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(Q)SARs as custodians against risk on chemicals and tool in decision-making frameworks to predict ecological effects and environmental fate of chemical substances

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ABSTRACT

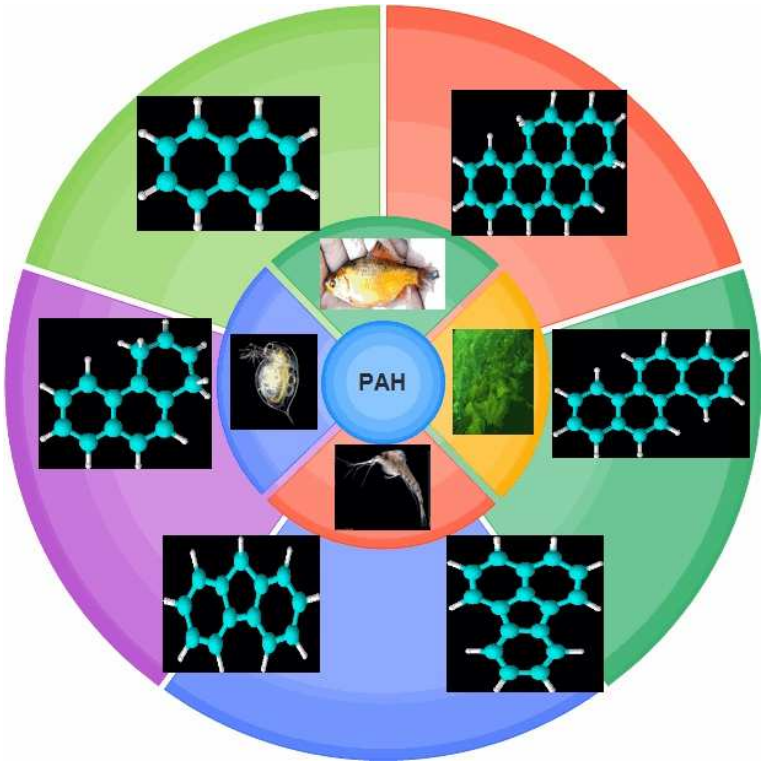
In the past few decades there has been increasing concern about the exposure and impacts of chemicals on humans and environmental organisms in the society. Water-based drilling fluids (WBMs) are the most common in exploratory and development drilling; they contain additives that can be extremely toxic, even in low concentrations. 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). Hence, the purpose of the present investigation was to evaluate the toxicological impacts in environment due to offshore drilling activities. The present study deals with determination of PAH concentrations in composite samples of WBM, and drill cuttings, which were obtained from three different wells in the Kaveri-Godavari (KG) Basin, East coast of India and the ecological toxicity prediction of these chemicals to the aquatic community. In both WBMs and drill cuttings, concentration of naphthalene was in highest concentration, while benzo (a) pyrene was lowest. 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. ECOSAR "estimation methods" can be used to fill data gaps where little or no experimental measured data exists. The toxicity of the PAHs (EC50/LC50) to fish, green algae, daphnid and mysid estimated can be used to predict toxicity to a general aquatic community. Monitoring of any chemical inputs from offshore exploration and oil & gas development in the offshore regions is important to be able to distinguish the "Environmental Baseline" from potential future impacts.

Keywords: Water Based Drilling Muds, Drill cuttings, Ecotoxicity, Polycyclic Aromatic Hydrocarbons, ECOSAR.

