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Petroleum Hydrocarbon Pollution after the Tasman Spirit Oil Spill of Coastal/Deep Sea Sediment along the Clifton Beach Karachi, Pakistan

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Abstract. An oil tanker, Tasman Spirit, carrying 67000 tons crude oil, got damaged near the Clifton Beach of Karachi, Pakistan and approx. 31,000 ton oil spilled into the sea. The distribution of aliphatic and aromatic hydrocarbons was determined in deep sea and surface sediment collected at 12 stations along the Clifton beach of Karachi, following the oil spill. Sampling was performed during 2003-2006, starting just after the accident of the oil tanker. Concentrations of PAHs (Σ16 parent components) and aliphatics were in the range of 0.09-560 µg/kg dw and 0.12-685 µg/kg dw, respectively, since the date of accident and after bioremedial measures. The highest concentrations were found within the radius of 50 km around the site, the area most heavily impacted by the spill, whereas at the stations, away from the ship, the concentrations were in the lower range without alkylated compounds. Addition of increasing amounts of ship fuel oil (taken from a Pakistani ship) to a representative sediment sample showed that measurable concentration of the Tasman Spirit oil was > 1 g/kg of sediment. The toxicity of selected samples of surface sediment from the coastal area near oil spill showed higher PAH concentrations; the average number of dead fauna was 90-95% within 3 days of oil spill which gradually decreased with the time.

Keywords: Tasman Spirit oil spill, Clifton beach, sediment, hydrocarbons, toxicity

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Introduction

The accident of grounding of oil tanker Tasman Spirit, transporting 67000 tons of Iranian crude oil, occurred near Karachi harbour along the Clifton beach, on the 27th July, 2003. The hull got perforated and approximately 31000 tones of crude oil spilled into the sea at the Karachi coast .The ship sank at 50 km offshore after leaking oil for 12 days. Being broken into two parts, it caused the largest oil spill that ever occurred at Karachi beach in the history of Pakistan.

Petroleum hydrocarbons (PHs) are composed of small and long chain aliphatic and aromatic hydrocarbons varying in molecular weight and toxicity. PAHs are mostly produced by incomplete combustion of organic matter or spillage of petroleum or petroleum by-products (Stark *et al.*, 2003; Mazeas and Budzinski, 2001; McRae *et al.*, 2000; Yunker *et al.*, 1999; Hammer *et al.*, 1998; Neff, 1995; 1979; O'Mally, 1994; Volkman *et al.*, 1992; Bjorseth and Ramdhal, 1983; Wakeham *et al.* 1980 a;b; Laflamme and Hites, 1978; Youngblood and Blumer 1975; National Academy of Science, 1972).

Immediately after oil spill more volatile compounds begin to evaporate increasing the viscosity and density of residues (Michel, 1992). Polyaromatic hydro-carbons (PAHs) are naturally present in crude oil (WHO, 1998) some of which are highly persistent in environment (Wong *et al.*, 2004; Machala *et al.*, 2001; Menzie *et al.*, 1992) and have strong bio-concentration capacity (Connell and Schuumann, 1988), toxicity, and sublethal effects on some aquatic organisms (Hartmann and Quinn, 1999) and creating diseases (Grimmer, 1983). Through bio-accumulation in the edible fishes and shell fishes, PAHs reach humans (Hartmann and Quinn, 1999) and due to their carcinogenic nature, may cause cancer (Freitag *et al.*, 1985). Sediment and biota have relatively strong affinity for lipophillic hydrocarbons and are their valuable indicators, (Kayal and Connell 1990; Connell and Hawker, 1986) in evaluating the petroleum effects; these are not affected by weathering conditions and seasonal changes (Zann, 1996).

In consideration of all the mentioned factors, the distribution of aliphatic and aromatic hydrocarbons was determined in deep sea and surface sediment collected at 12 stations along the Clifton beach of Karachi following the Tasman Spirit oil spill. Sampling was carried out during July 2003- December 2005. The sedimentary aromatic fractions were also analysed for

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possible effects of polyaromatic hydrocarbons (PAHs) on benthic biota.

Materials and Methods

Sampling. Sediment samples were collected from 12 sampling stations of the effected coastal area of Karachi (Fig. 1) located at five different points as indicated in Fig. 2; their GS values are given in Table 1. Samples were collected with stainless steel grab, deposited into new properly labelled plastic bags, placed in ice and brought to laboratory in intact condition. At laboratory all the samples were stored at -20 °C before processing and analysis.

