

PETROLEUM HYDROCARBONS DISTRIBUTION IN SEDIMENTS FROM THE THAMES ESTUARY, UK

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Sediment cores were collected from the Stanford-Le-Hope mudflats within 1 km distance from the Petroplus-Coryton BP and Shell Haven refineries located on the north shore of the Thames Estuary in Essex, 40 km east of Central London, UK (51 °30'N, 0 °27'E). The BTEX compounds (benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylenes) in surface sediment samples were non-detectable within the linear calibration range of 0 – 50 mg l⁻¹. *n*-Alkanes (C₁₁ - C₄₀) and polycyclic aromatic hydrocarbons (PAHs) quantified at different sediment depths (2 cm core portions up to a total depth of 18 cm) indicated a high distribution of *n*-alkanes in subsurface sediments at the 10 – 12 cm depth; up to an average concentration of 1353.4 µg g⁻¹ dry weight. The highest summed PAH (ΣPAH) concentration of 2.95 µg g⁻¹ dry weight was also found at the 10 – 12 cm depth. Source identification based on the ratio of low-molecular weight (LMW) to high-molecular weight (HMW) *n*-alkanes and the pristane/phytane ratio (Pr/Phy) indicated *n*-alkane input from biogenic sources. Nevertheless, the dominance of C₁-naphthalene among ΣPAH concentrations suggested possible input from petroleum-related sources.

Key words: Polycyclic aromatic hydrocarbons, Thames Estuary, BTEX, *n*-Alkanes, Gas chromatography, Extractable petroleum hydrocarbons, Solvent extraction

INTRODUCTION

Estuaries and surrounding shelf waters are vulnerable to hydrocarbon pollution globally due to their use as quays and the establishment of a succession of industries on the banks of such estuaries. Polycyclic aromatic hydrocarbons (PAHs) in marine environments have been described as adhering to and persisting in sediments due to their low water solubility and hydrophobic nature (Da Silva and Alvarez, 2007; Trabelsi and Driss, 2005). Like benzene, many of the PAH compounds have carcinogenic properties and have been listed as priority contaminants by the U.S. Environment Protection Agency (US EPA). The BTEX compounds (benzene, toluene, ethylbenzene and xylenes isomers), which may be found in association with PAHs in contaminated sites, have been widely recognized as toxins of concern in petroleum products such as gasoline. These volatile organic compounds (VOCs) are highly soluble and pose a drinking water hazard when accumulated in groundwater.

Several studies have reported the concentrations and distribution of various groups of

hydrocarbons in estuarine sediments around the UK as well as other parts of the world (Vane et al., 2007; Wetzel et al., 2013; Nicolaus et al., 2015; Oliva et al., 2015; Iwegbue et al., 2016). Studies involving the distribution of VOCs such as benzene and toluene, and PAHs in estuarine sediments are important for monitoring the levels of these chemical contaminants to avoid potential toxicity to humans and various sediment dwellers (Spencer and MacLeod, 2002; Williams et al., 2014; Oliva et al., 2015). Understandably, available data on the distribution of BTEX and other VOCs in sediment samples from estuaries around the UK is limited due to the high solubility and volatility of these compounds. However, there is a rich repository of published data on PAHs distribution, and to some extent heavy metals status of sediments from estuaries around the UK. For example, Spencer and MacLeod (2002) described the distribution and partitioning of heavy metals in estuarine sediment cores collected from the Thames, Medway and Blackwater estuaries in south-east England and concluded that over 70% of metals detected in subsurface sediments were labile in the Thames Estuary

with probable toxic effects to bottom-dwelling organisms. In a recent study by Vane et al. (2015), the Thames Estuary was described as one of the world’s most contaminated river–estuarine sediment systems. This summation was based on the profiling of mercury (Hg) pollution in sediment cores as having a rise-peak-fall pattern that reflected changing anthropogenic inputs over time. In particular, sediments at >40 cm depth were considered highly contaminated, with detected Hg levels over 7 mg kg⁻¹. In recent times, the British Geological Survey (BGS) has embarked on a study to identify and map pollution in the Thames estuary; the goal is to gain understanding of the processes that influence pollution distribution in tidal Thames.

