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PAH Composition of Water Based Drilling Mud and Drill Cuttings in the Offshore Region, East Coast of India

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Abstract As a consequence of offshore drilling, used Water Based Drilling Muds (WBMs) are typically disposed off, by discharging into the sea; such a disposal does not fully eliminate the environmental hazards. Hence, in this study, 2, 3, 4 and 5 ringed polycyclic aromatic hydrocarbons (PAHs i.e. naphthalene, fluorene, phenanthrene, fluoranthene, chrysene and benzo (a) pyrene) were determined from the WBMs and associated drill cuttings obtained from varying depths(viz. 150, 300 and 600 m) from three offshore wells present in East coast of India. In both WBMs and drill cuttings, concentration of naphthalene was maximum i.e. 81.59 ± 2.73 and 39.87 ± 2.40 mg/kg respectively, while benzo (a) pyrene was minimum i.e. 0.19 ± 0.07 and 0.12 ± 0.03 mg/kg respectively. The WBMs contained significantly ($p < 0.05$) higher PAH concentration than drill cuttings. The individual PAH concentration significantly ($p < 0.01$) increased with increasing depth in each well.

Keywords Water based drilling muds · Drill cuttings · Disposal · Environmental hazards · Polycyclic Aromatic Hydrocarbons

The major discharges associated with exploratory and development drilling are drill cuttings and drilling fluids. It has been reported that from 200 to about 1,000 metric tons of drilling fluid solids and a similar amount of drill cuttings may be discharged intermittently to the ocean during drilling of an offshore well (Neff 1987). The drilling of wells generate significant quantities of wastes, which have been estimated to account for up to 2% of the total waste volume generated in the United States. This waste comprises of drilling fluids and the cuttings generated during drilling. Drilling fluids (drilling muds) are used to remove cuttings from the hole, prevent blowouts by controlling back pressure, and maintain the integrity of the hole to permit the installation of a casing, and to cool and lubricate the drill bit. The three major types of drilling fluids are: water based where the fluid phase is water, oil-based where the fluid phase is oil, and synthetic-based where the fluid phase is a synthetic base compound such as an ester (Burke and Veil 1995). Water-based drilling fluids are the most common and often contain a variety of chemicals, which are formulated as required from a generally limited list of additives. More than 90% of the total ingredients of most water-based drilling fluids used offshore in US waters consist of four materials: barite, bentonite, lignite and lignosulphonate (Hinwood et al. 1994). While more than 1,000 products are available for formulating drilling fluids, the total number of ingredients in most drilling fluids is in

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the range of 8–12. The large numbers of oil-production wells in the North Sea and concurrent activities (e.g., drilling, pipelines, shipping) have generated concern in respect to the associated hydrocarbon contamination by organizations such as ICES, OSPARCOM and NSTF (Ferm 1996). It has been reported (AURIS 1993) that a large proportion of the oil and other hydrocarbons first deposited onto the seabed of the North Sea are still unchanged with time. The loss to the water column during settlement of cuttings, and further loss due to microbial and chemical degradation of hydrocarbons, has not resulted in a substantial decrease in quantities following discharge (AURIS 1993). The quantity and integrity of hydrocarbons still remaining in the piles is a result of the piles' depleted dissolved oxygen content, the type of drilling fluids used, the low temperatures encountered, and the resulting decimation of benthic communities present due to cuttings deposition (smothering) and composition. Investigations into environmental effects associated with North Sea (offshore) drill cutting piles have shown a significant impact on the benthic environment within close proximity (<500 m) to the drilling platforms (Hartley and Ferbrache 1983; Davies et al. 1984; Gray et al. 1990; Kroncke et al. 1992; Plante-Cuny et al. 1993; Daan and Mulder 1994, 1996; Daan et al. 1992).