Chemicals and reagents. Standard PAHs (16 compounds, each at 100, 200, 1000 or 2000 mg/mL), surrogate (d_{12}-chrysene) and internal standards (d_8-naphthalene) were all obtained from Dr. Ehresnstorfer's laboratory, Germany, and CRM from IAEA. Working standards of the micro-pollutants were prepared by combining the standard mixture with the corresponding IS stock solution. These solutions were further diluted with hexane to prepare calibration solution in the range of 0.001-10 ng/mL. All solvents used for sample processing and analyses (dichloromethane, hexane and methanol) were HPLC grade.

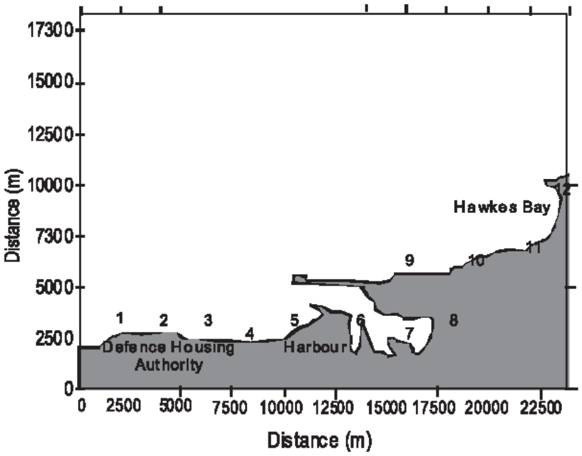

Fig. 2. Distance of selected sampling stations from the accident site and their location along the Clifton Beach.

Analytical procedure. Sample preparation (pre-GC). At the laboratory, samples were dried for 24 h at 60 °C, then copper powder was added and mixed well to remove sulphur from the sediment. Sediment sample

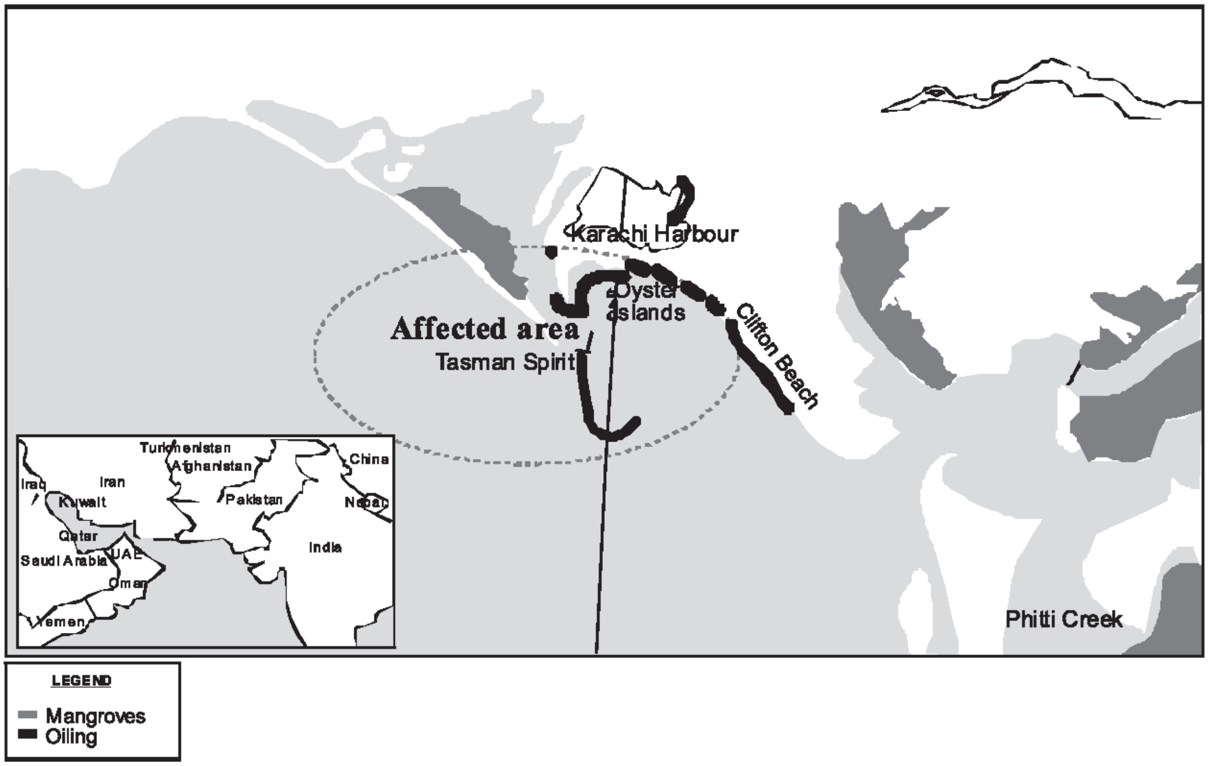

Fig. 1. Location of Tasman Spirit oil spill incident at Clifton Beach Karachi (Pakistan) on July 27, 2003.

