

# **Organic and Metal Contamination in Surface Mangrove Sediments of South China**

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Mangrove forests, the intertidal wetlands of the tropics and subtropics, are key ecological habitats that link terrestrial and marine environments. Mangrove forests and adjacent mudflats are increasingly impacted by urban/industrial development in the tropical coastal zone, suffering pollution from multiple sources including but not limited to municipal waste, aquaculture, mariculture and shipping as well as onshore industries and run-off from urban centres (Cuong et al. 2005; Huang et al. 2003; Zheng et al. 2000). Sediments that accumulate in mangroves are potential repositories of anthropogenic pollution because of high total organic carbon content, anaerobic properties and rapid turnover and burial (Marchand et al. 2005; Tam and Yao, 2002). The world wide denigration and loss of mangrove habitats is of global concern given they account for an estimated 11 % of the input of terrestrially-derived carbon into the ocean and about 10 % dissolved organic carbon (DOC) sourced from land; the long term effect of altering the carbon cycle is uncertain (Dittmar et al. 2006; Jennerjahn and Ittekkot, 2002). It has been widely postulated that mangroves afford physical protection against catastrophic storm events such as hurricanes and tsunamis (Alongi, 2007). Recent post-impact surveys along the Tamil Nadu coast following the 2004 Indian Ocean tsunami confirmed this notion and demonstrated that man-made structures built behind mangroves were significantly less damaged than their unprotected counterparts (Alongi, 2007).

Historically, mangrove swamps bounding the South China Sea have been exploited for a variety of economic purposes and in some instances entirely destroyed (Morton and Blackmore, 2001). In mainland China, mangrove forests once fringed the majority of the south coast, since 1940's rapid urbanization, agricultural development

in the form of rice farming and embankment for aquaculture ponds has resulted in the loss of 66% of mangrove forests (Li and Lee, 1997). Today, natural mangrove forests occur sporadically from 18 °N to 27°N latitude along the coasts of Hainan, Guangdong, Guangxi, Fujian and Taiwan provinces, covering an area of about 22,639 ha (Li and Lee, 1997). However, artificially introduced mangrove forests comprised of *Kandelia candel* were successfully transplanted in Zhejiang province at 28° 25' N in the 1950's. Overall a total of 36 true and semi mangrove plant species are distributed in China, 35 in Hainan, 19 Guangdong, 18 Guangxi, 17 in Taiwan, 11 in Hong Kong, nine in Fujian and five in Macau, and one introduced species in Zhejiang (Fan, 2004). Recent recognition of the importance of ecological, biogeochemical and hydrological functions of mangroves has led to 6 state and 17 local protected reserves being established (Fan, 2004).

Persistent organic pollutants (POPs) such as polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and total petroleum hydrocarbons (TPH) are of particular concern because of the effect these may have on fauna and flora of mangroves. Monitoring of organic pollutants can therefore alert coastal managers of possible impacts upon the detritus driven food web which can potentially lead to the bioaccumulation of contaminants in organisms which may ultimately be consumed by humans as food. Furthermore, organic pollutants at high concentrations can cause growth impairment of halophytic plants which in turn may limit buffering of storm events and stabilisation of coastal sediments (Mrozek et al. 1983; Tam et al. 2005).

Studies of organic pollution in mangrove sediments of China have primarily focused on sites in close proximity to heavily populated/urbanized industrial centres such as Hong Kong, Shenzhen and Guangzhou. Temporal monitoring of a major discharge of fuel oil onto Sheung Pak Nai Mangrove (Hong Kong) revealed a decrease in TPH concentrations from 60-80 µg/g to 30-40 µg/g after one year, the decline in TPH being attributed to weathering of the oil (Tam et al. 2005). However, the same study also reported TPH concentrations as high as 1000 µg/g in the root zones of mangrove sediments, suggesting that oil pollution from a single point source can lead to highly variable TPH values even in the same mangrove swamp. Sediment samples collected from mangrove forest and mudflats of Inner Deep Bay (Mai Po Wetlands) in Shenzhen in 1999 reported TPH concentrations ranging from 267 to 363 µg/g, confirming that concentrations were similar in both mangrove forest and mudflat sediment (Zheng et al. 2000).

Accumulation of PAHs in mangrove sediments of China has been previously observed. Sediment samples collected from mangrove forest and mudflats of Inner Deep Bay (Mai Po Wetlands) in Shenzhen in 1999 showed PAH concentrations of 180 to 830 µg/kg and 630 to 960 µg/kg respectively (Zheng et al. 2002). Comparison of total PAH concentrations along transects revealed a decline in values from the edge of mangrove forest to sea, where mudflat sediment cores (0-35 cm) showed little vertical change in PAH content (Zheng et al. 2002). The variation in PAH content along

transect was attributed to an increase in depositional flux of PAH into the sediment associated with loss of tidal current energy, in contrast the uniform down core PAH profiles were suggested to be caused by a high degree of sediment mixing (Zheng et al. 2002). Ascription of petrogenic/combustion PAH input using isomeric ratios revealed a mainly combustion related source derived from local anthropogenic pyrolytic sources. Another study of twelve surface sediments from Futian mangrove which lies approximately 2 km NE of the Mai Po and inner Deep Bay site reported PAH concentrations 237 to 726  $\mu\text{g}/\text{kg}$  (Zhang et al. 2004).

Polychlorinated biphenyls pose significant health risks to humans and are listed as one of the "dirty dozen" contaminants, their current production and use being restricted in countries that are signatories of the Stockholm convention (May 22, 2001). The contamination of ten mangrove sites by PCBs in Hong Kong showed relatively low total concentrations ranging from 0.5-5.8  $\mu\text{g}/\text{kg}$  with the exception of mangroves from Yi O, Tolo Pond and Lai Chi Wo which were identified as hot spots and gave PCB concentrations in the range of 11 to 25  $\mu\text{g}/\text{kg}$  (Tam and Yao, 2002). Similar concentrations of PCBs (4.9 to 27.6  $\mu\text{g}/\text{kg}$ ) were reported from mangrove sediments at Mai Po marshes nature reserve in Hong Kong (Zheng et al. 2000).

In the light that only a small proportion of mangroves in China have been examined for POPs we undertook a screening survey of mangrove surface sediments from mainland sites in the southwest (Beihai, Zhanjian) south (Shenzhen) and south eastern coast (Xiamen) as well as Hainan Island. The primary aim of this study was to determine individual concentrations of PAHs, PCBs and saturate and aromatic hydrocarbons as well as trace metals. The focus of the study was to determine concentrations of organic and metal pollution in mangrove sediments from developed and less developed coastal sites, along with evaluating potential sources of accumulating pollutants.

Mangrove sediments were collected from October to November 2006 using pre-determined GPS co-ordinates to accurately locate each position (Fig. 1). Polycarbonate tubes, fitted with stainless steel basket core catcher at the base were manually driven into the exposed sediment and extracted to recover the core material. At each mangrove swamp, five sediment cores within an approximately 100  $\text{m}^2$  area were collected from depths of 0-30 cm. Sediments were then transported back to the laboratory at  $\sim 0^\circ\text{C}$  where each of the five batches of samples were mixed in equal proportion in order to minimize the influence of highly localized hot-spots and stored at  $-70^\circ\text{C}$ . The samples were freeze-dried, sieved to pass a brass mesh of aperture 2 mm and a portion of the  $<2$  mm fractions analysed for PAH. The remainder was ground to a fine powder using a Retsch PM400 ball mill and analysed for TOC, TPH and PCB content. Thus each of the nine samples represents a composite of five surface sediments. The principal advantage of this approach being that a more representative "background" sample is captured.

All concentrations herein are reported on a dry weight basis. Silver-foil cups containing 100-1000 mg dried mangrove sediment were treated with excess acid (HCl, 50% v/v) to remove inorganic carbon and then oven dried at 100°C ±5°C for 1.5 h. Total Organic Carbon (TOC) was determined using a Elementar VarioMax C, N analyser controlled using 'VarioMax' software. The limits of quantification reported for a typical 300mg sample were 0.18%.

For each TPH preparation dried sediments (~2 g) were extracted with dichloromethane (DCM) / acetone (1:1 v/v) mixture using a ASE 200 (Dionex) system operated at 175°C, pressure 2000 psi, heat-up time 1 min, static time 8 minutes, flush volume 120%, purge time 60 s, total solvent used 37-44 mL per sample. The resulting solvent extract was rotary evaporated to 5 mL, quantitatively transferred to a glass vial (10mL), reduced to dryness using a stream of nitrogen gas and stored in darkness at 4°C. Prior to analysis each sample was dissolved in 1 mL toluene. A 5 µL aliquot was spotted on to silica rod (Chromarods-S III) using a programmed auto-spotter fitted with a 10 µL syringe. The rods were developed for 21 min using 100 mL n-hexane and then for 8 min with toluene 100 mL. The concentration of saturated and aromatic hydrocarbons was determined using by an Iatroscan Mk6s instrument fitted with a flame ionization detector (FID) and operated using Chrom Star software. Using the standard method for substitution of non-detects *i.e.* 0.5 x LOD all TPH concentrations below LOD (Limit of Detection 3 mg/kg) were assessed as contributing 1.5 mg/kg (Helsel, 2006).

