Spatial and Temporal Distribution of Polycyclic Aromatic Hydrocarbons in the Northern Arabian Gulf Sediments.

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Introduction

The major sources of PAHs in coastal marine sediments include (i) direct deposition from the atmosphere, (ii) runoff from land, (iii) inputs from industrial and wastewater treatment plant[1-2].Since they are hydrophobic they preferentially associate with suspended particulate material and sediments upon entry into the marine environment and transported to bottom sediments where their incorporation can be delayed due to recycling processes like bioturbation and resuspension. The main objectives of this study were to (i) undertake a comparative assessment of the state of PAH contamination within Kuwait Bay, a relatively large embayment covering an area of approximately 850 km^2 and the open Arabian Gulf, and (ii) to reconstruct the depositional history of these compounds in the northwestern Arabian Gulf. The Arabian Gulf is a “semi-enclosed” sea connected to the Indian Ocean through the Strait of Hormuz. Sediments can thus provide an important record of contamination. The use of dated sediment cores is a well-established means of reconstructing historical chronologies of contaminant inputs [3].

Materials and methods

Surficial sediment samples were collected using a van Veen grab sampler from 25 stations within Kuwait Bay (KB) and in the open Arabian Gulf. The samples were immediately transferred into clean, solvent-rinsed, amber glass jars and stored in a cool box for transport to the laboratory, where they were kept at -20^{o}C prior to analysis. The sampling strategy adopted in the study allowed for a comparative assessment of the status of pollution within and outside the Bay. The sampling locations were at least 10 km from the shoreline to minimize the influence of point sources emanating from land-based sources. Sediment cores were collected from four locations within Kuwait’s territorial waters using a freeze corer. The freeze corer comprised of a rectangular aluminium frame (16 x 8 x 150 cm) with a tapered end for easy penetration into sediment [4-5]. The corer was filled with dry ice and ethanol before lowering into the water. The corer was allowed to drop freely from approximately 5 m from the sediment-water interface into the sediment and left there for between 15 and 20 min. When retrieved thick slabs of sediment was frozen on both faces of the corer. The slabs of sediment were gently scraped off the metal plate, wrapped in aluminium foil, kept frozen on dry ice in coolers for transport back to the laboratory where it was stored at -18^{o}C until sectioning. One side of the sediment core was used for contaminant analysis and the other side for radiochemical dating. The core was sectioned at approximately 2 cm intervals. The sectioning materials were washed and solvent-rinsed between each section. The samples were stored in clean, solvent-rinsed, amber glass jars and kept at -20^{o}C prior to analysis.

Dating. The unsupported ^{210}Pb (total – supported) radioisotopes was used to determine sedimentation rates. The specific activity of total ^{210}Pb and ^{137}Cs radioisotopes were determined using ultra low background γ-spectrometry with HPGE detectors. Supported ^{210}Pb was obtained by indirectly determining the activity concentration of the supporting parent ^{226}Ra. The unsupported ^{210}Pb was calculated by subtracting the ^{226}Ra activity from the measured ^{210}Pb. The mean sedimentation rate determined from the unsupported ^{210}Pb profiles in the upper portion of the sediment column was determined to be 1.22±0.17 cm y^{-1}. The dates shown in Fig. 3, for Stations 26, are those based on the ^{210}Pb-derived mean sedimentation rate.

Extraction and Analyses

Sediment (20 to 40 g) samples were dried using anhydrous sodium sulphate and Soxhlet-extracted for 12 to 16 h using hexane. Prior to extraction, the samples were spiked with deuterated PAH surrogates (acenaphthylene-d_8, pyrene-d_{10}, phenanthrene-d_{10}, naphthalene-d_8, fluoranthene-d_{10}, benzo[a]pyrene-d_{12}, and benzo[*ghi*]perylene-d_{12}); to monitor analytical recoveries. Copper turnings were added to the flasks during the extraction stage to remove elemental sulphur from the sediment samples.