The Stanford-le-Hope tidal mudflats on the area for shipping activities involving crude oil and related petrochemical products (Figure 1), making the mudflats target for long-term petroleum hydrocarbon contamination. Although it is expected that sampling from the Stanford-le-Hope mudflats would form part of the BGS’s ongoing programme of work, there are presently no records of comparability data describing PAHs or *n*-alkanes distribution in sediments from the Stanford-le-Hope mudflat area. Therefore, this study though preliminary in terms of extent of coverage of sampling area, represents the first set of data for *n*-alkanes and PAHs concentrations in sediments from Stanford-le-Hope mudflats on the Thames estuary.

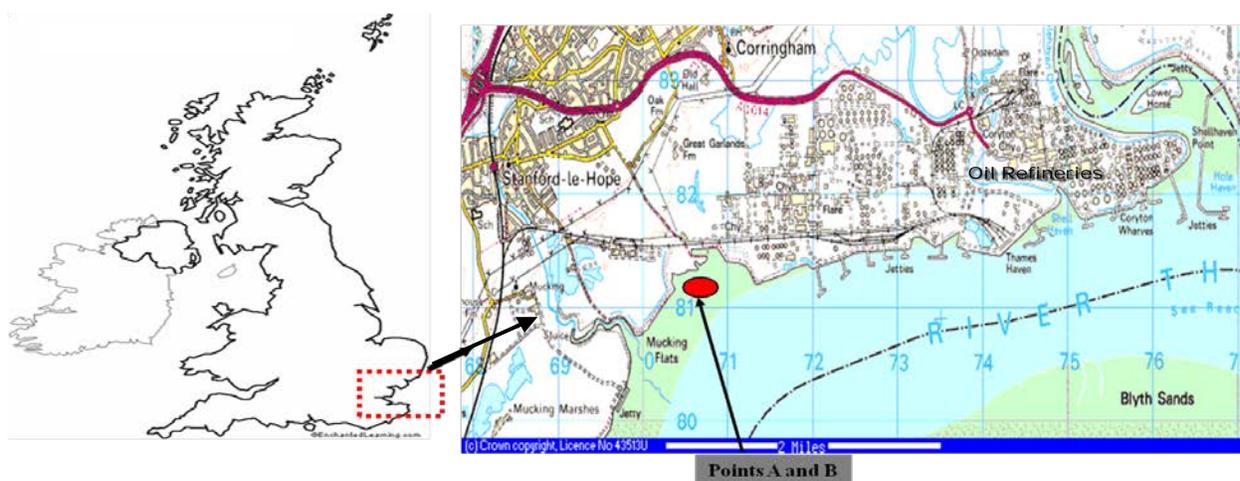


Figure 1. Map showing Stanford-le-Hope mudflats on the River Thames Estuary, the location of the Petroplus-Coryton and Shell Haven refineries and sampling points - A and B. Sources: <http://www.multimap.com>; <http://www.energyinst.org.uk/education/refineries/coryton.html>.

It involved the quantification of background concentrations of a range of volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH), PAHs and *n*-alkanes from C₁₁ to C₄₀ using headspace analysis, solvent extraction and subsequent detection/quantification by gas chromatographic methods (GC-FID and GC-MS).

MATERIALS AND METHODS

Site description and sampling

Sediment samples were collected from a randomly identified location on the Stanford-le

-Hope mudflats (Figure 1) at approximately 1 km distance from the Petroplus-Coryton and Shell Haven oil refineries. Sediments were collected at low tide between 10:00 – 13:30 to an approximate depth of 18 cm using plastic cores (25 cm long and 4 cm in diameter). Sediments were collected in cores within one marked 10 cm radius at two points that were approximately 150 cm apart. Cores were sealed immediately with rubber bungs before freezing in an ice box. Despite the proximity of the two sampling points, it was anticipated that sediment samples differed sufficiently to reflect the complexity and diversity common to such estuarine

environments. For BTEX determinations, an additional 10 g of sediment was collected using sterile 10 ml syringes with the tapered ends cut off. Triplicate sediment samples were placed in sterile 110 ml serum vials, crimp sealed immediately with PTFE-lined septa and frozen for headspace analysis.