For each total mercury (THg) preparation 0.5 g sediment was transferred to a 50 mL graduated glass stoppered boiling tube and 5 mL deionised water and 5 mL of aqua regia added. The combined solutions were left connected to an air condenser overnight at room temperature then subsequently heated to boiling point and maintained at that temperature for a minimum of 2 h. Once cooled to room temperature the solution was diluted to 50mL with deionised water and shaken to mix. After settling a 5 mL aliquot was removed by pipette and diluted with × 5 (4+1 v/v) using deionised water to give a 2% solution with respect to HCl. The samples were analysed using a PSA atomic fluorescence spectrometer system comprising a XYZ Autosampler and a Millennium Merlin operated with an Ar flow rate of 30-50 psi and detector set at 253.7 nm. The limit of detection for this set of analyses was 0.04 mg/kg. Quality control was achieved by subjecting two certified reference materials to the above procedure.

For the other trace metals pressed powder pellets were prepared by grinding 12.00 g of sample and 3.00 g of binder in an agate planetary ball mill for 30 minutes. The mixture was then pressed at 25 tons load into 40 mm diameter pellets. The binder used is a mixture of 9 parts EMU120FD, a styrene copolymer, and 1 part Ceridust 3620, a micronised polyethylene wax. The XRFS Spectrometer used for major elements was an Axios Advanced with a 60 kV generator and 4 kW rhodium (Super Sharp Max) end-window X-ray tube controlled via PC running PANalytical SuperQ XRF Pro-Trace application package. For trace element analysis, a set of

synthetic standards (Pro-Trace) was used to calibrate the instruments and to determine background and spectral interference correction factors. The PANalytical Pro-Trace calibration algorithm is used to fit calibration lines, applying matrix correction using mass attenuation coefficients. The calibrations were validated by analysis of a wide range of Reference Materials. Quality Control was maintained by regular analysis of two glass monitor samples containing 47 elements at nominally 30 µg/g and 300 µg/g and the results entered into run charts for statistical analysis using a SPC package. Lower limits of detection (LLD) are theoretical values for the concentration equivalent to three standard deviations (99.7% confidence interval) above the background count rate for the analyte in an iron-rich alumino-silicate matrix.

PAH analysis was based on a previously published HPLC method employed for the determination of PAHs in estuarine sediments (Vane et al. 2007a; Vane et al. 2007b). For the PAH extraction of each sample, approximately 15g was weighed into a pre-cleaned 50 mL amber bottle. To this was added 25 mL of a 1:1 v/v mix of acetonitrile and tetrahydrofuran (THF), both of HPLC grade. The bottle was sealed with a screw-cap closure containing a PTFE-faced silicone rubber septum. After sealing the bottle was shaken to suspend the contents, which, were then sonicated in a heated ultrasonic bath (Camlab, 300W) for 45 minutes at 50°C. During this period the bottle was occasionally inverted and shaken to continually re-suspend the sample. The bottle was then stored in the dark for about 2 hours, to permit some clarification of the supernatant, before taking a 2 mL aliquot in a gas-tight glass syringe, attaching a 0.2 µm in-line syringe filter (25 mm dia. - Nylon 66), and filtering the extract into an amber 4 mL vial (with PTFE-faced screw cap closure) having first discarded the first few drops of filtrate. The clarified extracts were stored in a refrigerator to await analysis which took place as soon as possible after extraction.

Quality control was achieved by subjecting a well-characterised, low-level PAH proficiency-testing marine sediment (Quasimeme – QPH048MS) to the above procedure (except that a weighed 2.5 g was used) and analysing it by the same method as for the samples. A procedural blank prepared from 15g white quartz sand (Sigma Aldrich, UK) – a material devoid of PAH - was treated in a similar fashion.

Filtered sample extracts (including those of the QCs and the procedural blanks) were injected into the HPLC system (Waters 600E) *via* a 5 µL sample loop (Rheodyne). The eluent flowrate through the separation column (Lichrospher®PAH 250 mm x 4.0 mm i.d.) was 0.7 mL/min. The column was surrounded by a column heater/chiller (Grace/Vydac 7995R) to maintain it at a constant 25.0°C ± 0.1°C. Separation of 17 PAHs was achieved within 45 mins by gradient programming the eluent. Far-UV HPLC grade acetonitrile (Rathburn Ltd.) and HPLC grade water (Milli-Q) were pumped as a 65% : 35% mix, respectively, at the start of each chromatographic run. Immediately thereafter, up to 14 minutes, the proportion of acetonitrile was continuously increased from 65% to 100% using a concave gradient (Waters curve 9).

From 14 minutes until the end of the run (45 mins.) elution with 100% acetonitrile was maintained.

As the PAHs exited the column they were directed into a scanning fluorescence detector (Waters 474). The detector was programmed so that optimized excitation and emission wavelengths for the PAHs were selected based on their retention times. The following 17 PAHs were included in this study: acenaphthene, anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*k*]fluoranthene, chrysene, dibenz[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*c,d*]pyrene, 1-methylnaphthalene, naphthalene, perylene, phenanthrene, pyrene.

The method used to extract and determine PCB concentrations, was based on that described by Ayris et al. 1997. Briefly, sediments were spiked with authentic standards, mixed with an equal amount of anhydrous sodium sulphate and extracted with hexane/acetone (1:1 v/v) in an accelerated solvent extraction system ASE 200 (Dionex). Extracts were eluted through a Pasteur pipette containing anhydrous sodium sulphate (1g) and Florisil with 10 mL of *n*-hexane. The eluant was extracted with dimethylsulphoxide (DMSO, 2 × 12 mL) and diluted with 18 MΩ de-ionised water (25 mL) prior to extraction with *n*-hexane (50 mL). The *n*-hexane extracts were combined and the volume reduced to 5 mL and passed through anhydrous sodium sulphate (1g) and the volume reduced to approximately 100 μL using a gentle stream of nitrogen gas.

Combined gas chromatography-mass spectrometry (GC-MS) was performed on a Carlo Erba Mega 500 series gas chromatograph (GC) directly coupled to a Varian 1200L triple quadrupole mass spectrometer operating in full scan mode (ionization energy 70 eV, mass range 39-550 amu). Sample application (1 μL) was by split/splitless injection; the GC was fitted with a fused silica ZB-5 column (60 m length x 0.32 mm i.d. x 0.25 μm film thickness). The GC oven was temperature-programmed from 100°C (1 min. isothermal) to 200°C (at 5°C / min.) to 280°C (at 2.4°C / min.) to 320°C (at 20°C / min.) and held isothermally at 320°C for 5 min and helium was used as carrier gas at 16 p.s.i. The limit of detection (LOD) based on the minimum concentrations that gave clearly defined peaks was between 0.1-0.20 μg/kg. Quality control was achieved by subjecting a PCB certified reference material (LGC 6113 – Soil) to the above procedure and analysing it by the same method as for the samples. A procedural blank prepared from white quartz sand (Sigma Aldrich, UK) – a material devoid of PCBs - was treated in a similar fashion.

The saturated hydrocarbon concentrations of sediments from selected mangroves ranged from 32-533 mg/kg and the aromatic hydrocarbon concentrations ranged from <3 to 37 mg/kg (Table 1). Total petroleum hydrocarbons (TPH) ranged from 32-570 mg/kg (Table 1). Sediments from Shenzhen (6) exhibited higher TPH concentrations at 570 mg/kg than other mangrove sites reflecting a possible localized urban pollutant

discharge source, hydrocarbons from vehicle exhausts or combustion products from factories. In contrast the TPH concentrations in Hainan Island mangrove sediments, namely stations 2, 7, 8 and 9 had a mean of 51 mg/kg, confirming low levels of hydrocarbons. This was not unexpected given that much of Hainan Island has a lower proportion of urban/industrial land use than other mainland coastal cities such as Shenzhen. Unpolluted sediments have been shown to contain up to 100 mg/kg of hydrocarbons derived from biological inputs such as algae and plant waxes, whereas heavily contaminated estuarine and coastal sediments yield approximately 1000 mg/kg hydrocarbons or more (Volkman et al. 1992; Volkman and Nichols, 1991). Using this benchmark, it is clear that only the sediment from Shenzhen (6) is polluted with petroleum hydrocarbons. However, there are no widely recognised toxicological benchmarks for the evaluation of TPH in marine sediments.