Even though the used Water Based Fluids are typically disposed off, by discharging into the sea, in accordance with local regulations (Int. Ass. of Oil & Gas Producers 2003), such disposal does not fully eliminate the environmental hazards. Some comparative studies showed that WBF do not always meet strict ecological requirements (Sorbye 1989; Wills 2000). As reported by Patin (1999), Water Based Drilling Muds (WBMs), while preferred over Oil Based Muds or Synthetic Based Muds (OBMs or SBMs) for obvious environmental reasons, can still damage marine life. Although the main components of WBMs maybe relatively harmless when heavily diluted in the sea, like other muds, they commonly contain additives that can be extremely toxic, even in low concentrations (Wills 2000). The comprehensive studies by Patin (1999) and Wills (2000) point outs that despite moves to increase reinjection and shipment ashore for disposal, up to 80% of drilling wastes and chemicals still enter the sea in one way or another. The PAHs are the organic compounds sometimes present in used WBM and associated drill cuttings that pose the greatest risk of bioaccumulation and toxicity to the marine organisms such as fishes (Neff 2005). The rapid growth of offshore oil and gas exploration and production on the eastern Indian continental shelf has generated the need for both general and region specific scientific information on the environmental consequences of drilling activities. In India, WBMs are currently used in the KG Basin, Block 98/4, which has an area of approx. 9,940 km^2 with Bathymetry ranging from 800 to 3,100 m along the East Coast of India (Fig. 1). The discharge of drilling wastes poses the greatest risk of bioaccumulation and toxicity to the marine organisms such as fish of ecological and commercial value (which are subsequently consumed by the humans). Generally, the WBMs are synthesized in such a way so as to avoid inclusion of aromatic hydrocarbons however; crude oil may contaminate the mud

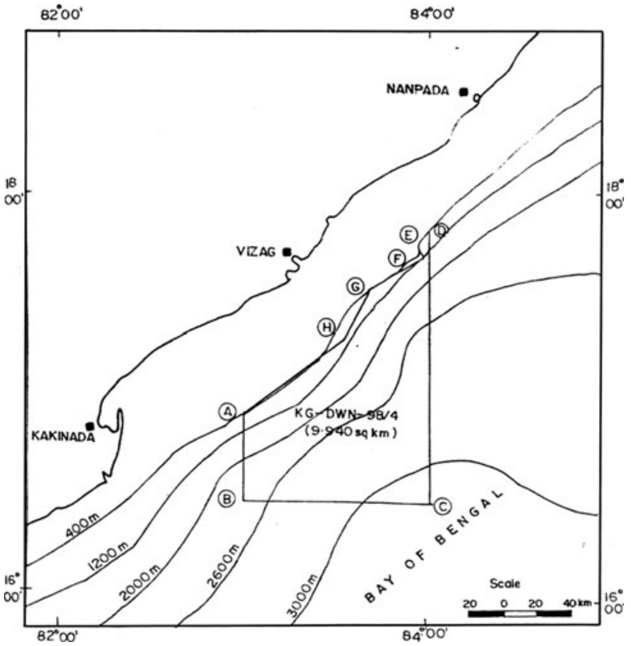

Fig. 1 KG-Basin, Block 98/4 along with wells 1, 2 and 3 in the study area

Table 1 Composition of Water Based Mud used for drilling ultra deep-water wells in Kaveri-Godavari (KG) Basin, Block 98/4 region, East coast of India

Product	Generic name	Conc. (ppb)	Order of addition
Sodash		0.5	1
Caustic soda		0.5	2
M-IPAC Ul	Poly anionic cellulose	1.5	3
M-IPAC R	Poly anionic cellulose	0.5	4
DUOVIS	Xanthan gum	1.5	5
Potassium chloride		40	6
Sodium chloride (%)		25	7
GLYDRILL MC (PAG)	Poly alkylene glycol	12	8
MIcide	Biocide	0.3	9
CONQOR 303A	Corrosion Inhibitor	0.1	10
MEG	Monoethylene glycol (As per requirement)	10%	11
Barite	As per requirement		12