INTRODUCTION

In the past few decades there has been increasing concern about the exposure and impacts of chemicals on humans and environmental organisms in the society. This has led to the implementation of stringent chemicals legislation in many industrialized countries and initiation of ambitious risk assessment and management programmes. Such a realization, coupled with increasing awareness to animal welfare concerns, has prompted the development and application of various (computer-based) estimation methods in the regulatory assessment of chemicals [1]. Amongst the available options for environmental cleanup, technologies based on biological remediation have emerged as low-cost, low-maintenance, environment-friendly, and renewable technologies for potential *in situ* remediation of organic and inorganic contaminants. However, there are certain limitations in biological species used in these technologies and it is desirable to know in the first instance whether a contaminant would need remedial action, and whether a biological process would be suitable to breakdown or remove it from the environment. This is where

computational models based on structure-activity relationship can provide a quick assessment to support decision making. The (Q)SAR models and expert systems can help prioritize contaminants on the basis of potential toxicities, and inform on their likely behavior and fate in the environment. This information is in turn helpful in the choice of appropriate remediation technologies, as well as in identifying the recalcitrant chemicals that can be monitored as markers for the success of remediation action [2].



While a large body of information is available on the environmental effects of chemicals, we know much less about their ecological effects. An understanding of the ecotoxicity of chemicals is therefore essential if we are to accurately assess the environmental risks of synthetic chemicals [3]. The fundamental hypothesis behind a quantitative structure-activity relationship (QSAR) model is that a chosen property (*e.g.* toxicity) can be described in relation to a chemical, which at the same time is described using certain parameters. An approach close to QSAR is the so-called structure-activity relationship (SAR) model. These models express the relationship between a certain chemical property (*e.g.* fragment) and the effect (*e.g.* carcinogenicity) in a qualitative way (carcinogenic or non-carcinogenic), without assigning a continuous numerical value to the toxicity, such as a specific quantitative dose, which can have a wide range of values. In the field of aquatic toxicology, QSARs have been developed as alternative tools for predicting the toxicity of chemicals, when little or even no empirical data are available. Elaboration of SARs (structure-activity relationships) or some other computational toxicity prediction models is primarily based on experimentally measured toxic effects of chemicals. Therefore, there is a direct relationship between the amount and quality of available information on toxicity of different chemicals towards different test species and adequacy of the models. The majority of toxicity data for chemicals available for standard freshwater test organisms have been generated using standard test media; as a result, the information concerning toxicity of chemicals in natural waters is limited. Environmentally irrelevant conditions in standard toxicity tests reduce their predictive power for environmental risk assessment. The application of predictive QSARs has the ability to not only provide a high level of protection of human health and the environment, but also can reduce animal testing to a minimum for the assessment of the hazardous properties of substances. Thus, expectations towards *in vitro* studies and QSARs (quantitative structure-activity relationship) are very high. EPA/OPPT [U.S. EPA's Office of Pollution Prevention and Toxics (OPPT)] has developed a screening level model ECOSAR. If no measured or analog data are available, screening level models such as the ECOSAR may be used to predict toxicity values that can be used to indicate which chemicals may need further testing or characterization. The information generated will be available to industry and other stakeholders. The use of such models in the early stages of research and development or prior to submission of notifications to the Agency, will result in safer chemicals entering commerce and prevent an unreasonable risk to human health or the environment.

Drill cuttings and drilling fluids are the major discharges associated with exploratory and development drilling [4]. 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 mud (WBM) where the fluid phase is water, oil-based mud (OBM) where the fluid phase is oil, and synthetic-based mud (SBM) where the fluid phase is a synthetic base compound such as an ester [5]. Water-based drilling fluids (WBFs) are the most common and often contain a variety of chemicals, which are formulated as required from a generally limited list of additives. Investigations have shown a significant impact of drill cutting piles on the benthic environment within close proximity (<500 m) to the drilling platforms [6,7]. Some comparative studies showed that WBF do not always meet strict ecological requirements [8,9]. The comprehensive studies by Patin[10] and Wills[9] 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 (Water Based Drilling Muds) and associated drill cuttings that pose the greatest risk of bioaccumulation and toxicity to the marine organisms such as fishes[11]. 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 800-3100 m along the East Coast of India (Fig. 1). Generally, the WBMs are synthesized in such a way so as to avoid inclusion of aromatic hydrocarbons however; crude oil may contaminate the mud as well as the drill cuttings, introducing them when drilling through hydrocarbon bearing formations[12]. 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). Hence, the purpose of the present investigation was to evaluate the impacts in aquatic environment due to offshore drilling activities. The present study deals with determination of PAH concentrations in composite samples of WBM, and drill cuttings, which were obtained from three different drilling depths viz. surface (150 meters), middle (300 meters) and bottom (600 meters), in three wells in the Kaveri-Godavari (KG) Basin, Block 98/4, East coast of India and predicting the ecological toxicity of these chemicals to the aquatic community by applying USEPA's ECOSAR.