Table 1. Sampling stations according to GPS

Sampling station	Longitude	Latitude
Sampling station # 1	65.58.46 E	23.47.25 N
Sampling station # 2	66.59.48 E	24.48.26 N
Sampling station # 3	67.01.43 E	24.47.53 N
Sampling station # 4	67.01.43 E	24.47.36 N
Sampling station # 5	66.59.24 E	24.47.16 N
Sampling station # 6	66.01.43 E	21.47.53 N
Sampling station # 7	77.01.43 E	30.47.36 N
Sampling station # 8	60.59.24 E	22.57.16 N
Sampling station # 9	67.59.48 E	23.48.26 N
Sampling station # 10	57.59.48 E	22.48.26 N
Sampling station # 11	57.01.43 E	29.47.36 N
Sampling station # 12	66.59.48 E	24.48.26 N

was spiked with surrogate (d12-cheysene) standard solution and homogenized well.

Saponification. All dried samples were saponified with 50 mL of 0.5 N methanolic potassium hydroxide solution for 10 h, filtered and evaporated to 1-2 mL on rotary evaporator and passed through silica gel column for purification and fractionation.

Purification/isolation. Saponified samples were purified through removing the interfering substances by adsorption column chromatography using silica gel as sorbent (WHO, 1998).

The concentrated extracts of saponification were fractionated by a deactivated silica gel/alumina column. The column was eluted first with 100 mL hexane containing aliphatic hydrocarbons then with 100 mL benzene containing aromatic hydrocarbons. Prior to injection, d8-napthalene was added as an internal standard. Finally, both fractions of aliphatic and aromatic hydrocarbons were evaporated down to 1-2 mL separately and run on GC.

Sample analysis. The samples were analyzed by the gas chromatograph (Perkin-Elmer Clarus 500) equipped with a fused silica capillary column (Elite-1; 30 m long, 0.53 mm i.d., 1.5 mm film thickness). FID was used as detector. The oven temperature programme was set at 60 °C (initial time, 10 min) to 140 °C at a rate of 2 °C/min and held for 10 min, 140 °C to 230 °C at a rate of 3 °C/min for 10 min. The inlet mode chosen was split-less and helium was used as carrier gas. Inlet and detector temperatures were 270 °C and 285 °C, respectively.

Quality control. The quality of data was assured through the analyses of appropriate certified reference materials. Deutrated surrogates and internal standards were used to compensate for losses involved in the sample extraction. The surrogate standard was used to monitor the method performance for each sample, while the internal standard was used to compensate for variance in final extracted volume, injection volume and instrument sensitivity. Analysis of blank samples was also carried out with each batch. Compounds were identified mainly by retention time. All the results for fishes and shellfishes were reported on wet-weight basis.

Results and Discussion

A total of 100 samples were collected at different times of the day from 12 sampling stations located at 5 points of the affected area. Complete sampling schedule and site information are given in Table 2.

Table 2. Sampling schedule and details

Position/location from the effected area	Distance	No. of samples	Sample description
Near the beach	5 km	40	Fishes
Latitude 24.48.26° N, Longitude 66.59.48° E	23.48 miles 37.7 km	15	Crabs, sediment, water and snails
Latitude 24.47.53° N, Longitude 67.01.43° E	25.64 miles 41.2 km	15	Crabs, sediment, water and snails
Latitude 24.47.36° N Longitude 67.01.43° E	27.3 miles 43.9 km	15	Crabs, sediment, water and snails
Latitude 24.47.16° N, Longitude 66.59.24° E	28.08 miles 45.1 km	15	Crabs, sediment, water and Snails

The study is spread over 4 years, from the year 2003 to 2006; yearly data are given in order in Table 3-6. In 2003 and 2005, 5 stations were covered while 12 stations were covered in 2004 and 2006 along those 5 points. Total concentration of 16 parent sedimentary PAHs were determined for comparison with the other data of incidents similar to that of Tasman Spirit that occurred in other parts of the world and a general ecotoxicity assessment was made. The GC profile of the Σ PAH fractions recovered from sediment samples exhibited general features of the coastal environment, with the predominance of aliphatic and polyaromatic compounds based on dissolved and unsolved hydrocarbons.