Quantification of BTEX, *n*-alkanes and PAHs in sediments

BTEX concentrations was measured using a Philips PU4500 gas chromatograph with a glass packed column (10% apiezon on chrommowax, 60-80 mesh) and nitrogen as carrier gas. GC conditions were: injector 160°C, column 100°C, and detector 160°C. For calibrations, an external standard solution mix containing benzene, toluene, and ethylbenzene; and a separate xylene standard solution was used at the concentrations: 0 - 50 mg l⁻¹. Samples were allowed an initial equilibration time of 2 h at 20°C prior to injection; and sample temperature was kept constant while measurements were taken.

Cores were sectioned into 0 – 2 cm, 2 – 4 cm, 4 - 6 cm, 6 – 8 cm, 8 – 10 cm, 10 -12 cm, 12 – 14 cm, 14 – 16 cm, and 16 – 18 cm portions and duplicate extractions carried out to determine the concentrations of 17 PAHs and *n*-alkanes from C₁₁ to C₄₀ in sediments. The solvent extraction method used is based on the relative solubility of analytes in two immiscible liquids; it also allowed the removal of interfering substances and concentration of analytes prior to quantification using gas chromatography-mass spectrometry (GC-MS). The protocol for the solvent extraction method used was previously described by Coulon et. al. (2004) and the steps involved are as follows: wet sediment (2 g) in 25 ml Oakridge centrifuge tubes was mixed thoroughly with 8 g of anhydrous sodium sulphate to dry sediments, this was followed by the addition of 6 ml of hexane: dichloromethane, (1:1). Using the sonication technique, samples were extracted in the solvent (hexane: dichloromethane, 1:1) by sonicating for 30 min at 20°C and were left to shake horizontally overnight (approximately 16 h) on a mechanical shaker (Stuart flask shaker) at 12°C. This was followed by centrifugation at 1300 g for 20 min (centrifuge model: Biofuge Stratos, Heraeus); and extracts were cleaned by elution through solid phase extraction (SPE) columns

according to the manufacturer's instructions (SPE Supelclean Envi™-18, Supelco Bellefonte, USA).

Extracts were initially collected in 15 ml conical falcon tubes and evaporated with oxygen-free nitrogen to 1 ml over an ice bath to minimize loss of light PAHs; concentrated extracts were then transferred into amber coloured glass vials, sealed with PTFE-lined caps and frozen until required for GC-MS analysis. Prior to GC-MS analysis, extracts were diluted to appropriate concentrations by adding hexane. Deuterated alkanes (C₁₀^{d22}, C₁₉^{d40}, and C₃₀^{d62}) and deuterated PAHs (naphthalene^{d8}, anthracene^{d10}, perylene^{d12}, and chrysene^{d12}) internal standards were added at required concentrations (5 and 2 mg l⁻¹ respectively). The mass spectrometer was operated in full-scan mode (range m/z 50-600), with identification of target analytes based on retention times of analytical standards and quantification performed by integrating the peaks of target analytes at specific mass-charge (m/z) ratios. Duplicate extraction and quantification of the same sample was carried out to check for variations in the reproducibility of the extraction method and quantification of samples.

Statistical analysis

Statistical analyses were carried out using Minitab version 15 (English) after ensuring that the data met with the assumptions and criteria of the test being used. One-way ANOVA followed by multiple comparisons with Tukey's test was used to determine whether concentrations obtained for TPH determinations were significantly different.

RESULTS AND DISCUSSION

BTEX quantification in Stanford-le-Hope sediments

Headspace analysis using GC-FID revealed no background concentrations of benzene, toluene, ethylbenzene and the xylenes isomers in surface sediments sampled. The BTEX compounds were not detected within the linear calibration range of 0 – 50 mg l⁻¹ and were thus below the limit of detection (< 0.25 mg l⁻¹). A detection limit of 0.005 mg l⁻¹ for benzene was measured previously in a separate analysis using the highest GC-FID machine sensitivity and high temperature conditions (injector and detector: 250°C and column: 155°C). Though

GC measurements in this study were carried out at lower temperature conditions (injector 160°C, column 100°C, and detector 160°C) to allow for separation of BTEX mix, the same high machine sensitivity was used. Estuarine sediments are generally not regarded as repositories for monoaromatics due to their very volatile nature; this could be an explanation for the absence of BTEX in the sediments studied. Furthermore, the BTEX compounds are readily soluble in water and easily degraded, and could have been washed away from sediments due to frequent tidal movements. In general, the detection of volatile organic compounds in estuarine sediments has been reported as often occurring within low limits of detection (Dewulf et al. 1996; Roose et al. 2001).