Previous studies of total petroleum hydrocarbon pollutants in Chinese mangroves and near-shore sediments reported concentrations in the range of 6-1996 mg/kg with the highest values observed in Victoria Harbour, Hong Kong and the lowest at Shek O Beach (Zheng and Richardson, 1999). With the exception of Shenzhen (6) the values reported in the current study fall at the lower end of TPH concentrations observed in mangrove sediments from China and are broadly comparable to those from Sheung Pak Nai Mangroves, Hong Kong but lower than Mai Po Mangroves, Hong Kong (Table 2) (Tam et al. 2005; Zheng et al. 2000).

The elemental composition of mangrove sediments are presented in Table 3. Concentrations of Hg in surface sediments from S. China mangroves ranged from <0.04 to 0.17 mg/kg (dry wt) (Table 3). Similarly Hg values of about 0.020 to 0.127 mg/kg have been reported in the South China Sea off the Malaysian coast (Kannan and Falandysz, 1998). World wide, marine, coastal and estuarine sediments have Hg background levels of approximately 0.02-0.1 mg/kg (Kannan and Falandysz, 1998; Shi et al. 2007), on this basis seven of the samples had Hg concentrations close to background and two sediments had concentrations just above that expected from a coastal sediments with little or no anthropogenic Hg input. In this current study of mangrove sediments, sites in close proximity to Shenzhen (6) and Xiamen (5) had the highest Hg values whereas those from Wengchang (1) and Haikou (2, 7, 8, 9), Hainan Island were three to four times lower (<0.04-0.06 mg/kg) (Table 2). One plausible explanation for this difference maybe due to the greater discharge of Hg from the major urban/industrial centers of Shenzhen (6) and Xiamen (5) as compared to the other less urbanized mangrove sites, alternatively the elevated concentrations maybe due to an unidentified local point sources.

Comparison of these sediment Hg concentrations from S. China mangroves (<0.04 to 0.17 mg/kg) indicated that they were less less contaminated than other coastal/estuarine areas: Seine estuary, France (0.46 mg/kg) San Francisco Bay, USA (0.2 mg/kg), Victoria Harbour Hong Kong (0.247 mg/kg), Gdansk, Poland (0.32 mg/kg) or the Anadyr estuary, Russia (339 mg/kg) (Kannan and Falandysz, 1998; Shi

et al. 2007).

The significance of the As, Cr, Cu, Pb, Ni and Zn concentrations were evaluated by comparison with threshold effect concentrations (TEC) and probable effect concentrations (PEC) for metals which provide a benchmark above and below which adverse effects on sensitive sediment dwelling organisms maybe observed in the field (Table 3) (MacDonald et al. 2000; Long et al. 1995). For the Beihai (3) mangrove, all elements were less than published TEC and PEC, indicating that they were toxicologically unimportant. In contrast, for Hainan mangroves (1,2,7,8,9) sediment Cr and Ni ranged from 109 to 437  $\mu\text{g/g}$  and 50 to 159  $\mu\text{g/g}$  (Table 3), respectively, exceeding their PEC benchmarks (MacDonald et al. 2000). Previous surveys of heavy metals in sediment cores from Mersey Estuary, UK have shown that grain-size can greatly alter the contaminant profile due to complexation and sorption of metals with clays and that normalization to Ga, a proxy for grain-size is required in sediments of variable composition (Ridgway et al. 2003; Ridgway and Shimmield, 2002). In this current study, non-normalized and Ga-normalised Cr and Ni concentrations were similar suggesting that these metals may adversely affect sediment dwelling biota. Although Cr and Ni values for four of the Hainan mangroves were above PEC this does not necessarily indicate an anthropogenic source since these could be of geogenic origin (natural background); this notion was confirmed in part upon comparison of Fe element with Cr and Ni (Table 3). However unequivocal identification of metals from anthropogenic and natural sources in estuaries and coastal zones is complex and requires assessment of sediment samples from uncontaminated rivers, catchment area and downstream of contaminant sources (Ridgway et al. 2003).

Overall As, Cu, Pb, and Zn concentrations were relatively low and either below or between TEC and PEC values for all mangrove sites (Table 3). Other studies have noted that mangrove roots contain Cu, Pb, Zn in about equal concentrations as the surrounding sediment where as those in leaf tissues were at most about half that of the roots (MacFarlane et al. 2007). From a sediment quality guideline standpoint (TEC and PEC) the Hg concentrations encountered at Shenzhen (0.17 mg/kg) and Xiamen (0.12mg/kg) are below the 0.18 mg/kg threshold effect concentration (TEC) for THg in freshwater sediments (MacDonald et al. 2000). Studies performed on marine and estuarine sediments using various indicator species have reported that Hg concentrations below 0.15 mg/kg have minimal effect on certain sediment dwelling animals and plants, where as for concentrations between 0.15 and 0.71 mg/kg effects are possible and at or above 0.71 mg/kg the effects are probable (Long et al. 1995). Comparison of the Hg mangrove sediment concentrations to soil quality benchmark criteria suggested that sediments from these S. China mangrove sites (1, 2, 3, 4, 7, 8, 9) are below concentrations predicted to harm the biota, where as those from Xiamen (5) and Shenzhen (6) maybe threatened with adverse effects from Hg exposure. Overall the Hg concentrations were below that expected to pose a major detrimental threat to benthic organisms.



In addition to PAH sediment analyses a three QCs, three procedural blanks and nine duplicate sample determinations were conducted at regular intervals. The results of the QC analysis, together with information on wavelength programming, are presented in Table 4. The limits of quantification (LoQ) are shown in Table 5, and were determined from the analysis of the procedural blanks, (*i.e.* the areas of peaks in the blanks with the same retention times as a given PAH were averaged and three times the standard deviation was added to that average to give the LoQ of that PAH). Certified reference material analyses were within certified values (Table 4).

Total (*i.e.*  $\Sigma 17$  PAHs) and individual PAH concentrations are displayed in Table 5. It will be observed that the totals ranged from 24  $\mu\text{g}/\text{kg}$  to 238  $\mu\text{g}/\text{kg}$ . In some cases (Samples 1, 2, 4 & 9) it was not possible to quantify the pyrene content of the samples because of the extensive overlap, during HPLC analysis, of a large peak of an unknown material with a retention time very close to that of pyrene. For these samples, therefore, the total PAH concentrations are  $\Sigma 16$  PAHs. It can be seen that the total PAH concentrations revealed by this study are low compared with those obtained from similar investigations of surface sediments from mangrove communities (Tables 6 & 7). Nevertheless, they are substantially higher than the total of 7.25  $\mu\text{g}/\text{kg}$  determined for the coastal sediment from a pristine site at Kat O Wharf, Hong Kong (Zheng & Richardson, 1999). A study of the available literature, typically reveals large variations in total PAH concentrations even for surficial mangrove sediment samples taken from the same locations (Table 6), *e.g.* Ho Chung: 189-329  $\mu\text{g}/\text{kg}$  (Guo et al. 2005) *cf.* 1273-11098  $\mu\text{g}/\text{kg}$  (Tam et al. 2001) and similarly for Mai Po: 212-1042  $\mu\text{g}/\text{kg}$  (Zheng et al. 2000) *cf.* 1007-4842  $\mu\text{g}/\text{kg}$  (Tam et al. 2002).

The samples in this study emanated from widely geographically separated sources along the coasts of S. China. Any commonality displayed in their PAH distribution patterns may therefore be presumed to result from either their being collected from sites specifically within mangrove systems, or from their exposure to ubiquitous influences that globally affect surficial sediments, *e.g.* deposition of pyrolytic PAHs that have undergone aeolian transport (Jaward et al. 2004).

All, to a greater or lesser extent, possess significant concentrations of those PAHs taken to characterise pyrolytic sources. Thus, all contain measurable quantities of pyrolytic-originating PAHs: fluoranthene, pyrene, chrysene, benzo[*b+k*]fluoranthenes, benzo[*a*]pyrene, benzo[*g,h,i*]perylene, benz[*a*]anthracene and indeno[*1,2,3-c,d*]pyrene (Table 5). Even in those cases where the quantification of pyrene was confounded by the presence of an unknown interfering material its presence was still discernible in the form of a distortion to the unknown's chromatographic peak shape. These nine, together with phenanthrene - which also can arise from combustion processes (Budzinski et al. 1997) - were, of course, found at comparatively low concentrations in those samples where the total concentrations of PAH were low and as such may probably be attributed, in the main, to the global background atmospheric deposition

of pyrolytic emissions.