PAHs concentration in the analyzed sediment samples collected from different sampling stations was different with respect to individual components and concentration which may be due to the spreading pattern of the spilled oil as well as adsorbing properties of the sediment for

Table 3. PAHs contamination level in sediment samples in 2003 (ppm)

Components	St 1, A	St 2, A	St 3,A	St 1, B	St 2, B	St 3,	St 4
Naphthalene	0.176	4.862	0.242	0.623	<LOR	<LOR	<LOR
Acenaphthylene	<LOR	4.118	<LOR	<LOR	<LOR	<LOR	<LOR
Acenaphthene	<LOR	3.569	<LOR	<LOR	0.481	<LOR	1.181
Fluorene	<LOR	3.841	<LOR	<LOR	<LOR	<LOR	<LOR
Phenanthrene	0.508	3.504	<LOR	<LOR	0.096	<LOR	0.237
Anthracene	<LOR	3.518	0.571	<LOR	<LOR	0.979	<LOR
Fluoranthene	0.254	3.474	<LOR	<LOR	0.154	<LOR	0.378
Pyrene	<LOR	3.682	0.349	0.257	0.568	0.742	1.396
Benzo(a)anthracene+Chrysene	<LOR	6.886	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(b)fluoranthene+Benzo(k) fluoranthene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(a)pyrene+Dibenzo(a,h)anthracene	<LOR	6.214	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(ghi)perylene+Indeno(1,2,3-c,d)pyrene	<LOR	5.034	<LOR	<LOR	<LOR	<LOR	<LOR
Sum	0.937	48.704	1.163	0.880	1.299	1.721	3.191

*LOR= Limit of reporting; ** A & B= are the two points at a station at a distance of 5 km.

Table 4. PAHs contamination level in sediment samples in 2004 (ppm)

Components	St 1	St 2	St 3	St 4	St 5	St 6	St 7	St 8	St 9	St 10	St 11	St 12
Naphthalene	0.225	0.255	0.255	0.236	0.173	0.247	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Acenaphthylene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Acenaphthene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.003	<LOR	0.134
Fluorene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.002	<LOR
Phenanthrene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.20
Anthracene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Fluoranthene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Pyrene	0.322	0.365	0.365	0.267	0.23	0.297	0.227	0.210	0.24	<LOR	0.002	0.25
Benzo(a) anthracene + Chrysene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.006	<LOR	<LOR
Benzo(b)fluoranthene+ Benzo(k) fluoranthene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(a)pyrene+ Dibenzo(a,h) anthracene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.108
Benzo(ghi)perylene+ Indeno(1,2,3-c,d)pyrene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Sum	0.548	0.620	0.620	0.503	0.376	0.544	0.227	0.210	0.204	0.009	0.005	0.721

*LOR= Limit of reporting.

PAHs. Average concentrations of Σ PAH and Σ C_5-C_{25} in the sediment (in ng/g of dry weight) of the most significant and representative 8 stations during the years 2003 and 2004 are shown in Table 7.

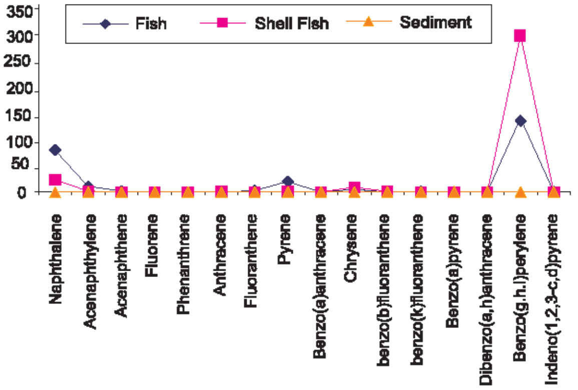

Fig. 3. Comparison of oil pollution status due to Tasman Spirit: PAHs trend in fish, shell fish and sediment.

