2-D ratio plot of MPHE/PHE vs. BaA/CHRY (Figure 4b) readily illustrates the differentiation of petrogenic and pyrogenic sources, and the 'mixed' nature of urban runoff and atmospheric fallout particles. For this data set, the plot failed to classify unburnt coal as petrogenic.

#### 4.4.2 *n*-Alkanes, UCM and hopanes

MC-1 and MC-2 sediment samples contained a pronounced UCM, which is diagnostic of petrogenic inputs. Similar UCMs were observed for atmospheric particles, road dust and particulates collected from the broken discharge pipe near site MC-2. The UCM of these materials showed the greatest similarity with bitumen and were considerably different from the very intense UCM of used sump oil and car tyre particles. Diesel soot exhibited a distinctive, bimodal UCM while coal, charcoal and coal tar pitch had no observable UCM.

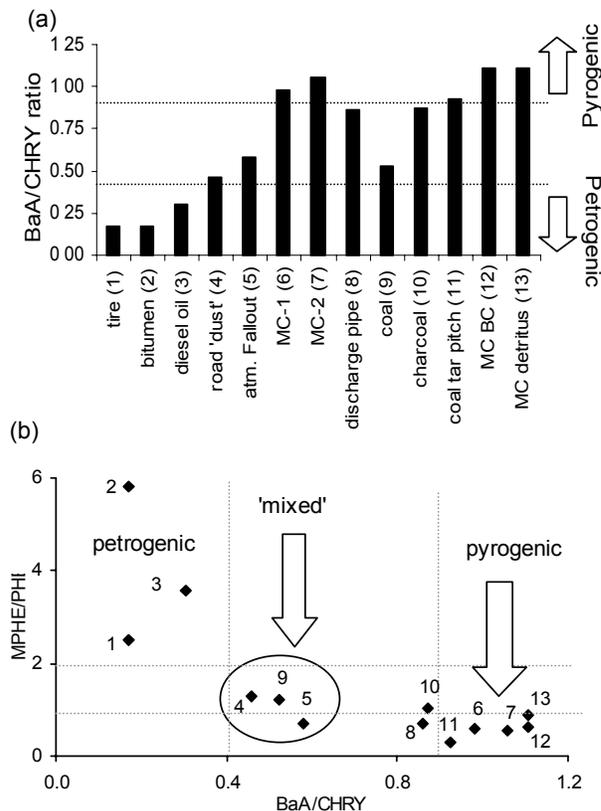


Figure 4. (a) Plot of BaA/CHRY ratios. (b) 2D-plot of MPHE/PHE vs. BaA/CHRY. Dashed grey lines indicate characteristic values for the ratios (refer Table 4) and number on 4b related to sample numbering on 4a.

Urban samples contained significant biogenic inputs (prevalence of odd numbered C<sub>25</sub>-C<sub>33</sub> *n*-alkanes), which was evident from the carbon preference index (CPI) calculated between C<sub>22</sub> and C<sub>35</sub>. Petroleum products are characterised by a CPI value of ca. 1. The CPI of road gutter debris and atmospheric settled particles was 3.8 and 2.9, respectively. Higher proportions of biogenic inputs are due to the larger particle sizes of mechanically generated leaf and soil/dust particle, which accumulate preferentially in road dust samples (Rogge et al., 1993). Particulate material sampled within the broken discharge pipe had a similarly high CPI of 3.7, and is consistent with the material being derived from

street runoff. Upstream sediment (MC-2) had a much lower CPI (1.9) than the estuarine sediment, MC-1 (4.7). This may indicate that much of the biogenic material (light material) entering the creek (via runoff) is preferentially transported down stream, although the abundance of mangroves would also contribute to the high CPI value of MC-1.

Consistent with the observed UCM, hopanes were present in MC sediments at both sampling locations. The hopane distribution was very similar to those for diesel soot, bitumen, car tyre particles and used sump oil, thus the qualitative analysis was of little use for source apportionment. However, the similarity of the UCM with bitumen suggests that asphalt abrasion particles may be the main input of petroleum hydrocarbons to MC sediment. Faure et al. (2000) similarly concluded that bitumen was the major source of diffuse sediment contamination in river sediments.