However, in the two samples with the highest total concentrations of PAH, *i.e.* samples Xiamen (5) and Shenzhen (6), elevated concentrations of the nine characteristic pyrolytic PAHs were encountered. This would seem to argue some localized input of pyrolytic PAH in these samples, probably from the proximity of the large cities of Xiamen and Shenzhen, whereas, for the other samples the presence of pyrolytic PAHs likely stems from the global aeolian deposition attending long-range atmospheric transport processes. A hierarchical cluster analysis of PAH composition patterns, based on the squared Euclidean distance metric and Ward's minimum variance algorithm (Ward, 1963), produced a dendrogram, shown in Fig. 2, that provided supporting evidence for the similarity of the samples from Xiamen and Shenzhen and their difference from the other samples.

Another indication that the Xiamen/Shenzhen samples differed from other samples was emphasised by the construction of a plot of total PAH concentrations against TOC% (Fig. 3, Table 6). A strong correlation between PAH and TOC ( $r^2 = 0.97$ ) was found to exist for all samples other than those from Xiamen and Shenzhen. When these latter were included the overall correlation was much weaker ( $r^2 = 0.11$ ). The strong correlation should not necessarily be taken to imply a causal relationship but it would seem that TOC has a controlling influence on PAH sorption to sediments with low total PAH concentrations. For the samples from Xiamen and Shenzhen, where PAH concentrations were higher than for the other mangrove samples, the likely contamination of the sediments by local PAH sources could be the reason for their non-correlation. Such interference of localized inputs of PAH pollution with a linear relationship between total PAHs and TOC has previously been invoked to explain the behaviour of mangrove sediments in the Hong Kong region (Ke et al. 2005).

Isomeric ratio cross plots were constructed based on the relative concentrations of isomeric pairs of PAHs whose ratios have been identified as diagnostic of PAH source (Yunker et al. 2002). Traditionally, the ratio between the concentration of fluoranthene and that of fluoranthene and pyrene summed is plotted as the abscissa of such cross plots. However, since a full set of pyrene data were unavailable (because of peak interference problems) our cross plots were performed employing the ratio between the concentration of anthracene and that of anthracene and phenanthrene summed as the abscissa (see Fig. 4). Two cross plots were established; the first using the ratio of the concentration of benz[*a*]anthracene to that of benz[*a*]anthracene and chrysene summed as the ordinate, and the second the ratio of the concentration of indeno[1,2,3-*c,d*]pyrene to that of indeno[1,2,3-*c,d*]pyrene and benzo[*g,h,i*]perylene summed as the ordinate. Again the similarity between samples Xiamen (5) and Shenzhen (6) and their difference from the other samples is highlighted, as is the predominance of combustion-related PAH sources for the Xiamen/Shenzhen samples.

The prominence of phenanthrene, perylene and naphthalene in all the samples is noticeable, and is pronounced in four of the samples (Stations 1, 2, 4 & 9) where these three PAHs predominate. The relative abundances of phenanthrene, perylene and naphthalene are indicated (as bold numerals) on the column charts employed to show the distribution patterns of the PAHs in the samples (Fig. 5). For all the samples at least one of the three is the dominant PAH. Thus, for five of the samples (Stations 3, 4, 7, 8 & 9) phenanthrene predominates and for four (Stations 1, 2, 5 & 6) perylene is the most abundant PAH. These results are interesting, particularly in light of a recent publication concerning the global patterns of PAHs in soils (Wilcke, 2007), where the author has suggested that PAH patterns in soils result from the combination of two main distinctive inputs, *i.e.* the first being a background pattern of biogenically-generated PAHs, dominated by naphthalene, phenanthrene and perylene which also includes the global background aeolian deposition, upon which is superimposed a second anthropogenic pattern consisting in the main of the high molecular weight pyrolytic PAHs. Our sediments appear to conform to, and support, the hypothesis of Wilcke. Because the anthropogenic loading for our samples, though significant, is low, the presence of the biological and diffuse source patterns associated with the biogenic/aeolian background become enhanced and, therefore, easily discerned. It also explains the notable instances of predominance of phenanthrene for our samples, compared with its frequent non-dominance in other mangrove sediments, as exhibited in the relative abundance order of the USEPA PAHs (Table 6).

There is also the possibility that the marked naphthalene and phenanthrene concentrations in some of the samples (Stations 1, 2, 4, 8 & 9) could betoken a petrogenic contribution to the PAH patterns arising, from unburnt petroleum (Aislabie et al. 1999), *e.g.* by oil spills and leakage from boats and ships. The presence of naphthalene in Hong Kong mangrove sediments at 10-20% of the total PAH concentrations was presumed to stem mainly from anthropogenic activities, especially petrogenic inputs (Tam et al. 2001). When the ratio of the concentration of naphthalene to that of phenanthrene is greater than one then fresh and unweathered petroleum is indicated (Dahle et al. 2003; Olajire et al. 2005). Inspection of Table 6 reveals that only one of our samples satisfied this condition, *i.e.* Haikou (2). However, militating against a primarily petrogenic origin for naphthalene, in those samples where its concentrations are pronounced (Stations 1, 2, 4, 8 & 9), are the comparatively low accompanying concentrations of 1-methylnaphthalene and acenaphthene. It might reasonably be expected that these would be comparable for either a weathered, or an unweathered, major petroleum contribution (Farias et al. 2008; Wang et al. 1999; Wang et al. 2004). It is also pertinent to note that in a study of the Mai Po marshes nature reserve, the naphthalene content of the mangrove sediments was high in contrast to the mudflat samples where naphthalene was largely undetectable (Zheng et al. 2000). This situation could conceivably arise from the much greater biological activity of the mangrove *cf.* mudflat environment (Marchand et al. 2005), with accordingly the possibility of naphthalene biogenesis in the former

(Wilcke, 2007; Krauss et al. 2005).

Inspection of Table 6 reveals that perylene formed between 11.2% and 20.8% of the total PAH concentrations, (except for the Behai (2) sediment where this was only 2.0%). Although there may well be a pyrolytic contribution to the perylene content, its relatively high concentrations in the majority of our sediments points to its having a primarily biogenic provenance (Venkatesan, 1988). Investigations of biomass and diesel burning reveal perylene to be a comparatively minor component of the total PAHs released by the combustion process, *e.g.* for a variety of cereals the maximum emission was 4.6% during corn burning (Jenkins et al. 1996); 2.4% was found in diesel soot (Wang et al. 1999) and 0.01-0.02% in unburned diesel (Wang et al. 1999; Mi et al. 2000). Accordingly, in a recent study, whenever perylene occurred at >10% of the total concentration of parent PAHs ( $\Sigma 17$  PAHs) its origin was attributed principally to biogenesis (Bicego et al. 2006). On this basis all our sediments, except for Behai (2), may be considered to possess a substantial biogenic component.

Total PAH threshold effect concentration levels (TEC) and probable effect concentration levels (PEC) in freshwater sediments are reported as 1610  $\mu\text{g}/\text{kg}$  and 22,800  $\mu\text{g}/\text{kg}$  respectively (Ingersoll et al. 2000; MacDonald et al. 2000). All of the sediments in this current work were below the TEC concentration, indicating that the PAH content was not toxic to organisms living in the sediment.

Total PCB concentrations ranged from 2 to 6  $\mu\text{g}/\text{kg}$  with a mean concentration of 4  $\mu\text{g}/\text{kg}$  (Fig. 6). The low values encountered in the surface sediments support the notion that the mangrove sites had not received any appreciable PCB contamination. Similarly moderate PCB concentrations (0.5-5.8  $\mu\text{g}/\text{kg}$ ) have been reported for Hong Kong mangrove sediments with the exception of mangroves from Yi O, Tolo Pond and Lai Chi Wo which were identified as hot spots and gave values in the range of 11 to 25  $\mu\text{g}/\text{kg}$  (Tam and Yao, 2002) and concentrations of PCBs (4.9 to 27.6  $\mu\text{g}/\text{kg}$ ) were reported from mangrove sediments at Mai Po marshes nature reserve in Hong Kong (Zheng et al. 2000). However a more recent spatial assessment of PCB pollution in China ( $n = 31$ ) showed that waters from the Mingjiang estuary contained 985  $\mu\text{g}/\text{kg}$  and that sediments in the Pearl River had PCB concentrations as high as 83  $\mu\text{g}/\text{kg}$  (Xing et al. 2005). Overall the concentrations of PCBs observed in this current work are very low and according to published TEC values do not represent a risk to sediment dwelling organisms (Ingersoll et al. 2000; MacDonald et al. 2000).