The extracts were reduced in volume on a Turbovap™, solvent exchanged to hexane and interfering compounds removed by column chromatography using 10-g silica and 5-g alumina and 0.5-cm anhydrous sodium sulphate (Na_2SO_4) at the top of the column to prevent the column from contact with air. The compounds of interest were eluted with 100-ml 1:1 mixture of hexane and dichloromethane (DCM). The eluent was then blown down on a Turbovap™ concentrator, transferred to 2-ml vials and blown down under a gentle stream of nitrogen. During this blow down stage 50-µl of dodecane was added to ensure that the samples did not dry out. The samples were then transferred to 100-µl glass inserts, and spiked with Mirex (10-µl of 10 ng/µl) internal standard, used for volume correction and to adjust for variations in instrument response.

The analytical data is reported on dry weight and organic carbon normalized basis. The percent dry weight was obtained by drying a sub-sample of the wet sediment in preweighed crucibles to constant weight at 105^oC and reweighing the crucible. The organic matter content was determined by igniting the crucible containing dried sediments from each core section at 550^oC for 4 h. The percent weight loss-on-ignition was converted to percentage of organic carbon by dividing by 1.72.

Instrumental Analysis

The sample extracts were analyzed for PAHs using a Shimadzu GC-2010 gas chromatograph (GC) (Shimadzu, Tokyo, Japan) using splitless injection on a 30-m DB5-ms column (0.25 mm i.d. and 0.25 µm film thickness) and helium as carrier gas. The oven program was 60^oC for 2 min, ramped at 20^oC min^{-1} to 180^oC, and further ramped at 6^oC min^{-1} to 280^oC and held for 20 min. The gas chromatograph was coupled to a Shimadzu 2010 Mass Selective Detector operated in electron impact (EI) mode using selected ion monitoring (SIM). The injector temperature was set at 290^oC and the interface temperature at 280^oC. Identification and quantification were carried out against five calibration standards of known concentration using the internal standard method. Fifteen PAHs (acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indo[1,2,3-*cd*]pyrene, and benzo[*ghi*]perylene) routinely detected in samples were quantified. The sum of these is referred to as ΣPAHs.

Results and discussion

The spatial distribution of ∑PAHs is given in Fig. 1. The mean±SD (and range) ∑PAH concentrations for all samples was 7.2±3.2 (2.2 – 17.2) ng g^{-1} dw. The highest PAH concentration of 17.2 ng g^{-1} dw. was measured at a Station about 40 km offshore but opposite oil-loading operations. Intersite differences in concentration exist although these differences are not statistically significant ($p=0.08$). For example, the average concentration of ∑PAHs within Kuwait Bay was only 1.4 times higher than the average concentrations outside the Bay. However, when these concentrations were normalized to the organic carbon content of the sediments, the concentrations within Kuwait Bay were 4 times higher than the average concentrations outside the Bay (Fig. 2) and were shown to be statistically significant ($p < 0.001$). The composition of PAHs in sediments is clearly dominated by the low molecular weight 3- and 4-ring PAHs at most locations. Phenanthrene, fluorene, fluoranthene, and pyrene, together constituted ca 60% of the total PAHs in over 80% of samples. The most abundant group are the tricyclic PAHs which contribute 40-43% followed in order of decreasing importance by the tetracyclic PAHs (28-36%), pentacyclics (12-15%), with the hexacyclic PAHs contributing 10-13%.

Vertical Profiles.