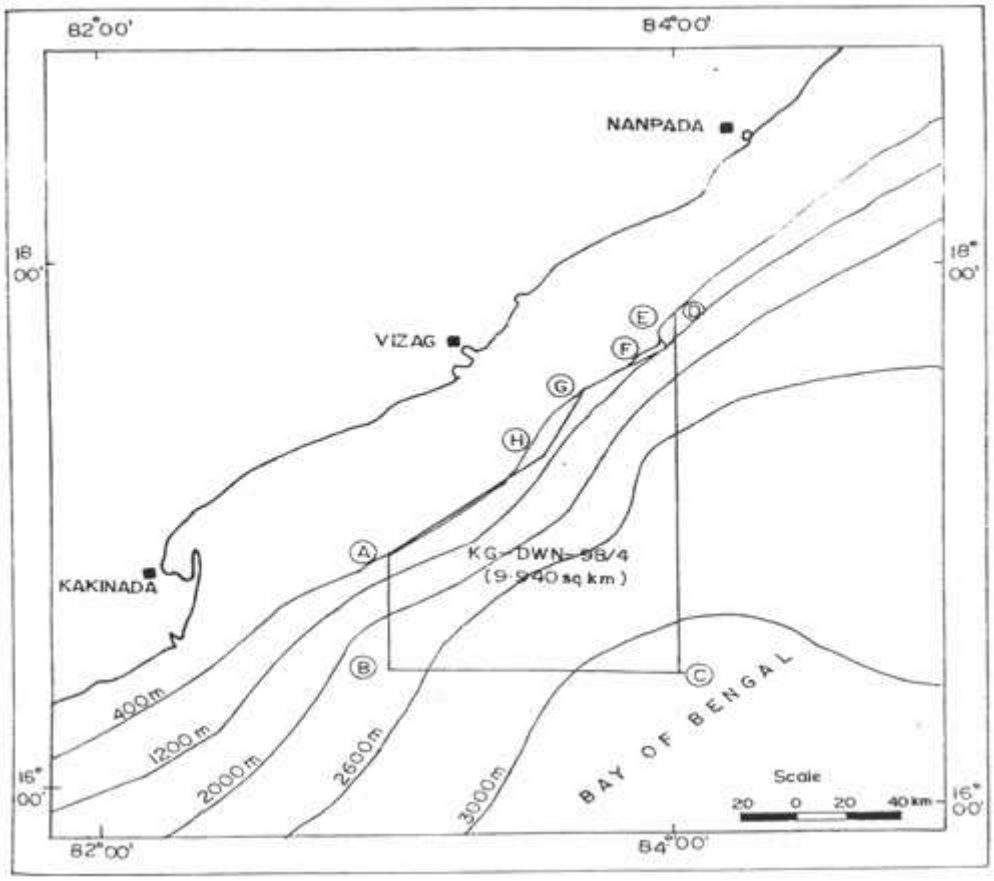


Figure 1: Study Area

EXPERIMENTAL SECTION

Use of ECOSAR for predicting the aquatic toxicity of PAHs

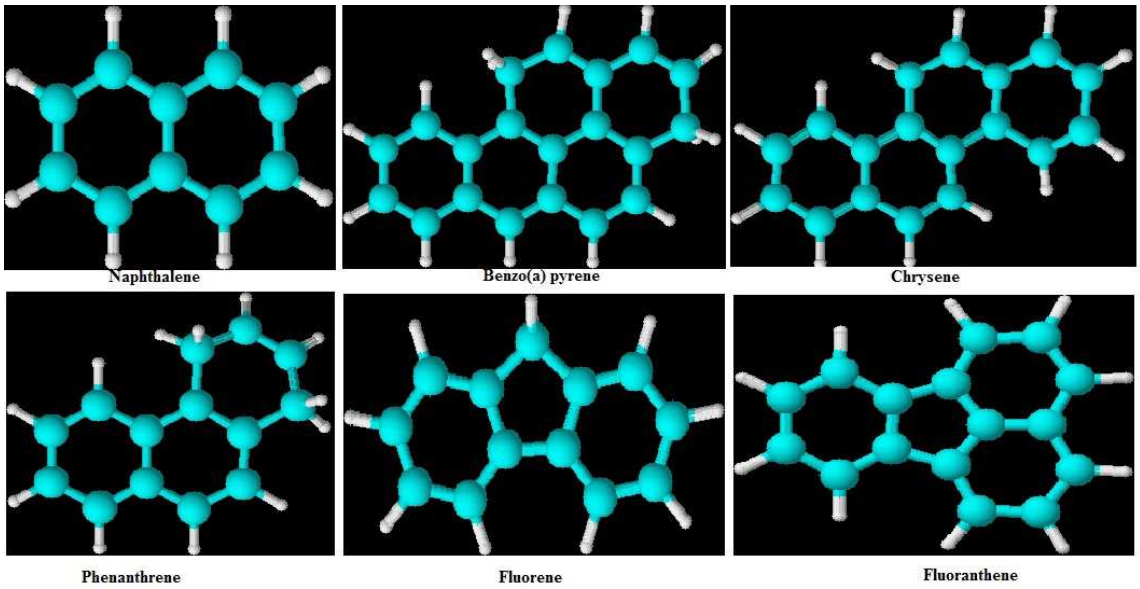
The toxicity of the PAHs (*EC*50/LC50) to *fish, green algae, daphnid and mysid* were calculated using the ECOSAR model – a computerized predictive system used by the United States Environmental Protection Agency (US EPA, 1994) [13] to estimate the aquatic toxicity of industrial chemicals. The ECOSAR model uses Structure Activity Relationships (SARs) for the prediction of the aquatic toxicity of untested chemicals based on their structural similarity to chemicals for which aquatic toxicity data are available [14]. The SARs in the ECOSAR model express correlations between the physico– chemical properties and aquatic toxicity of a compound within specific chemical classes. ECOSAR version 1.1 (2011) was used in the current study (Table 1).

Table 1. Ecotoxicity predictions of the chemicals by ECOSAR

PAH's	Log Kow*	Water Solubility (mg/l)	Fish (SW) 96hr LC50 (mg/l)	Daphnid 48hr LC50 (mg/l)	Green Algae 96-hr EC50 (mg/l)	Mysid 96-hr LC50 (mg/l)
Naphthalene	3.169	31	11.9	5.919	5.789	4.006
Fluorene	4.016	1.69	2.694[a]	1.439	1.538	0.511
Phenanthrene	4.345	1.15	1.464[a]	0.804	0.890	0.222
Fluoranthene	4.933	0.26	0.494[a]	0.285[a]	0.336[a]	0.050
Chrysene	5.521	0.002	0.166[a]	0.101[a]	0.126[a]	0.011[a]
Benzo(a)pyrene	6.109	0.00162	0.055[a]	0.035[a]	0.046[a]	0.003[a]

**EPISUITE Kowwin v1.68 Estimate ECOSAR*

[a] *= Chemical may not be soluble enough to measure this predicted effect. If the effect level exceeds the water solubility by 10X, typically no effects at saturation (NES) are reported.*