Coal tar pitch and the enriched BC particles from MC sediments (refer Figure 3a) were compositionally similar and characterised as having very low quantities of *n*-alkanes and no observable UCM or hopanes. Although only tentative, this supports the idea that a coal tar derived product may be responsible for the high PAH content of the MC BC particles. The plant detritus fraction (refer Figure 3b) similarly contained no hopanes or UCM, but did contain biogenic *n*-alkanes as expected (CPI 4.6 for C<sub>22</sub>-C<sub>33</sub>). These results strongly indicate that most of the PAH content of the detrital fraction (refer Section 4.2) can be attributed to incorporated BC particles.

#### 4.5 Implications for source apportionment

As mentioned in the introduction, pyrogenic or combustion sources, considered to be the major source of PAHs in urban runoff, are associated with very fine particulate, however, a number of studies (including this one) are reporting enrichment of pyrogenic PAHs in >125 µm particles. Therefore, if the major PAH source is fine combustion particles, what is the origin of the pyrogenic PAHs on >125 µm particles? A possible answer is perhaps post-depositional repartitioning, however, assuming combustion-derived PAHs are emitted pre-sorbed to a soot matrix, strong binding (Jonker and Koelmans, 2002; Bucheli and Gustafsson, 2000) means that pyrogenic PAHs are unlikely to undergo significant post-depositional change (McCready et al. 2000, and ref. therein). On this basis, post-depositional re-partitioning from fine combustion soot particles to larger particulates seems unlikely. Although interestingly, Ghosh et al. (2000) reported that the outer surface of sectioned BC particles from Milwaukee Harbour sediments had 100-fold higher levels of PAHs than interior regions, which is perhaps suggestive of post-depositional sorption.

Petroleum derived PAHs are considered less tightly bound to particulate matter, and reasonably susceptible to post depositional change (Readman et al. 1987, and ref therein), however repartitioning from these sources is inconsistent with the pyrogenic nature of PAHs in MC sediment. The mechanical nature of asphalt abrasion is conducive to

forming larger sized black particles that are observed in sediment (Faure et al., 2000; Wakeham et al., 1980). Hoffman et al. (1984) observed that urban runoff had a bimodal PAH distribution with maxima at 125-250 µm and <45 µm, and proposed that the smaller size fraction reflects atmospheric fallout particles (combustion), while larger particles were attributed to bitumen particles washed off roadways. Wakeham et al (1980) suggested bitumen was a major contributor of PAHs to urbanised lake sediments. Supporting evidence included the fact that PAH loadings in road dust from concrete roads were several times lower than road dust from similarly trafficked bitumen roads (Waibel et al., 1976). It is important to mention that the bitumen in the Waibel et al. study contained coal tar (binder consisted of 13% coal tar pitch and 87% bitumen), which contains up to 150000 µg/g of PAHs, compared to 10-24 µg/g for bitumen (Blackburn et al. undated). Therefore conclusions relating to the importance of asphalt abrasion to total sediment PAH loads are highly dependent on the presence of coal tar. Since not only does this result in 100-1000-fold higher PAH concentrations, but it also 'swamps' the petrogenic PAH signature of the bitumen. Blackburn et al. (undated report), reported that Danish asphalt roads laid between 1952 and 1970 contained up to 136-times more PAHs (up to 10340 µg/g, 16 EPA) than a 1991 sample.

Although we have no information relating to the prevalence or extent of coal tar in road construction, preliminary evidence suggests that coal tar inputs might be an important source of pyrogenic PAHs in certain urban-impacted sediments such as MC. The fact that MC BC particles contained at least 1000 µg/g, indicates that either a very contaminated source material is incorporated directly into the sediment, or, post-depositional enrichment of pyrogenic PAHs is occurring. If we assume the former, Table 3 indicates that, with the exception of coal tar, very few source materials contain the required levels of PAHs.

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