There are few studies of organic pollutants in mangrove sediments of Southern China and there is a particular paucity of contaminant survey information from the Island of Hainan. In combination the TPH (32,000 to 570,000  $\mu\text{g}/\text{kg}$ ), PAH (24  $\mu\text{g}/\text{kg}$  to 238), PCB (2 to 6  $\mu\text{g}/\text{kg}$ ) as well as Hg (<0.04 to 0.17 to  $\text{mg}/\text{kg}$ ) in the surface sediments from nine mangrove swamps indicate low pollution levels. The highest pollutant loadings were detected from sites in Shenzhen and Xiamen confirming the hypothesis that mangroves in close proximity to urban/industrial centers receive greater hydrocarbon sourced pollution inputs than those adjacent to

rural/non-urbanized areas such as those on the Island of Hainan. Isomeric cross plots of diagnostic ratios for PAH confirmed this relationship and suggested combustion-related PAH sources for the Xiamen and Shenzhen mangroves.

None of the sediments analysed in this study exceeded published threshold effects concentration levels, suggesting that they would not harm sensitive biota or humans; although the possibility that certain lipophilic pollutants could accumulate via biomagnification at higher trophic levels cannot be entirely discounted. The low amounts of anthropogenic organic pollutants from Haikou, Wengchang, Beihia and Zhanjiang mangroves exposed what is most likely the combined natural biogenic and aeolian transported background pollution as evidenced by elevated abundances of phenanthrene, perylene and naphthalene relative to other other PAH compounds. This observation supports recently developed theories on the source and alteration of PAH in terrestrial soils from tropical and subtropical zones.

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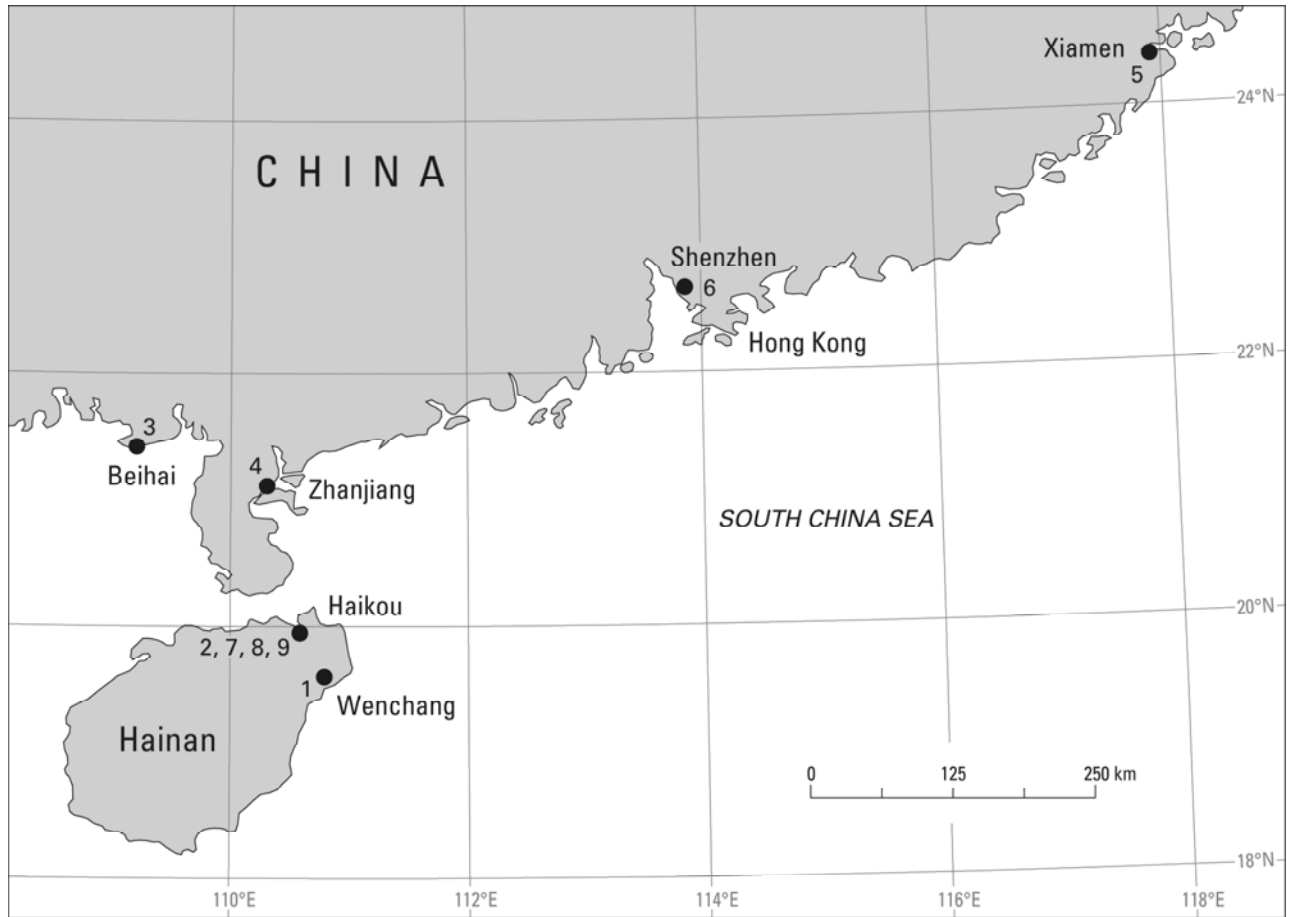
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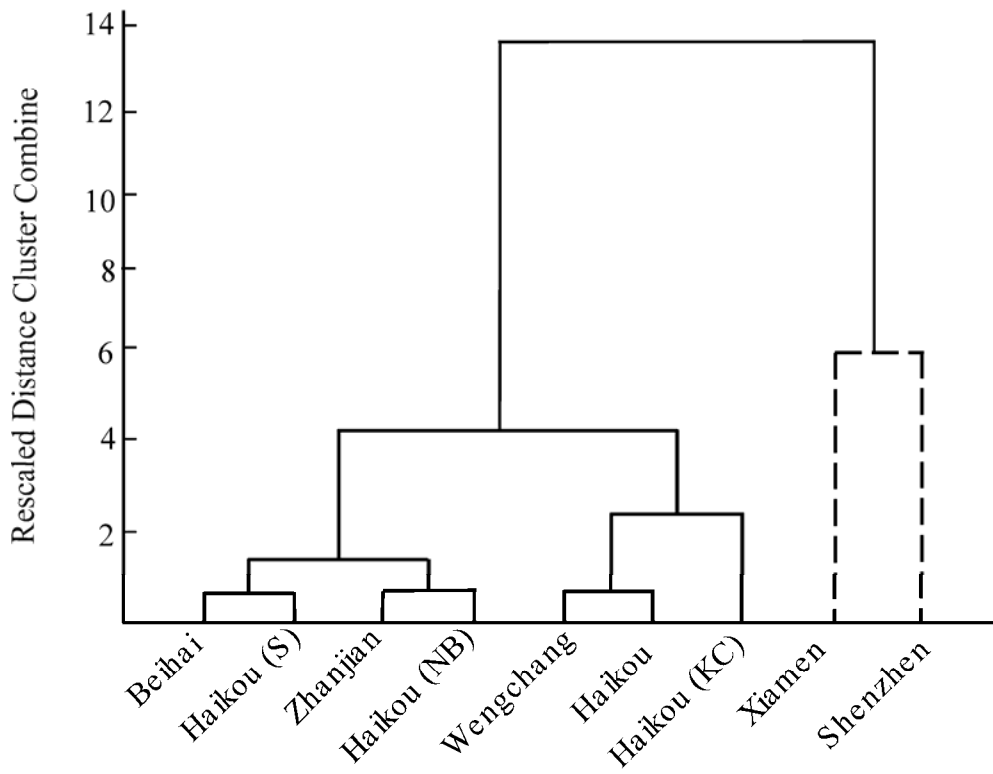
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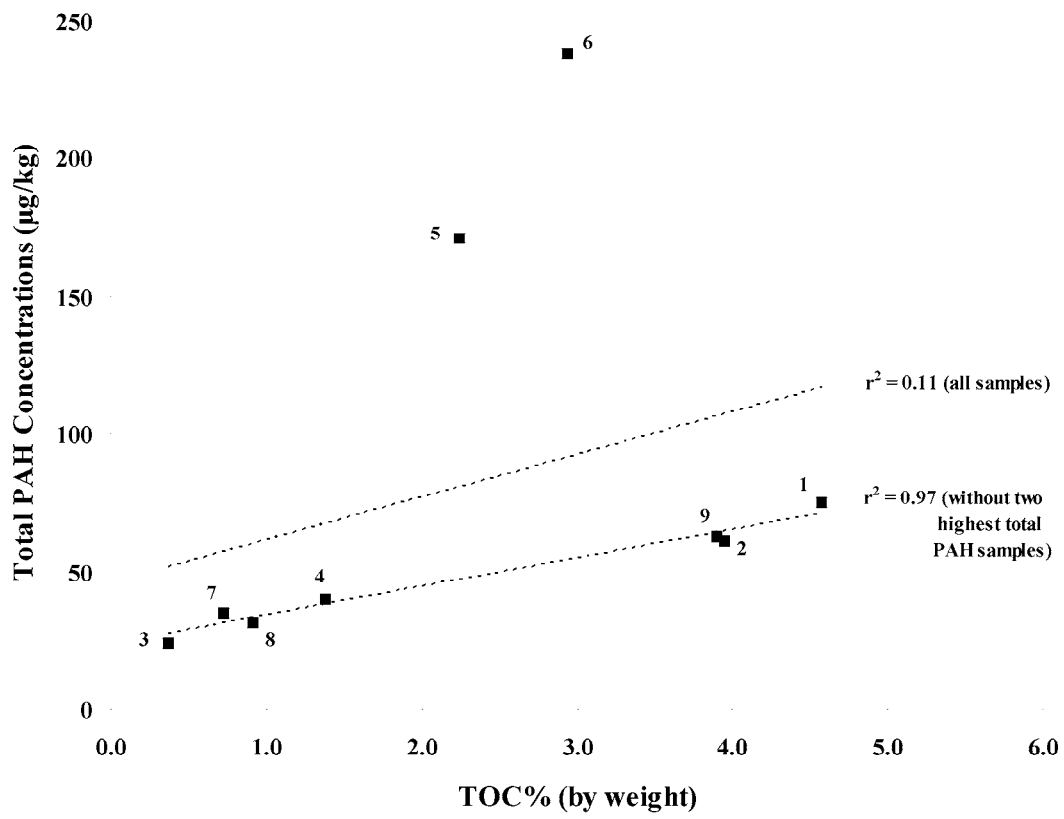
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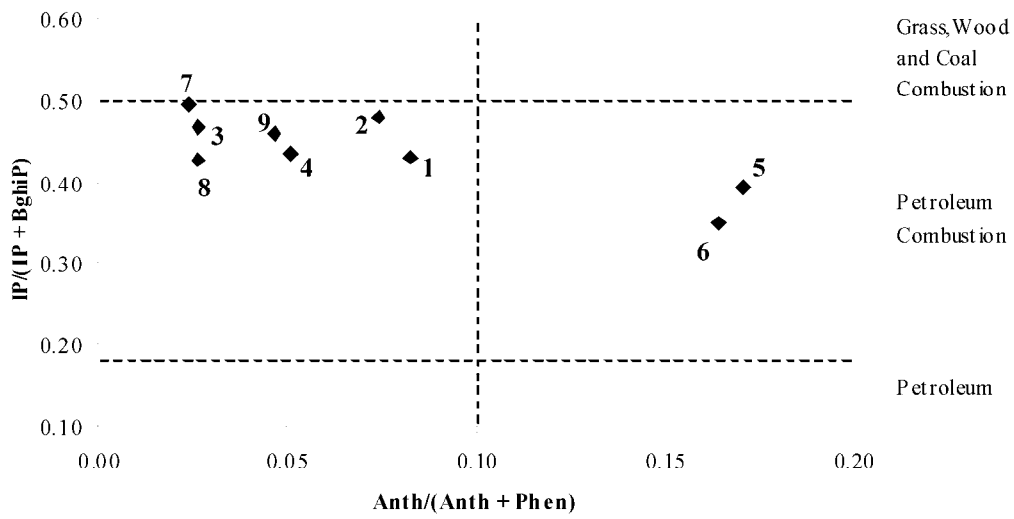
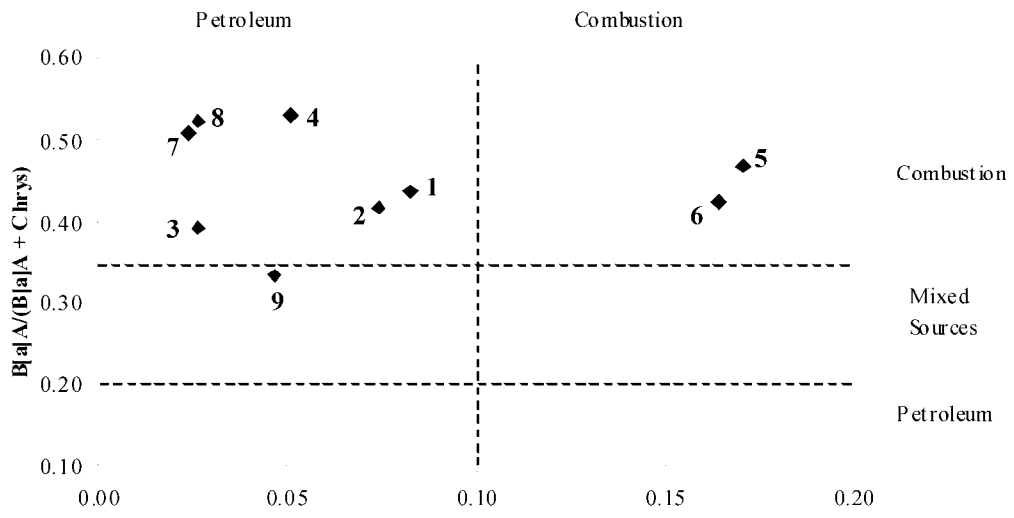
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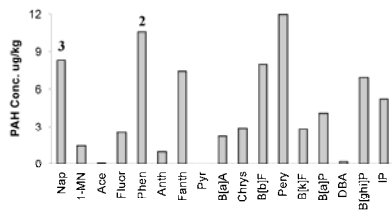