Table 2 Quality control data of synthetic samples

SN	Naphthalene		Fluorene		Phenanthrene		Fluoranthene		Chrysene		Benzo(a)pyrene	
	OC (μg/l)	PR	OC (μg/l)	PR	OC (μg/l)	PR	OC (μg/l)	PR	OC (μg/l)	PR	OC (μg/l)	PR
1	1	96.0	1	96.3	1	96.6	1	96.3	1	98.3	0.1	95.9
2	5	97.0	5	96.5	5	97.2	5	97.6	5	97.9	0.5	96.3
3	10	97.3	10	95.0	10	95.8	10	97.8	10	96.8	1.0	96.9
4	15	95.0	15	92.5	15	94.0	15	96.0	15	97.5	1.5	97.3

OC original concentration, *PR* percent recovery

Spiked with Certified Reference Material, obtained from M/s Acros Organics Ltd. Belgium

For each spiked sample, a total of 3 trail runs (n = 3) were carried out. The data was collected and mean ± standard deviation was computed. The standard deviation values for each of the spiked PAH sample were less than 8% of the mean value. Furthermore, the percent recovery for all the PAHs was more than 92.0%. This indicated a fairly consistent result and ensured desired quality control. Method detection limits were found to be 0.05–0.617 μg/kg

Table 3 Concentrations of PAHs recovered from drilling mud (mg/kg) (n = 15)

Depth	Mean ± SD	Minimum	Maximum	*p*
Naphthalene				
S	1.93 ± 0.64	1.38	2.84	<0.01
M	10.03 ± 0.14	9.84	10.22	
B	81.59 ± 2.73	79.24	85.82	
Fluorenes				
S	0.04 ± 0.04	0.00	0.10	<0.01
M	0.83 ± 0.15	0.60	0.99	
B	8.60 ± 0.78	7.55	9.44	
Phenanthrenes				
S	0.57 ± 0.08	0.47	0.72	<0.01
M	0.48 ± 0.24	0.26	0.82	
B	9.97 ± 1.05	8.54	11.15	
Fluoranthenes				
S	0.14 ± 0.04	0.09	0.20	<0.01
M	0.36 ± 0.20	0.09	0.56	
B	0.73 ± 0.28	0.46	1.15	
Chrysenes				
S	0.10 ± 0.02	0.08	0.15	<0.01
M	0.33 ± 0.14	0.18	0.54	
B	0.58 ± 0.13	0.40	0.79	
Benzo(a)pyrenes				
S	0.01 ± 0.01	0.00	0.02	<0.01
M	0.08 ± 0.01	0.07	0.10	
B	0.19 ± 0.07	0.10	0.30	

S surface (150 m), *M* middle (300 m), *B* bottom (600 m)

Table 4 Concentrations of PAHs recovered from drill cuttings (mg/kg) (n = 15)

Depth	Mean ± SD	Minimum	Maximum	*p*
Naphthalene				
S	0.46 ± 0.48	0.03	1.20	<0.01
M	5.73 ± 0.49	5.00	6.30	
B	39.87 ± 2.40	36.70	42.48	
Fluorene				
S	0.01 ± 0.01	0.00	0.03	<0.01
M	0.38 ± 0.08	0.24	0.48	
B	3.57 ± 0.94	2.36	4.70	
Phenanthrene				
S	0.25 ± 0.05	0.16	0.34	<0.01
M	0.40 ± 0.21	0.14	0.76	
B	4.60 ± 0.53	3.86	5.20	
Fluoranthene				
S	0.08 ± 0.06	0.00	0.18	<0.01
M	0.13 ± 0.09	0.03	0.26	
B	0.43 ± 0.06	0.35	0.54	
Chrysene				
S	0.03 ± 0.02	0.01	0.06	<0.01
M	0.14 ± 0.05	0.09	0.24	
B	0.47 ± 0.25	0.26	0.85	
Benzo(a) pyrene				
S	0.00 ± 0.00	0.00	0.00	<0.01
M	0.02 ± 0.02	0.00	0.05	
B	0.12 ± 0.03	0.09	0.16	

S surface (150 m), *M* middle (300 m), *B* bottom (600 m)

as well as the drill cuttings, introducing aromatic hydrocarbons when drilling through hydrocarbon bearing formations (Neff et al. 2000). Hence, the purpose of the present investigation was to evaluate the impacts in environment due to offshore drilling activities. In view of the present marine environmental circumstances the generated information necessitates wider distribution.