Determination of extractable petroleum hydrocarbons (EPH) in Stanford-le-Hope sediments

The concentrations and distribution of *n*-alkanes from C₁₁ to C₄₀, the isoprenoids (pristane and phytane), and 17 PAH compounds was determined in sediment cores collected from the Stanford-le-Hope mudflats; the results obtained are presented in Figures 2 and 3. The quantification of *n*-alkanes at different depths in the sediments indicated that subsurface sediments at the 10 – 12 cm depth had the highest \sum *n*-alkane concentrations of 1353.4 $\mu\text{g g}^{-1}$ dry weight (Figure 2). This trend was also observed for core portions sampled from a second point within the same location. For PAHs, highest average concentrations were found at the 10 – 12 cm depth for point A core portions and at the surface (0 – 2 cm depth) for point B core portions (Figure 3). Considering mean concentrations across the different depths analysed, tetradecane, pentadecane, and pristane levels were highest among the \sum *n*-alkane concentrations detected at the 10 – 12 cm depth (Figure 2). Overall, high levels of *n*-alkanes and PAHs was observed within the 10 – 12 cm depth for the two sets of sediment core portions analysed; in fact, \sum *n*-alkanes concentrations contributed at least 99% of the petroleum hydrocarbons detected at the various depths. The detection of high petroleum hydrocarbon levels at the 10 – 12 cm depth is in agreement with the report that petroleum hydrocarbons persisted at the 12 – 14 cm and 14- 16

cm depths in sediments analysed 30 years after the West Falmouth oil spill (Reddy et al., 2002). Oil penetration into deeper sediment layers, persisting anoxic conditions in subsurface sediments and limited bioavailability to degrading-microbes were some factors reported as possibly responsible for the detected high petroleum hydrocarbon levels at the 12 – 14 cm and 14 – 16 cm depths in the West Falmouth sediments. Although no oil spill incidents have been reported on the Stanford-le-Hope mudflats, the estuary is subject to pollution discharges from industries located along the banks as well as domestic sources. For this reason, the characterization of the nature of pollutants in sediments of the Thames estuary by the British Geological Survey is a much needed venture. Specifically, organic pollutants under study include: total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Publications on the outcomes of this study are yet to be made available at the time this report went to press; however, it is expected that the data generated would be useful in the separation of what constitutes natural background and anthropogenic inputs into sediments of the Thames estuary. In line with this, the detection of significant amounts of *n*-alkanes (mainly *n*-C₁₄, *n*-C₁₅ and Pristane; Fig.2) in the Stanford-le-Hope sediments indicated inputs from mixed sources, terrestrial biogenic and contributions from petroleum inputs (Vane et al., 2011; Iwegbue et al., 2016). As confirmation, diagnostic parameters were tested to identify the sources of *n*-alkanes detected in the sediments. The ratio of low-molecular weight *n*-alkanes/high-molecular weight *n*-alkanes (LMW/HMW) and the isoprenoids ratio, pristane/phytane (Pr/Phy) was determined to distinguish inputs from petroleum, marine biogenic and terrestrial biogenic sources. For the LMW/HMW ratio, values near 1 indicated input from petroleum sources; values less than 1 implied natural input from terrestrial plant sources and values above 1 are indicative of natural input from marine biogenic sources (Fagbote and Olanipekun, 2013; Iwegbue et al., 2016). Similarly, the pristane/phytane ratio is usually larger for sediments with input from biogenic sources and near 1 or equal to 1 in sediments with petroleum inputs (Volkman et al., 1992; Wang et al., 2012). In this