The GC profile of the Σ aliphatic and polyaromatic fractions represented the level of the individual PAH and AH analyzed not only in sediments but also in samples of marine fauna as well as water samples collected from the affected area during the study; their comparison is given in Fig. 3. High levels of PAHs were observed in all sediment samples collected nearest to the oil impacted area after 28 months of the spill comparative to the previous monitoring made after 18 months at the same site which is the evidence of bio-accumulation of PAHs. Unfortunately, any background data for the area prior to the Tasman Spirit oil spill is not available. It is, therefore, suggested that the contamination found in the marine environment is not solely but mainly due to this spill. Intact hydrocarbons enter the oceans from a variety of sources, including decaying phyto- and zoo-planktons, routine tanker and shipping operations, terrestrial runoffs, atmospheric fallouts,

Table 5. PAHs contamination level in sediment samples in 2005 (ppm)

Components	St 1	St 2	St 3	St 4	St 5
Naphthalene	0.009	<LOR	0.139	<LOR	<LOR
Acenaphthylene	<LOR	<LOR	<LOR	<LOR	<LOR
Acenaphthene	<LOR	<LOR	<LOR	<LOR	<LOR
Fluorene	<LOR	<LOR	<LOR	<LOR	<LOR
Phenanthrene	0.023	<LOR	<LOR	<LOR	<LOR
Anthracene	<LOR	<LOR	<LOR	<LOR	<LOR
Fluoranthene	0.026	<LOR	<LOR	<LOR	<LOR
Pyrene	<LOR	0.028	<LOR	0.164	0.172
Benzo(a)anthracene+Chrysene	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(b)fluoranthene+Benzo(k) fluoranthene	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(a)pyrene+Dibenzo(a,h)anthracene	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(ghi)perylene+Indeno (1,2,3-c,d)pyrene	<LOR	<LOR	<LOR	<LOR	<LOR
Sum	0.0586	0.028	0.139	0.164	0.172

*LOR= Limit of reporting.

Table 6. PAHs vontamination level in sediment samples in 2006, (ppm)

Components	St 1	St 2	St 3	St 4	St 5	St 6	St 7	St 8	St 9	St 10	St 11	St 12
Naphthalene	0.001	<LOR	<LOR	0.002	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Acenaphthylene	<LOR	<LOR	<LOR	<LOR	<LOR	0.009	<LOR	<LOR	<LOR	0.001	<LOR	0.006
Acenaphthene	<LOR	0.003	<LOR	<LOR	<LOR	<LOR	<0.005	<LOR	0.003	<LOR	<LOR	<LOR
Fluorene	<LOR	<LOR	<LOR	0.006	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.008	<LOR
Phenanthrene	<LOR	<LOR	0.005	<LOR	<LOR	0.004	<LOR	0.005	<LOR	<LOR	<LOR	<LOR
Anthracene	0.002	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.005
Fluoranthene	<LOR	<LOR	<LOR	<LOR	0.006	<LOR	<LOR	<LOR	<LOR	0.003	<LOR	<LOR
Pyrene	<LOR	<LOR	0.004	<LOR	<LOR	<LOR	<LOR	<LOR	0.004	<LOR	0.004	<LOR
Benzo(a)anthracene+Chrysene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	0.008	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(b)fluoranthene+Benzo(k) fluoranthene	<LOR	0.001	<LOR	<LOR	<LOR	<LOR	<LOR	0.0061	<LOR	<LOR	<LOR	<LOR
Benzo(a)pyrene+Dibenzo(a,h)anthraene	<LOR	<LOR	<LOR	<LOR	0.012	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Benzo(ghi)perylene+Indeno(1,2,3-c,d)pyrene	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
Sum	0.003	0.004	0.009	0.014	0.018	0.013	0.013	0.011	0.007	0.004	0.012	0.011

*LOR = Limit of reporting.

natural seepage and from shipping and offshore well disasters.

Individually, minimum concentration (0.014 ppm) was found to be that of naphthalene while maximum (11.923 ppm), that of dibenzo (a,h)anthracene; concentration of the 7 of 14 compounds increased in the order of fluorene (0.012), anthracene (0.027), chrysene (0.057), pyrene (0.188), benzo(a)anthracene (0.012), phenanthrene (0.027), and benzo(a) pyrene (0.612 ppm). Also the average minimum concentration (0.008 ppm) was that of naphthalene and maximum (1.325 ppm) that of dibenzo (a,h)anthracene (Fig. 4).