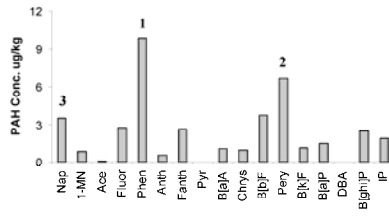




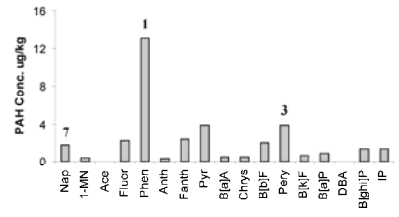
1. Wenchang ( $\Sigma 16\text{PAHs } 75 \mu\text{g/kg}$ )



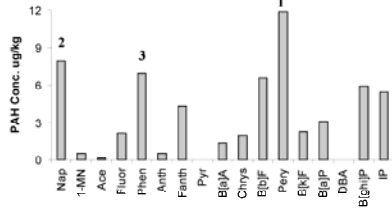
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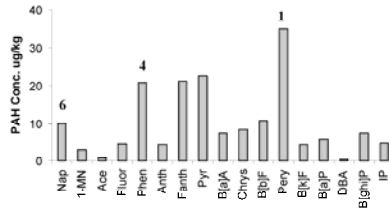
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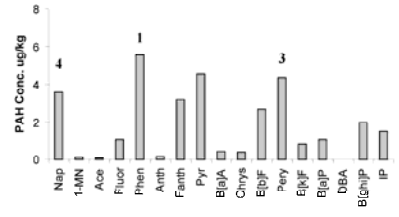
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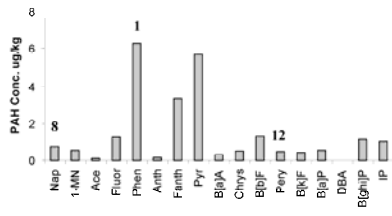
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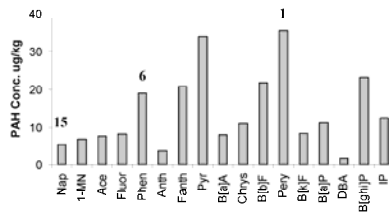
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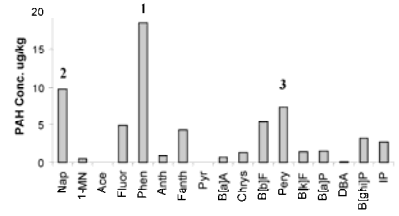
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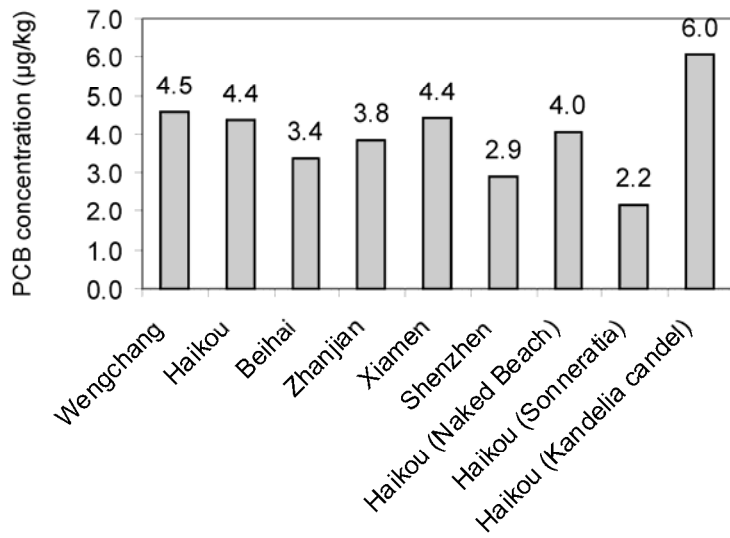
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I.D.	Location	Saturate HCs (mg/kg)	Aromatic HCs (mg/kg)	Total Hydrocarbons (mg/kg)
1	Wenchang	65	28	93
2	Haikou	70	13	83
3	Beihai	58	ND	58
4	Zhanjian	32	ND	32
5	Xiamen	74	13	87
6	Shenzhen	533	37	570
7	Haikou (nakedbeach)	37	ND	37
8	Haikou ( <i>Sonneratia</i> )	38	ND	38
9	Haikou ( <i>Kandelia candel</i> )	47	ND	47