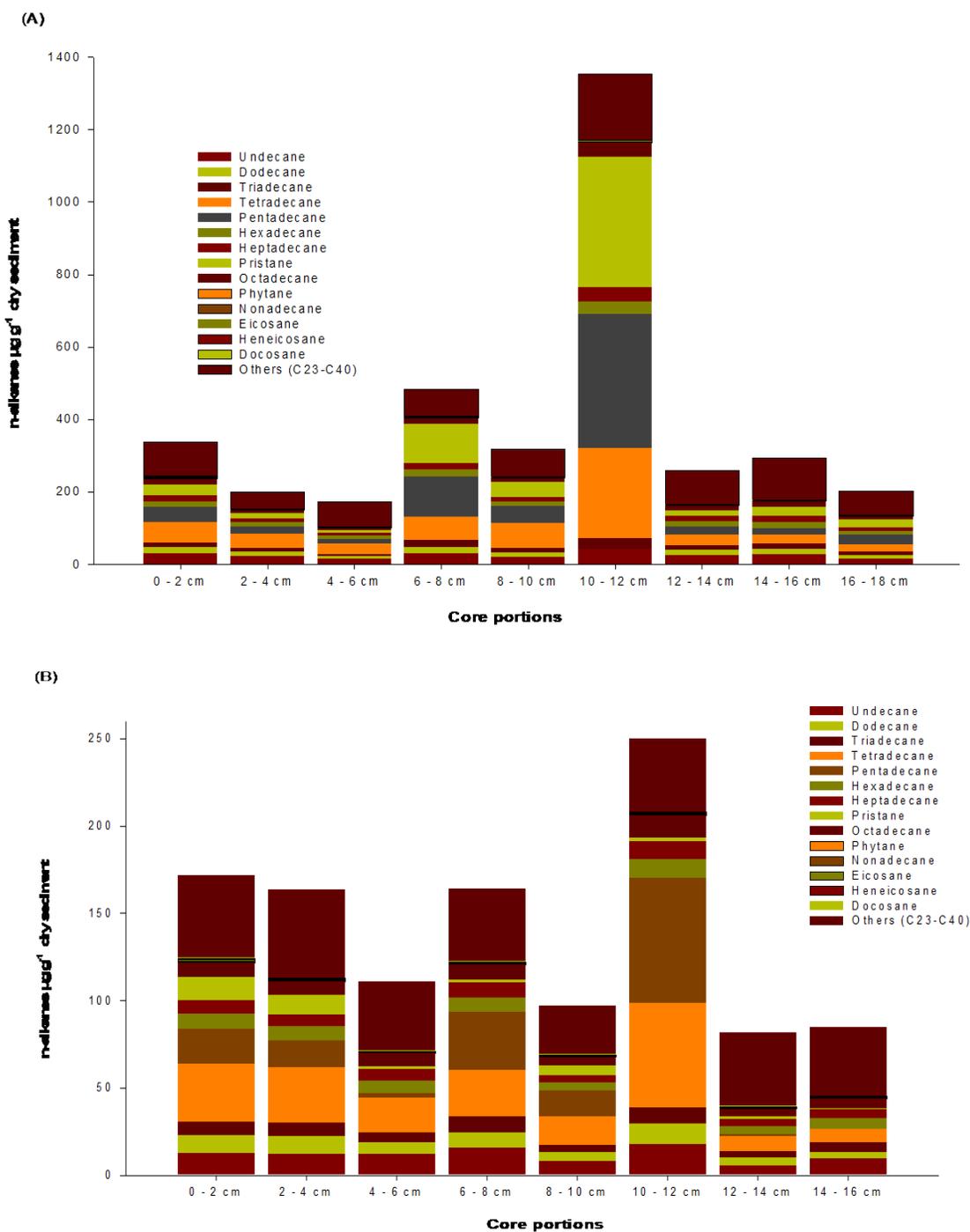


Figure 2. Mean *n*-alkane concentrations ($\mu\text{g g}^{-1}$) in surface and core sediments from Stanford-le-Hope, subdivided into 14 individual alkanes ($\text{C}_{11} - \text{C}_{22}$) and others (sum of concentrations for $\text{C}_{23} - \text{C}_{40}$ alkanes). **A**, point A sediments; **B**, point B sediments; $n = 2$ extractions.

study, *n*-alkanes in sediments at 0 - 2 cm, 2 - 4 cm, 6 - 8 cm and 10 - 12 cm depth for point A samples had LMW/HMW ratios of about 1 (0.71 - 0.85), indicating contamination from petrogenic sources. For sampling point B, the LMW/HMW ratio for *n*-alkanes in sediments at 6 - 8 cm and 10 - 12 cm

depth was 0.79 and 0.93 respectively, again indicative of contamination from petroleum sources. In contrast, the pristane/phytane ratios in sediments at the various depths from both sampling points were mostly larger than 1 (lowest = 2.2; highest = 260.5), indicating that aliphatic hydrocarbons were