Although four sediment cores were collected and analyzed for PAHs, the discussion here is primarily focus on the core collected at the entrance of Kuwait Bay (Station 26), close to the navigation channel. The concentration of ΣPAHs at Station 26 fluctuated between 12 and 25 ng g^{-1} from the bottom of the core to a depth of about 40 cm when concentrations increased to a maximum of 45 ng g^{-1} around the late 1970s and early 1980s corresponding to a depth of ~35 cm (Fig 3a). This was followed by a sharp decrease in concentration to pre-1970 "background" concentrations of between 12 and 25 ng g^{-1}. PAHs and other hydrophobic organic compounds are thought to be mainly associated with organic-rich particles in aquatic and terrestrial systems. As a result, their concentrations are often normalized with respect to organic carbon. The vertical profiles of the organic-carbon-normalized ΣPAH concentrations measured at Station 26 are presented in Fig. 3b. The vertical profile of the organic carbon-normalized ΣPAH concentrations is slightly different from that of the dry weight profiles as there are three distinct peaks in the depth profiles. The first peak in the organic-carbon-normalized concentrations occurs at a depth of 70 m in sediments dated around the mid-1950s. This is followed by a decrease in concentrations from that point until the early 1970s after which the concentrations increase rapidly to the maximum recorded concentrations in the late-1970s to early 1980s. This was followed by a sharp decrease in concentrations to near background concentrations of 480 ng g-^{1} OC. The third peak in the organic-carbon-normalized concentrations similar in magnitude to the peak in the mid-1950s occurs in the early 1990s followed by a steady decrease until the early 2000s after which there have been another steady increase in concentration to the present. The peak in the organic-carbon-normalized concentrations occurring in the mid-1990s may be related to the Arabian Gulf War of 1991 whereas the most intense peak in the depth profiles occurring in the 1980s may also be related to war-related activities as the First Gulf War (the Iran-Iraq war) was fought between 1980 and 1988. This sediment core at Station 26 is close to the navigation channel of ships transporting crude oil. PAH inputs to this site may therefore come from spillages from ships in addition to atmospheric deposition and land-based sources, as the site is close to the shore.

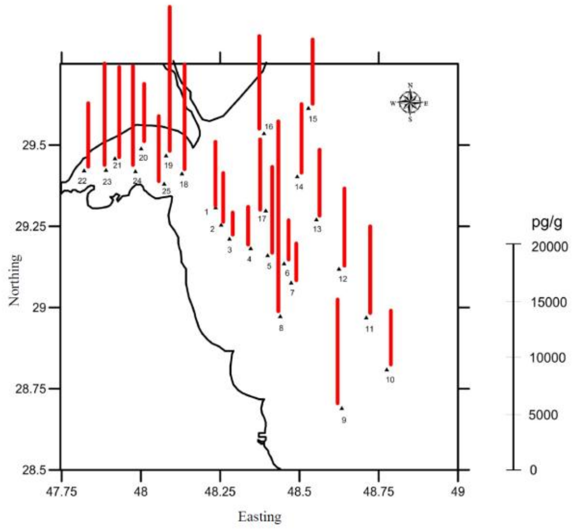

Fig. 1. Spatial distribution of ∑PAHs in Kuwait's territorial water.

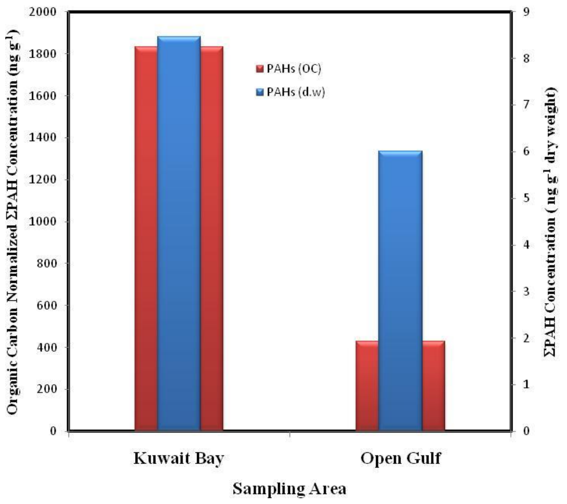

Fig. 2. Comparison between PAH concentrations measured in Kuwait Bay and the open Gulf waters.