ND = not detected, beneath limit of quantification 3 mg/kg; Aromatic hydrocarbons detected at concentrations beneath the sample quantitation limit (SQL) were given a zero value to avoid artificially elevating concentrations. TPH = Sum of aromatic and saturate hydrocarbons.

Location	Range (mg/kg)	Reference
Xiamen Harbour, Fujian	133-943	Ou <i>et al.</i> , 2004
Pearl River Estuary, Guangdong	14-146	Fung <i>et al.</i> , 2005
Hong Kong, Coastline	6-1996	Zheng and Richardson, 1999
Mai Po Mangroves , Hong Kong	267-363	Zheng <i>et al.</i> , 2000
Sheung Pak Nai Mangroves, Hong Kong	60-80	Tam <i>et al.</i> , 2005

ID.	Location	As	Cr	Cu	Pb	Hg	Ni	ZnFe <sub>2</sub> O <sub>3</sub> %
1	Wenchang	15	109	27	30	0.06	50	89 6.82
2	Haikou	13	122	27	33	0.06	54	92 7.07
3	Beihai	<3	9	3	7	<0.04	<3	9 0.55
4	Zhanjian	16	68	19	36	0.04	27	69 4.84
5	Xiamen	14	56	37	95	0.12	26	194 6.17
6	Shenzhen	15	81	93	77	0.17	45	252 6.11
7	Haikou (nakedbeach)	9	437	53	16	0.05	159	110 15.89
8	Haikou ( <i>Sonneratia</i> )	8	363	50	20	<0.04	134	97 14.03
9	Haikou ( <i>Kandelia candel</i> )	13	118	25	27	0.06	51	74 6.75
Threshold Effect Concentration (TEC)		9.79	43.40	31.60	35.80	0.18	22.70	121
Probable Effect Concentration (PEC)		33	111	149	128	1.06	48.60	459
Stream Sediment GSD-7, Certified Value		84 ±9	122 ±10	38 ±2	350 ±26		53 ±5	238 ±19
QC Run 1		82	118	37	357		55	248
QC Run 2		81	120	36	359		57	249
QC Run 3		82	116	37	360		57	248
QC Run 4		82	117	36	356		58	244
QC Run 5		83	119	37	359		56	248

Quasimeme Marine Sediment QPH048MS	Naph	Ace	Fluor	Phen	Anth	Fanth	Pyr	B[a]A	Chrys	B[b]F	Pery	B[k]F	B[a]P	DBA	B[ghi]P	IP
Assigned Value	290	148	132	1164	198	2046	1845	1008	1158	1249	317	652	878	201	1047	1043
Uncertainty	73	37	33	291	50	512	462	252	290	313	40	163	220	50	262	261
Permissible Max.	363	185	165	1455	248	2558	2307	1260	1448	1562	357	815	1098	251	1309	1044
Permissible Min.	217	111	99	873	148	1534	1383	756	868	936	277	489	658	151	785	782
QC Run 1	268	124	111	1167	165	2444	1805	882	1059	1293	336	683	967	167	1065	956
QC Run 2	337	125	110	1189	168	2442	1900	893	1073	1338	317	696	978	189	1034	810
QC Run 3	321	123	108	1182	165	2441	1842	872	1041	1315	348	689	963	232	1106	1042
Excitation Wavelength (nm)	275	275	275	253	240	240	240	254	254	350	350	350	350	300	300	300
Emission Wavelength (nm)	325	325	325	373	425	425	425	395	395	440	440	440	440	470	470	470
Retention Times (mins)	9.5	14.5	15.1	17.7	19.9	21.2	22.2	24.8	25.7	28.2	28.7	30.0	32.0	35.2	37.5	40.0

**PAH Abbreviations :** Naph: naphthalene, 1-MN: 1-methylnaphthalene, Ace: acenaphthene, Fluor: fluorene, Phen: phenanthrene, Anth: anthracene, Fanth: fluoranthene, Pyr: pyrene, B[a]A: benz[a]anthracene, Chrys: chrysene, B[b]F: benzo[b]fluoranthene, Pery: perylene, B[k]F: benzo[k]fluoranthene, B[a]P: benz[a]pyrene, DBA: dibenz[a,h]anthracene, B[ghi]P: benzo[g,h,i]perylene, IP: Indeno[1,2,3-c,d]pyrene

Sample Location	Naph	1-MN	Ace	Fluor	Phen	Anth	Fanth	Pyr	B[a]A	Chrys	B[b]F	Pery	B[k]F	B[a]P	DBA	B[ghi]P	IP	Total
1. Wenchang	8.26	1.41	<LoQ	2.50	10.5	0.95	7.36	intf	2.18	2.83	7.91	11.9	2.80	4.02	<LoQ	6.88	5.19	74.7
2. Haikou	7.88	0.56	0.13	2.11	6.97	0.56	4.32	intf	1.39	1.94	6.57	11.9	2.28	3.10	<LoQ	5.92	5.47	61.1
3. Beihai	0.77	0.55	0.11	1.27	6.30	0.17	3.34	5.69	0.34	0.52	1.31	0.47	0.44	0.55	<LoQ	1.17	1.03	24.0
4. Zhanjian	3.49	0.83	<LoQ	2.75	9.80	0.52	2.60	intf	1.09	0.97	3.72	6.67	1.15	1.50	<LoQ	2.48	1.93	39.5
5. Xiamen	9.93	3.06	0.88	4.48	20.8	4.29	21.3	22.6	7.32	8.33	10.6	34.9	4.35	5.82	<LoQ	7.31	4.78	170.7
6. Shenzhen	5.41	6.82	7.55	8.11	19.0	3.75	20.9	33.9	7.97	10.9	21.7	35.5	8.30	11.2	1.70	23.1	12.5	238.1
7. Haikou (Naked Beach)	1.72	0.37	<LoQ	2.21	13.0	0.32	2.38	3.91	0.47	0.45	1.97	3.86	0.66	0.91	<LoQ	1.35	1.33	35.0
8. Haikou ( <i>Sonneratia</i> )	3.60	<LoQ	<LoQ	1.07	5.52	0.15	3.21	4.57	0.42	0.39	2.71	4.35	0.82	1.06	<LoQ	2.00	1.49	31.4
9. Haikou ( <i>K. candel</i> )	9.74	0.46	<LoQ	4.90	18.5	0.90	4.29	intf	0.71	1.42	5.44	7.35	1.43	1.53	<LoQ	3.28	2.79	62.7
Limits of Quantification (LoQ)	0.19	0.20	0.10	0.03	0.13	0.08	0.35	0.45	0.16	0.14	0.19	0.30	0.14	0.16	0.37	0.31	0.25	-

**N.B.** intf = Pyrene quantification by HPLC confounded by interference from large peak of a closely eluting unknown compound in chromatogram