It was observed that the spilled oil rarely dispersed in the water column and mainly sedimented in the form of tar balls in the deep sea sediments which was attributed

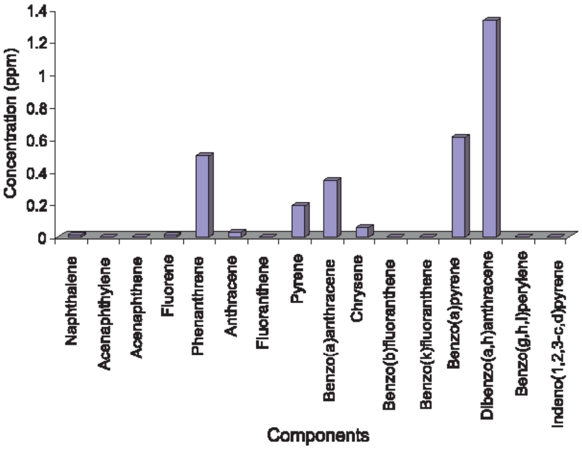

Fig. 4. Average PAH concentration of individual component.

to the heavy nature of the spilled oil. Concentrations in the range of 3-450 mg of total PAHs per kg of dry wt sediment were reported in subtidal sediments (Pastor *et al.,* 2001) from the Arabian Gulf following War (Readman *et al.,* 1992). However, average concentration of individual component of PAHs in this study (Fig. 4) was found lower than the value reported ten years later in 1999; the median sediment concentration was of 117 mg/kg (Page *et al.,* 2002).

After analysis of a number of sediment samples, average concentrations of polyaromatic and aliphatic hydrocarbons from different sample stations during 2003-2006 are given in Table 3-6 in order and level of the oil pollution is given year-wise given in Fig. 5.

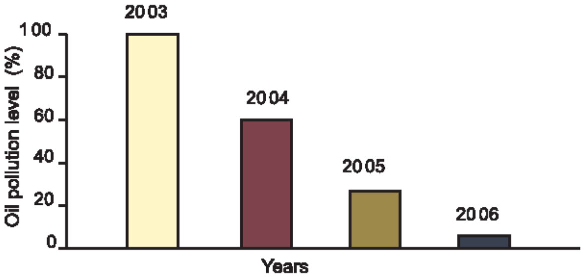

Fig. 5. Level of oil pollution at Clifton beach, during the period of study.

Table 7. Average concentrations of ΣPAH and ΣC5-C25 in sediments (ng/g dry weight) at 8 representative stations

Area	Survey year	ΣPAHs (ng/g)	ΣAliphatic (ng/g)
Clifton beach,			
Station # 1	August, 2003	10.9–5.4	5.0–7.0
Station # 2	March , 2004	<0.04–109	<0.04–5.0
Station # 3	August, 2003	8.2–7.2	n.d
Station # 4	March , 2004	35–65	4.3–2.3
Station # 5	August, 2003	11.6–72	0.2–40
Station # 6	March. , 2004	23.3–12	n.d*
Station # 7	August, 2004	10.56–13.4	0.20–1.5
Station # 8	March , 2004	20.06–3.9	0.03–0.7

* n.d. = not detected.

The components of Tasman Spirit oil, found in sediment samples collected during 2003, varied from those found in 2006. Concentration of components also varied with respect to the sampling stations, the lowest PAHs concentration 0.089 ppm being at sampling station 2 and the highest 0.556 ppm, at sampling station 4.

Physicochemical properties of the oil were measured and showed high density (0.97 kg/L) and viscosity (29, 500 cSt at 15 °C) as well as a high content of resins. The stable emulsions with water were broken-up into fragments of enough density to sink during its way towards the shore, favoured by the humid weather conditions following the spill. These conditions helped wash the beached oil back into the sea, mixed with sand. In fact, tar aggregates of 1-20 cm in diameter, amounting upto 300 kg/km^2 were found in January 2003, during sampling of bottom fauna by beam trawling, in areas of the continental shelf below the main drifting path of the spill (Fig. 1). The oil spill, immediately after the accident caused colossal damage to the environment, marine life and human beings covering approx. 2062 km marine area exposing about 300,000 persons to toxic VOCs released by evaporation into the air from the oil spill.

Conclusion

Studies have demonstrated that levels of PAHs and AHs as low as 1 µg/g in sediments cause toxic and long-term effects. The present detailed study was spread over four years; the monitoring of the levels of PAHs and AHs, from July 27,2003 up to December 2006, started with making an initial survey so as to know the current situation concerning PAH levels at the spill affected area. Though it is concluded that no harmful oil pollution persisted up to 2006 due to considerable bioremedial measures that were taken in this area, regular monitoring for at least the next 10 years is recommended for recording the decrease and/or the increase in hydrocarbon level. The studies should be focused on determining the effects of oil on the changes in surface and deep sea sediments and strict improvements in the existing environmental legislation should be made to cover all aspects of pollution control management, within the country.

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