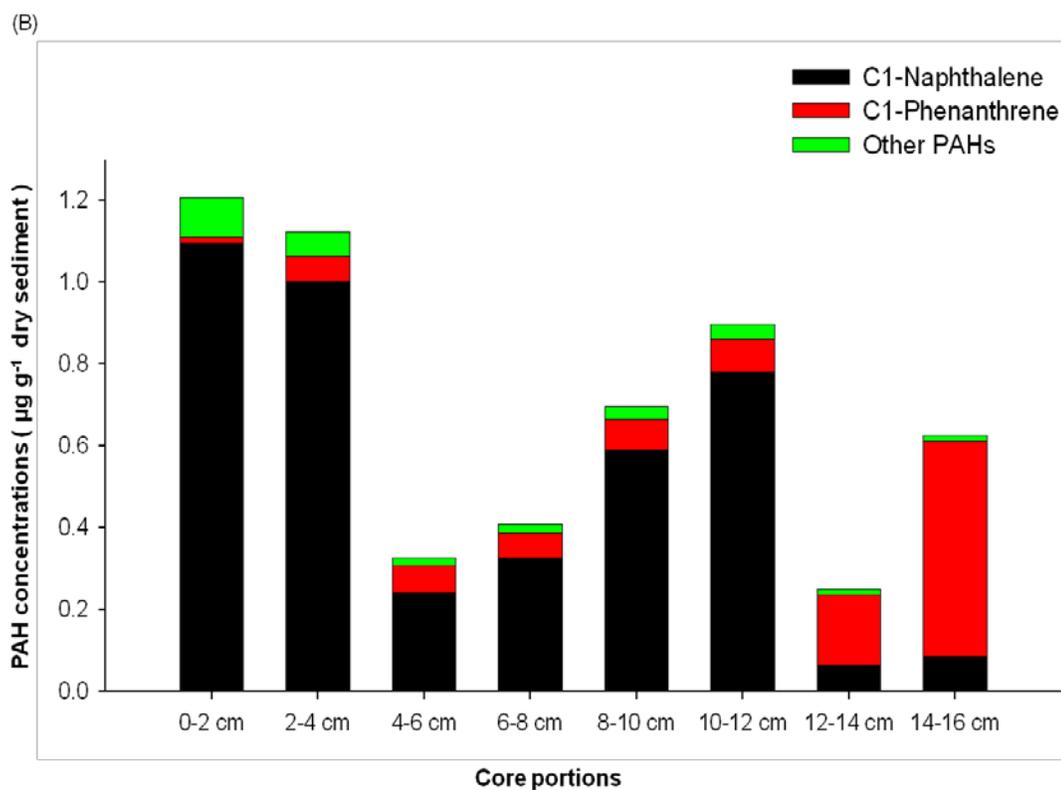
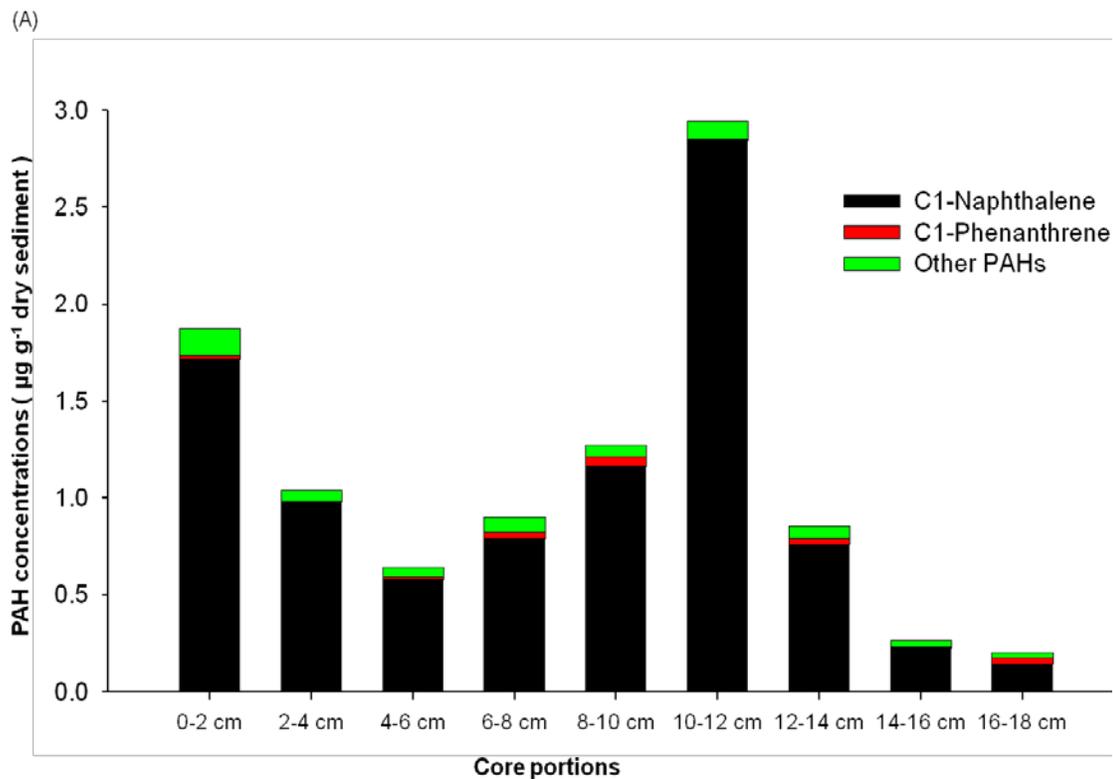