Scheme 1: 3D View of selected PAHs*

**Note: Structures drawn by Chemsketch (ACD labs Version 11.0)*

Drilling Mud and Cutting Samples

The drill mud & associated cuttings used in this study were obtained from three wells at three different depths viz. surface (150 meters), middle (300 meters) and bottom (600 meters) on the east coast of India. Three replicate composite samples were collected and were refrigerated at 4^0C and protected from light. Table 2 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, whereas the drill cutting samples (2g each) were subjected to soxhlet extraction 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) (Method 6410B, Standard Methods, APHA, AWWA, WEF, 2001). 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 (Scheme 1). The standards were obtained from M/s Acros Organics Ltd., Belgium. The PAHs structures were drawn by Chem Sketch Version 11.0, available from ACD labs (Scheme 1).

Table 2. 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

Statistical Analyses

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

Over 100,000 chemicals are released into the environment, and as few as 1 – 5% have toxicity data available. There is scarcity of information regarding the toxicity of most of the chemicals released into the environment. The cost of obtaining such information experimentally would be enormous in terms of money, time and animals. Companies and regulatory agencies are therefore turning to the prediction of environmental toxicity and fate through the use of quantitative structure-activity relationships (QSARs) [15]. Currently, there is lack of monitoring activities in various countries to assess the environmental concentrations of chemicals or their potential ecotoxicological effects in the city's freshwater or estuarine environments. This lack of baseline data on exposure conditions impedes reliable estimates of their ecological risk [16]. The computational methods for predicting chemical toxicity are rapidly evolving. In recent years numerous initiatives and projects have begun, and there are high expectations for the potential roles that QSAR can play. QSAR is a tool for the prediction of biological activity, and thus lends itself readily to the prediction of environmental toxicity. Over the past few years environmental QSAR has increased steadily in importance. It has now reached the stage where some regulatory agencies, such as the U.S. Environmental Protection Agency, routinely use some QSAR–predicted toxicities for regulatory purposes; it is anticipated that such use will increase greatly in the future, as more assurances are sought on the safety of chemicals, and more public pressure is brought to bear against the use of animals in toxicity testing [15]. However, further research is needed and many challenges remain in addressing the broader targets. It is most likely that the integration of different models will become more and more important. The risk, of course, is that some models may yield conflicting results[17]. Accurate prediction of *in vivo* toxicity from *in vitro* testing is a challenging problem. Large public-private consortia have been formed with the goal of improving chemical safety assessment by the means of high-throughput screening. Zhu et al.[18] have successfully developed QSAR modelling approach that affords a successful prediction of acute toxicity (LD50) values from chemical structure for both rats and mice. ECOSAR "estimation methods" can be used to fill data gaps where little or no experimental measured data exists as also observed by Reuschenbach et al.[19] Moore et al.[20] Posthumus and Sloof [21]. Toxicity to these surrogate species (fish, aquatic invertebrates, and aquatic plants) stated in Table 1 can be used to predict toxicity to a general aquatic community. QSARs can be used as an initial evaluation of the toxicity of chemical; however tests with bioassays must be performed for confirmation as also observed by Sihtmäe and co-workers[14]. Tables 3-4 show that individual PAH concentrations in drill mud and drill cuttings increased with depth in each well. A similar trend was observed in the drill mud and cuttings samples in Point Arguello Field, California [11,22].

Table 3. Concentrations of PAHs recovered from Drilling Mud (mg/kg) (N = 15)

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

S: Surface (150meters) M: Middle (300 meters) B: Bottom (600 meters)

Table 4. Concentrations of PAHs recovered from Drill Cuttings (mg/kg) (N = 15)

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

S: Surface (150meters) M: Middle (300 meters) B: Bottom (600 meters)

Figure 2-3 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 [11,23] 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. However, WBM wastes have the potential to smother marine life with artificial sediments or suffocating it with plumes of superfine suspended particles [24]. 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 oil & gas development in the offshore regions is important to be able to distinguish the ″Environmental Baseline″ from potential future impacts. In view of the present marine environmental circumstances the generated information necessitates wider distribution.