The present study deals with determination of PAHs concentrations in composite samples of WBM, and drill cuttings, which were obtained from three different drilling depths viz. surface (150 m), middle (300 m) and

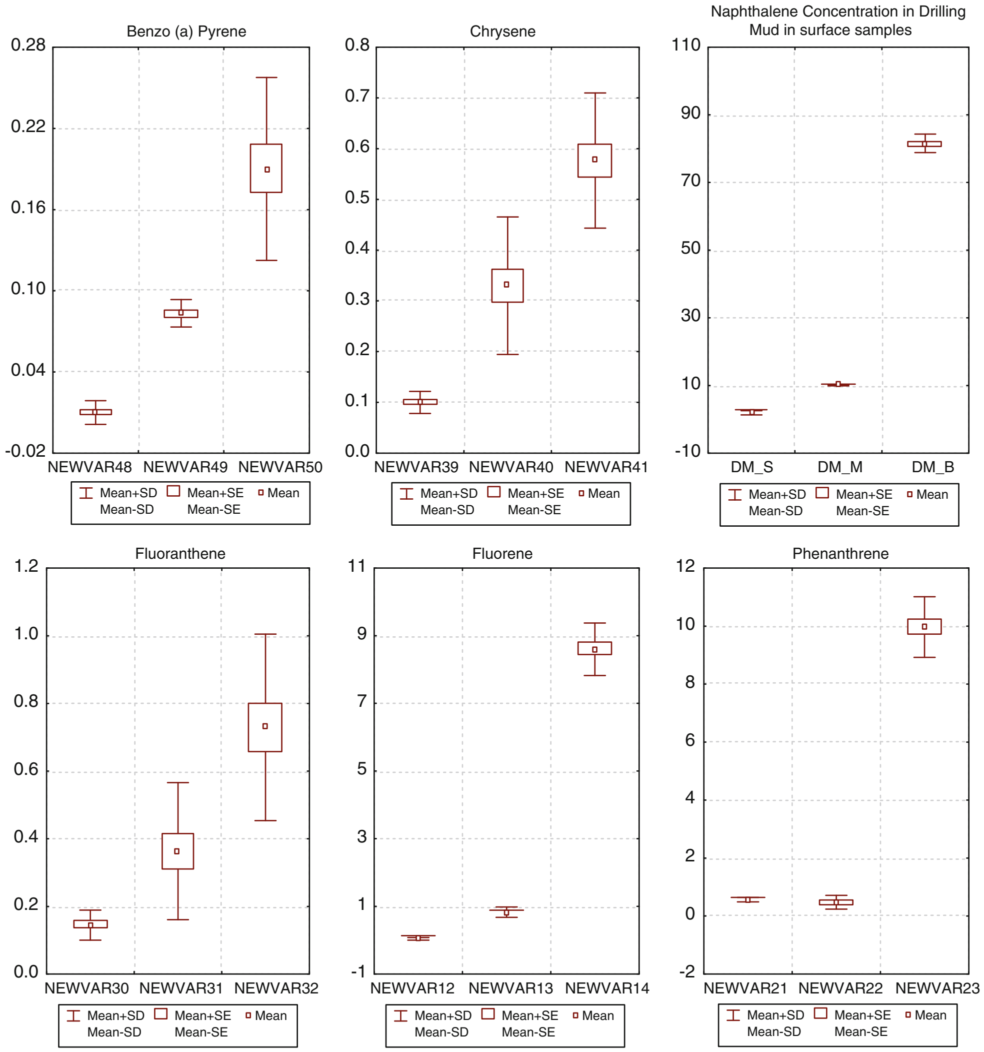

Fig. 2 PAH composition of drilling muds. The new variables depicted in the column 1, 2 & 3 indicate the concentration of individual PAHs at the three drilling depth viz. surface (150 m), middle (300 m) and bottom (600 m) respectively

bottom(600 m), in three wells in the Kaveri-Godavari (KG) Basin, Block 98/4, East coast of India.