Sources of PAHs to Kuwait's Marine Environment

The two main sources of PAHs in coastal marine sediments are petrogenic (petroleum) and pyrogenic (combustion) in origin [6-8]. It was estimated that between 1997 and 1987, 3339 mT of crude oil (21 million barrels) were introduced into the northern Arabian Gulf [9]. In the 1980s another major oil spill occurred from the Nowruz oil field (offshore oil well in Iran) where an estimated 2-4 million barrels (318 – 636 mT) were introduced into the Arabian Gulf over a 10-mo period [10]. The 1991 Gulf War also led to the release of an estimated 11 million barrels (1749 Tm3) in the Arabian Gulf besides the torching of 727 oil wells resulting in the additional 8 million barrels of oil released into the environment. Petrogenic PAHs primarily originate from land-based sources and enter the marine environment either directly by atmospheric deposition or from point source discharges, such as wastewater inputs and surface runoff.

Several approaches have been used in the literature for source apportionment of PAHs measured in the environment [11-14]. The most widely used technique is the concentration ratios between different PAH compounds since some of the ratios are known to be diagnostic of particular sources [15]. Single compound ratios like the ratio of Phen/Ant and Fla/Py have been used to distinguish petrogenic from pyrogenic sources [13]. It has been suggested that the use of double compound ratios provides better accuracy with less uncertainty than interpretations using relative ratios determined by individual compounds since there are possibilities of overlaps of ratios of PAH profiles from different sources. The diagnostic ratio plots of BaA/(BaA+Chry) vs Flur/(Flur+Py) and InP/(InP+BghiP) vs BaA/(BaA+Chry) for the sediment core samples collected from all stations suggests that the source of PAHs to Stations 26 and 27 were primarily combustion, unburned petroleum source dominated the source profile at station 28 located in the southern part of Kuwait close to the refineries, and a combination of sources at station 30, the most remote station.

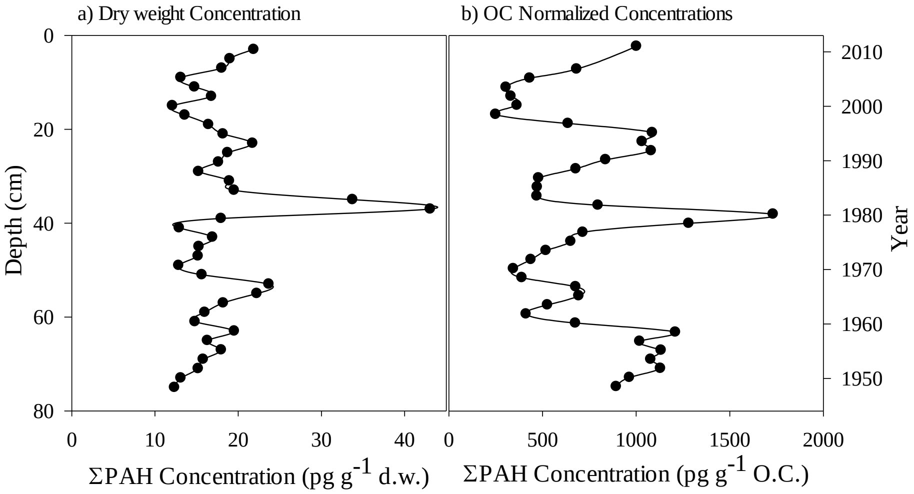

Fig 3. Historical profiles of ΣPAH concentrations in sediments at Station 26 on a (a) dry weight and (b) organic-carbon-normalized basis.

It can be seen that the concentrations of PAHs were higher within Kuwait Bay compared to the levels measured in the Open Gulf suggesting that point source inputs were important sources of POPs in Kuwait. The sedimentary record shows that the concentrations of most PAHs were low prior to the discovery of oil in Kuwait. The concentrations started to increase above pre-industrial background levels around the late 1970s and early 1980s with pulses in the profile corresponding to accidental or in some cases deliberate release of petroleum into the environment (e.g. the 1991 Gulf war)

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