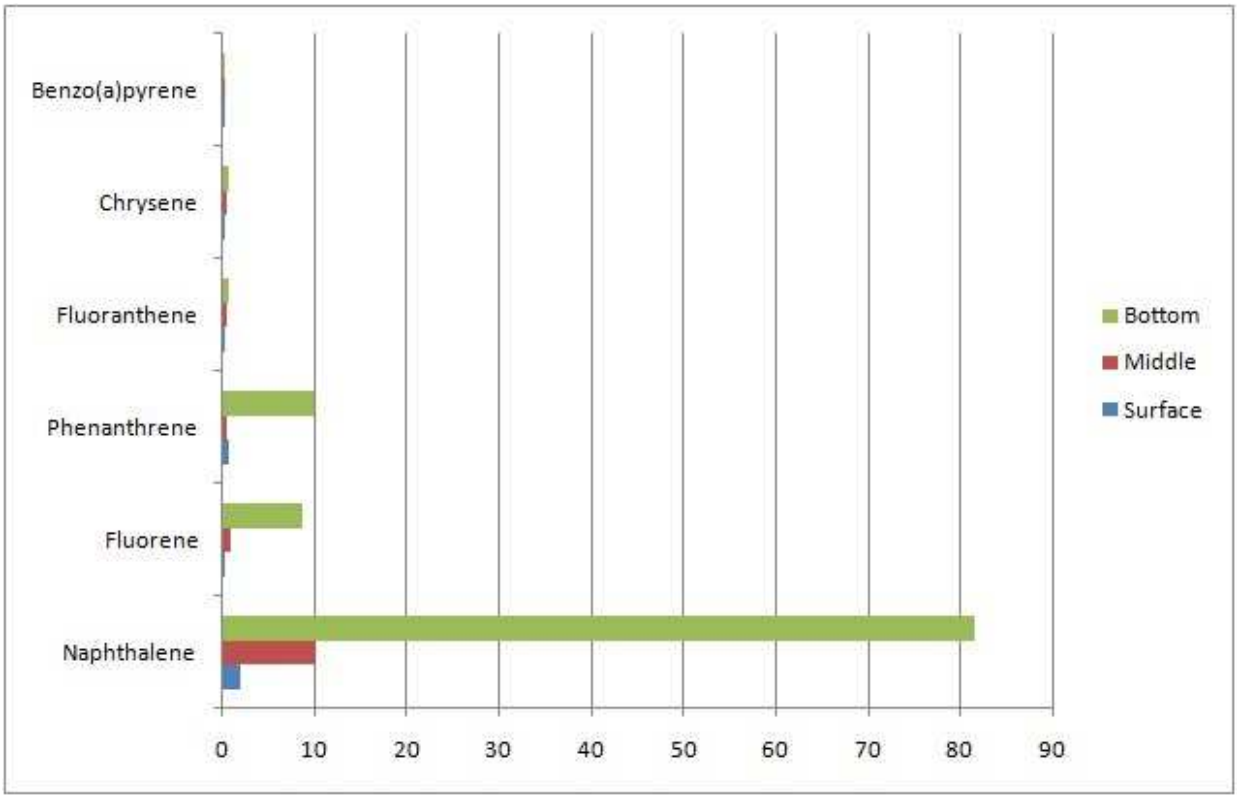


Figure 2: PAH in Drilling Mud

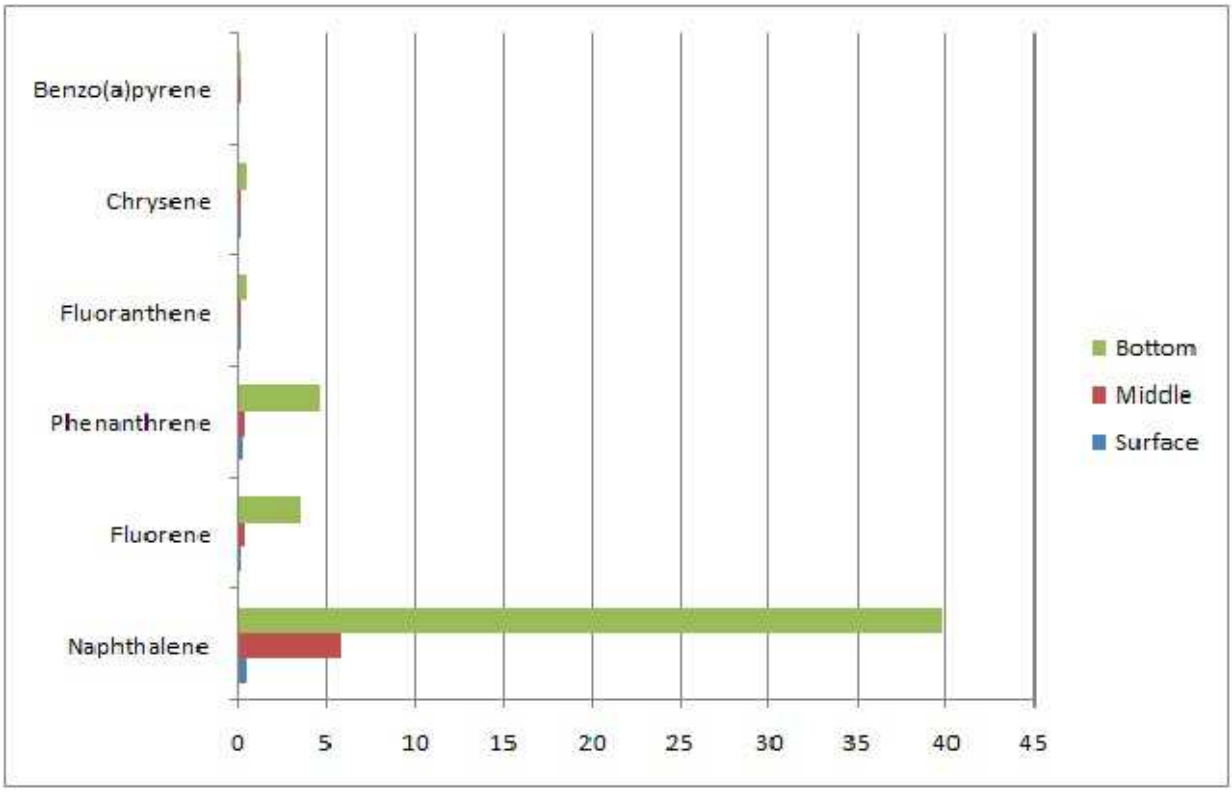


Figure 3: PAH in Drill Cutting

CONCLUSION

ECOSAR model has demonstrated the ability to predict the toxicity of chemicals to the aquatic community and the surrounding environment however tests with bioassays are required for the reliability and assurance. The ecotoxicity predictions from such models can aid in the decision making process by authorities. As also observed by Dearden [15] QSAR for the prediction of environmental toxicity is well established, although there is still a shortage of good quality toxicity data for the development of QSARs. Environmental fate (bioconcentration, soil sorption and biodegradation) can also be predicted by QSAR. The use of QSAR models should become part of a broader vision, that is, by combining *in vivo* and *in vitro* methods. QSAR models are robust and less expensive and ought to be used as the first step on this process [17]. The rapid growth of offshore oil and gas exploration activities in the coastal region of India has generated the need for both general and region specific scientific information on environmental consequences of such activities. Water Based Drilling Muds although preferred over Synthetic and Oil based formulations still have the potential to cause harm to the surrounding marine environment. Regular monitoring of offshore drilling activities will help to assess its impact and provide proper mitigation methods.

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