Sample Location	Relative Abundance Order														Other Properties			
	Nap	Ace	Fluo	Pha	Antl	Fant	Pyr	B[a]A	Chr	B[b+k]F	B[a]P	DBz	B[ghi]P	IP	Pery / Σ PAH %	Nap / Phen	Total PAHs	TOC %
1. Wenchang	4	14	10	<b>3</b>	12	<b>5</b>	nd	<b>11</b>	<b>9</b>	<b>2</b>	<b>8</b>	13	<b>6</b>	<b>7</b>	16.2	0.79	74.7	4.57
2. Haikou	3	13	9	<b>4</b>	12	<b>7</b>	nd	<b>11</b>	<b>10</b>	<b>2</b>	<b>8</b>	14	<b>5</b>	<b>6</b>	19.7	1.13	61.1	3.95
3. Beihai	8	13	5	<b>1</b>	12	<b>3</b>	<b>2</b>	<b>11</b>	<b>10</b>	<b>4</b>	<b>9</b>	14	<b>6</b>	<b>7</b>	2.0	0.12	24.0	0.37
4. Zhanjian	4	13	5	<b>1</b>	12	<b>6</b>	nd	<b>10</b>	<b>11</b>	<b>3</b>	<b>9</b>	14	<b>7</b>	<b>8</b>	17.2	0.36	39.5	1.38
5. Xiamen	5	13	11	<b>3</b>	12	<b>2</b>	<b>1</b>	<b>7</b>	<b>6</b>	<b>4</b>	<b>9</b>	14	<b>8</b>	<b>10</b>	20.8	0.48	170.7	2.24
6. Shenzhen	12	11	9	<b>5</b>	13	<b>4</b>	<b>1</b>	<b>10</b>	<b>8</b>	<b>2</b>	<b>7</b>	14	<b>3</b>	<b>6</b>	15.3	0.28	238.1	2.94
7. Haikou (Naked Beach)	6	13	5	<b>1</b>	12	<b>4</b>	<b>2</b>	<b>10</b>	<b>11</b>	<b>3</b>	<b>9</b>	14	<b>7</b>	<b>8</b>	11.2	0.13	35.0	0.72
8. Haikou (Sonneratia)	3	13	8	<b>1</b>	12	<b>5</b>	<b>2</b>	<b>10</b>	<b>11</b>	<b>4</b>	<b>9</b>	14	<b>6</b>	<b>7</b>	13.8	0.65	31.4	0.91
9. Haikou (Kadelia candel)	3	14	5	<b>1</b>	11	<b>6</b>	nd	<b>12</b>	<b>10</b>	<b>4</b>	<b>9</b>	13	<b>7</b>	<b>8</b>	11.8	0.53	62.7	3.90
<b>Mangroves (Mean Totals):</b>																		
Mai Po (2515 µg/kg)	3	9	2	<b>4</b>	11	<b>10</b>	<b>6</b>	<b>1</b>	<b>5</b>	<b>7</b>	<b>13</b>	12	<b>14</b>	<b>8</b>	Tam et al., 2002	<b>Rankings of the 9 PAHs associated with pyrogenicity appear in bold typeface</b>		
Mai Po (373 µg/kg)	3	14	12	<b>4</b>	11	<b>2</b>	<b>1</b>	<b>6</b>	<b>9</b>	<b>5</b>	<b>10</b>	13	<b>7</b>	<b>8</b>	Liang et al., 2007			
Ting Kok (119 µg/kg)	2	-	8	<b>4</b>	-	<b>6</b>	<b>5</b>	<b>7</b>	<b>1</b>	-	<b>9</b>	11	<b>10</b>	<b>3</b>	Ke et al., 2005			
Sheung Pak Nai (159 µg/kg)	9	12	8	<b>2</b>	11	<b>4</b>	<b>1</b>	<b>10</b>	<b>3</b>	<b>5</b>	<b>7</b>	13	<b>14</b>	<b>6</b>	Ke et al., 2005			
Sheung Pak Nai (157 µg/kg)	10	13	11	<b>5</b>	9	<b>3</b>	<b>4</b>	<b>2</b>	<b>8</b>	<b>7</b>	<b>12</b>	14	<b>1</b>	<b>6</b>	Tam et al., 2002			
Ma Wan (2071 µg/kg)	12	14	13	7	10	<b>3</b>	<b>2</b>	<b>1</b>	<b>5</b>	<b>4</b>	<b>6</b>	11	<b>8</b>	<b>9</b>	Ke et al., 2005			
Ma Wan (2063 µg/kg)	12	14	13	<b>8</b>	10	<b>3</b>	<b>1</b>	<b>2</b>	<b>5</b>	<b>4</b>	<b>6</b>	11	<b>7</b>	<b>9</b>	Tam et al., 2002			
Yi O (1196 µg/kg)	12	13	5	<b>1</b>	11	<b>8</b>	<b>2</b>	<b>4</b>	<b>6</b>	<b>3</b>	<b>10</b>	9	<b>7</b>	<b>14</b>	Ke et al., 2005			
Sai Keng (1460 µg/kg)	5	12	4	<b>3</b>	11	<b>9</b>	<b>7</b>	<b>1</b>	<b>6</b>	<b>10</b>	<b>14</b>	13	<b>8</b>	<b>2</b>	Tam et al., 2002			
Shenzhen (237 µg/kg)	3	14	12	<b>6</b>	10	<b>2</b>	<b>1</b>	<b>13</b>	<b>11</b>	<b>5</b>	<b>4</b>	9	<b>7</b>	<b>8</b>	Zhang et al., 2004			

**N.B.** The rankings only extend to 14 because B[b]F and B[k]F are added together to give B[b+k]F. This is because historically it was difficult to resolve these two chromatographically and so many relative abundance orders show the two combined. (e.g. McCready et al., 2000).

**Assumption** - in cases where pyrene could not be quantified it was assumed, on the basis of samples where it could, that it was the predominant of the 15 USEPA except when phenanthrene was dominant and in such cases pyrene was then regarded as the second most abundant USEPA PAH.

Location	Mean	Range	Total PAHs	Notes	References
This study	82	24-238	Σ 16/17 PAHs		
Hong Kong: Mai Po	373	311-435	Σ 16 PAHs	PAH inputs from wet deposition and Pearl River	Liang et al., 2007
Guanabara Bay, Brazil	14471	1232-28278	Σ 16 PAHs	Oil spill contaminated sites.	Maciel-Souza et al., 2006
Hong Kong: Mai Po	557	332-781	Σ 16 PAHs	Paper concerns PAH-degrading bacteria so no specific mention of PAH contamination at each site. However, notes that PAH contamination in mangrove sediments varies dependent on their proximity to human activities, source and types of pollution and sediment properties, e.g. organic matter content and particle size distributions.	Guo et al., 2005
Ho Chung	259	189-329			
Sai Keng	429	311-547			
Sheung Pak Nai	334	69-599			
Yi O	311	216-406			
Ma Wan	1058	695-1422			
Kei Ling Ha Lo Wei	169	117-221			
Hong Kong: Ting Kok	119	56-172	Σ 16 PAHs	Protected SSSI- slight pollution rural/recreational.	Ke et al., 2005
Sheung Pak Nai	159	59-241		Receives direct waste from fish ponds and villages.	
Yi O	313	73-1196		Remote – but had historical oil spill contamination.	
Ma Wan	2071	791-3758		Considerable pollution from refuse and discharges.	
Hong Kong: Ho Chung	2202	1162-3322	Σ 16 PAHs	Contaminated by vehicles, industry and wastes.	Yu et al., 2005
Deep Bay, Shenzhen, China	409	237-726	Σ 16 PAHs	Mangrove forest located at heart of modern city Suggested pollution mostly from combustion sources	Zhang et al., 2004
Hong Kong : Yi O	588	138-2135	Σ 15 PAHs	Oil spill contaminated sites (30 days after spill)	Ke et al., 2002
	315	73-1196	Σ 15 PAHs	Oil spill contaminated sites (126 days after spill)	
Hong Kong: Mai Po	2515	1007-4842	Σ 16 PAHs	PAH contamination attributed to petrogenic sources	Tam et al., 2002
Sai Keng	1460	839-2140		PAH contamination attributed to petrogenic sources	
Sheung Pak Nai	157	69-209		PAH contamination attributed to pyrolytic sources	
Ma Wan	2063	791-3751		PAH contamination attributed to pyrolytic sources	
Hong Kong: Mai Po	1945	685-4680	Σ 15 PAHs	Suggested industrial, shipping and sewage pollution for the higher values of PAHs.	Tam et al., 2001
Ho Chung	6186	1273-11098			
Sai Keng	1044	356-1811			
Tolo	1041	649-1485			
Hong Kong: Mai Po Marshes	610	212-1042	Σ 15 PAHs	Higher values attributed to specific HMW PAHs	Zheng et al., 2000
Guadeloupe Is., Caribbean	502	103-1657	Σ ? PAHs	Higher values from harbours with pyrolytic pollution	Bernard et al., 1996
S.W. Coast Puerto Rico	1820	500-6000	Σ ? PAHs	Higher values from oil spill contaminated sites	Klekowski et al., 1994



