Simulation of Polycyclic Aromatic Hydrocarbons Distribution at Different Depths and Times in Fresh and Saline Water Environments

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Abstract: *Simulation of the distribution of polycyclic aromatic hydrocarbons (PAHs) in aquatic environments were carried out in a specially designed 50L dispersion simulation tank by spiking fresh water and saline water with 1ml of crude oil. The required turbulence was achieved using a portable submersible pump. Six samples each were collected at three depths at 15 minutes intervals. Results showed that the concentrations of the PAHs changed with time. PAHs concentrations in fresh water ranged from 1.76ppm-3.31ppm at 5cm, 7.50ppm-40.46ppm at 10cm and 17.31 ppm-25.68ppm at 20cm while in the saline water, the PAHs concentrations ranged from 17.25ppm-20.63ppm at 5cm, 13.45ppm-25.02ppm at 10cm and 1.34ppm-3.31ppm at 20cm. The distribution of PAHs concentration with time and space showed that higher levels of PAHs were found at 5cm in saline water and at 20cm in the fresh water for the same time period, indicating that while oil can be held in the upper water column for longer resident time in saline water, the same oil will spread and reach the benthic environment faster in fresh water. With pH and total suspended solids of the two water matrices being almost the same, their influence in the spatial and temporal distribution of PAHs is negligible. TDS and salinity of surface water exposed to crude oil was found to be important factors to be taken into consideration in designing a strategy for PAHs remediation programme.*
Keywords: *Fresh water, Saline water, Simulation, crude oil, polycyclic aromatic hydrocarbons, water column,*

I. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are aromatic hydrocarbons with two or more fused benzene rings in different structural arrangements (Vichi, e*t al*.,(2005), Haritash and Kaushik (2009), Kim *et al*.,(2013), Jiang et al., (2014), Masih and Lal (2014),Nguyen *et al*.,(2014), Sharma (2014). They contain carbon and hydrogen bound in simple to intricate ring systems. Thearrangement of their benzene ring confers on them a wide variety of physical, chemical and toxicological properties (Cerniglia, 1992).They naturally occur as a composite mixture of hydrocarbons (Albers, 2003). PAHs can come in contact with the marine environments through natural oil seeps, inadvertent oil spills, swamp discharges, inland runoff, littoral erosion, and atmosphericremoval during precipitation (Dachs et al., 2002; Mitra and Bianchi, 2003, Tsapakis *et al*., 2006). Some of the PAHs like naphthalene, benzo(a)pyrene, benzo(e)pyrene and their metabolic products are ofmajor environmental health concerns because of their toxic, carcinogenic, genotoxic and mutagenicproperties (Samanta *et al*., 2002; Yan *et al*., 2004).

According to Meador *et al.,*(1995) PAHs can be classified as low molecular weight (2-3 benzene rings), middle molecular weight (4 benzene rings) and higher molecular weight PAHs (> 4 benzene rings). Eisler (1987) stated that the behavior, distribution, biological effects and physico-chemical properties of PAHs are largely dependent on their molecular weights. The solubility of PAHs and ability to vaporize diminishes with increase in molecular weight. However, their environmental persistence, boiling point, recalcitrance to biodegradation and partition coefficient increases with molecular weight (Albers, 2003; Kanaly and Harayama, 2000; May *et al*., 1978).

Natural oil seeps, forest fires, volcanoes and biosynthesis in plants, fungi and bacteria are

the natural contributions of PAHs to the environment (Albers, 2003; Wild and Jones, 1995).The other sources include cigarette smoke and as products of humous transformations by microorganism (Katarzyna *et al,* 2004). However, natural contributions to the environment include oil seepage, fossil fuel, coal, wood, bush burning and volcanic eruptions (Yunker *et al*.2002,2012).

The contamination of the aquatic ecosystems by PAHs poses a great danger to man and the environment. Both the parent PAHs, alkyl-substituted members and even their metabolites have been implicated

in either genotoxicity, mutagenicity,carcinogenicity or teratogenicity studies (Meador *et al* ,1995 ; (Heintz *et al*., 1999). The toxicity of PAHs is associated with the generation of $^1O_2$ via photosensitization when exposed to solar UV radiation with the production of toxic PAH quinones (Babu, *et al*., 2002).

Within the aquatic environment, under normal conditions and in the absence of surfactant-based formulations or dispersants, spreading of oil occurs either by wave action or turbulence which removes the oil from slick and brings it down by gravity into the water column (Lee, 2014).