Materials and Methods

The drill mud and associated cuttings used in this study were obtained from three wells at three different depths viz. surface (150 m), middle (300 m) and bottom (600 m) on the east coast of India, in the year 2008–2009. Three replicate composite samples were collected in amber glass bottles at each of the three prospective well sites for the purpose of estimating small-scale variability in this region. The samples were refrigerated at 4°C and protected from light. Table 1 gives the composition of Water based Mud used for drilling ultra deep-water wells in this region. The drill mud samples (250 mL each) were subjected to liquid–liquid extraction by means of a separatory funnel (Method 6410B, Standard methods, APHA, AWWA, WEF 2005), whereas the drill cutting samples (2 g each) were subjected to soxhlet extraction (Method 5520 D, Standard Methods, APHA, AWWA, WEF, 2005) and in both the cases, methylene chloride (Dichloromethane, DCM; HPLC grade, E. Merck, Germany) was used as the solvent. The extracts were cleaned up in a silica gel column, and then concentrated to 1 mL over a Kuderna Danish evaporating apparatus, on a boiling (100°C) water bath. The polycyclic aromatic hydrocarbons (PAH) analyses were performed using Gas chromatography (Agilent 5973N, USA) coupled to a Mass selective Detector (GC/MS) in Selective Ion Monitoring (SIM) mode (Method 6410B, Standard Methods, APHA, AWWA, WEF 2005). The following GC (Ultra 2, 0.17 μm capillary column, Supelco, USA) conditions were used for the analysis; split less injection