Figure 3. Mean PAH concentrations ($\mu\text{g g}^{-1}$) in surface and core sediments from Stanford-le-Hope, subdivided into three categories: C1-naphthalene, C1-phenanthrene and others (sum of concentrations for 15 PAHs). **A**, Point A sediments; **B**, point B sediments; $n = 2$ extractions.

derived from biogenic rather than crude oil-related sources.

With respect to PAH levels, the highest Σ PAH concentration of $2.95 \mu\text{g g}^{-1}$ dry weight was found at the 10 – 12 cm depth (Figure 3). Detected high Σ PAH concentration was largely due to high levels of C_1 -naphthalene (highest of $2.85 \pm 0.75 \mu\text{g g}^{-1}$ dry weight) at the 10 - 12 cm depth and across the sediment depths studied for sampling points A and B. Σ PAH concentrations obtained in these sediments were consistent with low values of total PAH concentrations found in sediments from the less industrialized Solway estuary UK (Rogers, 2002). These workers quantified 22 PAH compounds including alkyl-substituted PAHs in UK estuarine sediments. The highest total PAH concentration of $89.61 \mu\text{g g}^{-1}$ dry weight was found in sediments from Southampton water near a British Petroleum (BP) chemical facility; total PAH concentrations in sediments from the Mersey estuary were in the range $0.66 - 11.23 \mu\text{g g}^{-1}$ dry weight. Rogers (2002) recommended that sediments having PAH concentrations greater than $20 \mu\text{g g}^{-1}$ dry weight be classified as highly contaminated. Based on this requirement therefore, and in comparison to data for sediments from highly industrialized estuaries such as Mersey estuary, the total PAH concentrations found in the Stanford-le-Hope sediments (highest Σ PAH of $2.95 \mu\text{g g}^{-1}$ dry weight) were relatively low, despite the use of the estuary as a docking area and the location of nearby oil refineries. Nevertheless, the dominance of total PAHs by alkylated PAH compounds, specifically C_1 -naphthalene and C_1 -phenanthrene is suggestive of releases from oil and oil-related products (Law and Biscaya, 1994; Douglas et al., 1996; Wang et al., 2012).

The observed variability in petroleum hydrocarbons concentrations reported for the Stanford-le-Hope sediments reflected the heterogeneity common to such complex environmental matrices. Nevertheless, the fact that sampling was limited to just two points within the area makes it impossible to draw a generalized conclusion regarding the pollutant status of the Stanford-le-Hope mudflats. Conversely, the data presented in this study provides background

information for the sediments studied. More detailed studies are required on the current status of total petroleum hydrocarbons (TPH) in these sediments to include all hydrocarbons such as: *n*-alkenes, branched alkanes, branched alkenes, cycloalkanes, etc. as well as PAHs.

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