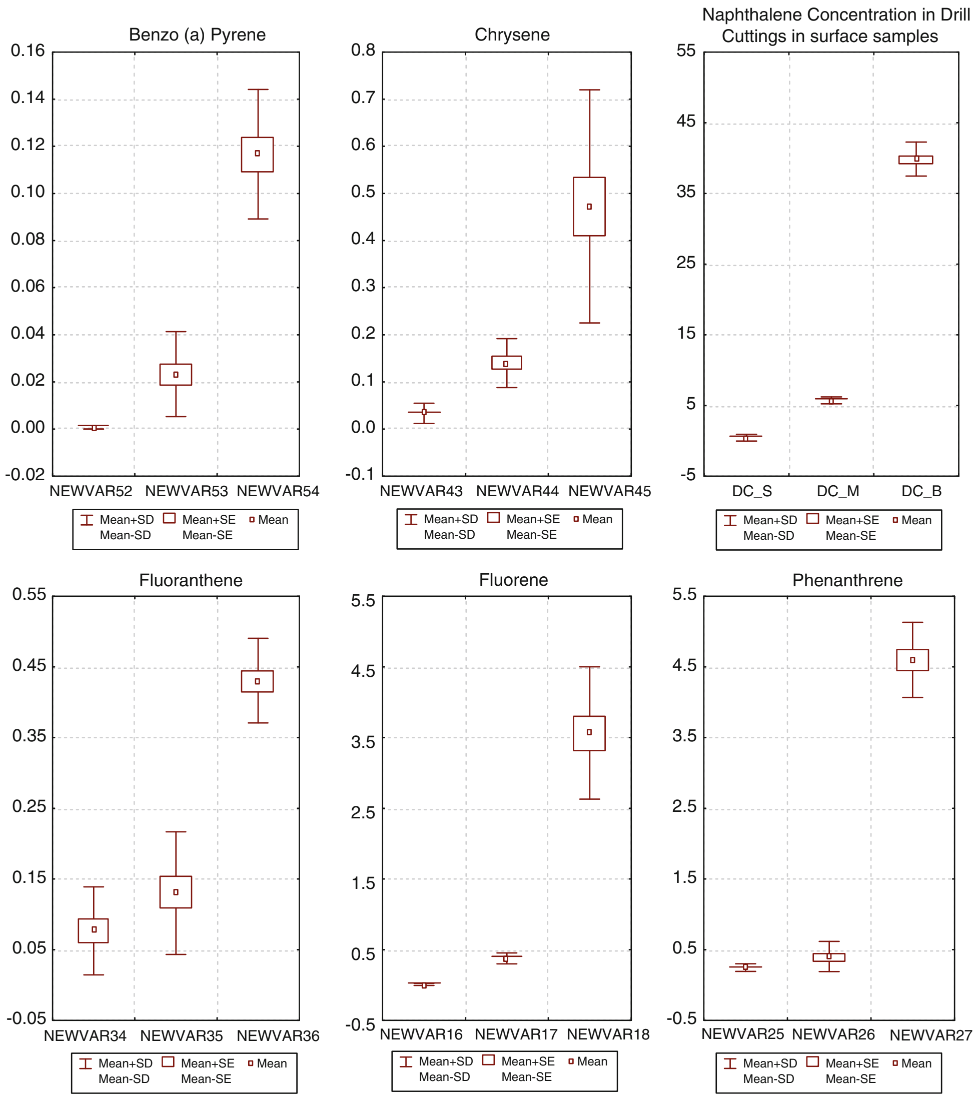

Fig. 3 PAH composition of drill cuttings. The new variables depicted in the column 1, 2 & 3 indicate the concentration of individual PAHs at the three drilling depth viz. surface (150 m), middle (300 m) and bottom (600 m) respectively

225°C; temperature programs 60°C hold 2 min ramp at 6°C/min to 300°C hold 13 min. A duplicate, certified reference material and operational blank was routinely performed with each batch of 10 samples. Six parent PAHs (Naphthalene, Fluorene, Phenanthrene, Fluoranthene, Chrysene and Benzo (a) pyrene) were quantified. The standards were obtained from M/s Acros Organics Ltd., Belgium. Table 2 presents the results of quality control and method detection limits.

Statistical analyses were performed using Statistica software (Texas, US). Data presented are the mean PAH concentrations estimated in select water based drilling mud and drill cutting samples. Data for each parameter was evaluated for statistical significance using one-way analysis of variance (ANOVA) to compare the means, considering exposure concentration as independent variable. The alpha level was set at 0.05.

Results and Discussion

Tables 3 and 4 show the average PAH concentrations determined from WBM and drill cuttings samples from KG-Basin, Block 98/4. Tables 3 and 4 show that individual PAH concentrations increased with depth in each well. A similar trend was observed in the drill mud and cuttings samples in Point Arguello Field, California (Neff 2005). EPA proposes to establish a PAH content limitation of 0.001%, or 10 parts per million (ppm), weight percent PAH expressed as phenanthrene for base fluids (USEPA 1999).

Both Drill Mud and Drill Cuttings Samples contained phenanthrene within this limit. Figures 2 and 3 depicts that at all depths the drilling muds contained higher concentrations of individual PAHs than the cuttings, suggesting that the PAHs were derived primarily from the petroleum additives in WBM and not the geological formation.

This may be explained based on the fact that small amounts of petroleum products (such as oils, synthetic liquids, graphite, surfactants, glycols, glycerin) may be added to WBM for lubrication (Neff 2005) with increasing depth in the wells. It was observed that the Naphthalene concentrations in DM samples of all 3 wells was of the highest order while the Benzo(a)pyrene concentrations were lowest. Although WBM containing PAHs are more toxic than those without any hydrocarbons, the drill cuttings in this case do not contain sufficient PAHs to harm bottom-living communities. Petroleum hydrocarbon concentrations greater than about 50–60 mg/kg in cuttings piles often are associated with altered benthic community diversity (Neff 2005). However, WBM wastes can smother marine life with artificial sediments or suffocating it with plumes of superfine suspended particles (USEPA 1999). It is therefore vitally important, even when no OBMs or SBMs are used to minimize the discharge of drilling wastes if at all possible. Monitoring of any chemical inputs from offshore exploration and oil and gas development in the offshore regions is important to be able to distinguish the “Environmental Baseline” from potential future impacts.

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