Studies at the Deep Water Horizon (DWH) blowout in 2010, indicated that contact with rivers below sea level and high speed floods can bring about oil dispersion in a water body (Zhao *et al*, 2014). Oil particles may remain suspended i.e. dispersed or may come back to the surface either as individual particles or as aggregates depending on the oil particle size, how active the system is, as well as the distance from the surface to the point in the water column where the activity is taking place (Figure 2).
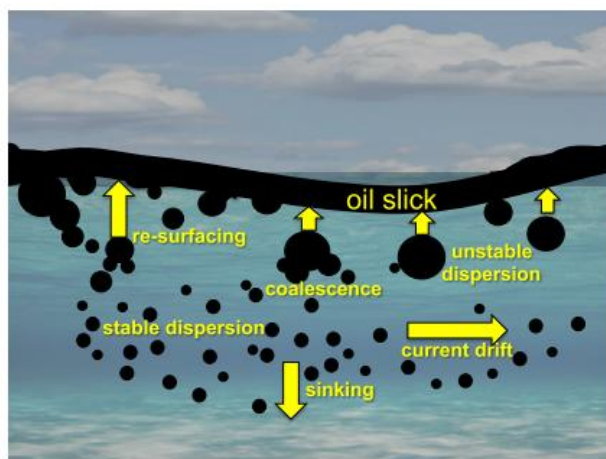

Figure 1: Dynamic processes in oil slick-water column interaction. (Lee *et al*., 2015)

According to Fingas (2014), oil particles with size less than 0.02mm can maintain stability in their dispersed state and not resurface for a long time. This phenomenon has been demonstrated by Valentine *et al*, (2014) in studies carried out in the case of the DWH incident.Whether in fresh or sea water, oil droplets within the subsurface can become trapped in sediments below through gravity deposition ('sedimentation'). Agitation, turbulence or any perturbation within this zone may throw them up as suspended droplets and subsequently back into the water column where they are redistributed. When such interactions exist between oil droplets and inorganic materials such as clay materials, oil mineral aggregates (OMAs) are formed while the interaction between OMAs and oil droplets associated with organic particles leads to the formation of oil particle aggregates (OPAs) (Lee, 2002). According to Fitzpatrick *et al*.(2015) and Waterman and Garcia (2015), OPAs does not only refer to OMAs plus organic particles but also includes detritus and cells of living microorganisms. OPAs may remain afloat due to up thrust or may sink to become part of the sediment. Studies have shown that incorporation of 2-3% of dissolved solids (minerals) into the oil phase is enough to cause some oils to be submerged (NRC, 1999); depending, of course, on the oil viscosity and the type of mineral (Omotosho *et al*., 2002).

Albers (2003) stated that the outcome of interactions between PAHs found in water and their surrounding aquatic environmental systems is a function of the processes at work and directly influencing them per time. These factors could be biological, chemical or physical and according to Berrojanbiz et al.,(2011),include vapourisation, distribution, breakdown by microbes, particulate suspension, gravity separation and multidirectional movements. One important means of PAHs removal from ocean waters is vertical gravity separation and ultimate burial in sediments (Dachs et al., 1997; Gustafsson, 1997a; Lipiatou et al., 1997). This is mainly true of organic-rich hydrophobics with high affinity for particulates (OPAs). As a result, the sedentary seafloor becomes the eventual depository for such PAHs (Marini and Frapiccini, 2013; Neff, 1979).

To appreciate the eventual outcome of PAHs interactions found in the aquatic environment, it becomes necessary to measure the route of PAHs (concentration?) to obtain information on their vertical distribution along the water column.

Studies carried out in the last twenty years have shown that OPAs can largely explain the fluctuations in concentration distribution of PAHs in the lower column of water bodies (Dachs et al., 1996; Deyme et al., 2011; Tsapakis et al., 2006) while information on events in the upper columns are still scarce due to paucity of strategies of measurements(Gustafsson et al., 1997a). This study therefore seeks to understand what happens

when PAHs leave their natural organic medium to an aquatic environment in terms of their distribution in space and time.

The Study Area

The three locations designated as Locations 1 , 2 and 3 are all within the riverine areas in the oil reach Niger delta region. The formations are prolific and currently producing. The samples were collected from the loading terminals and so are representative of the crude oils from the respective locations. The satellite imagery of the locations are shown in
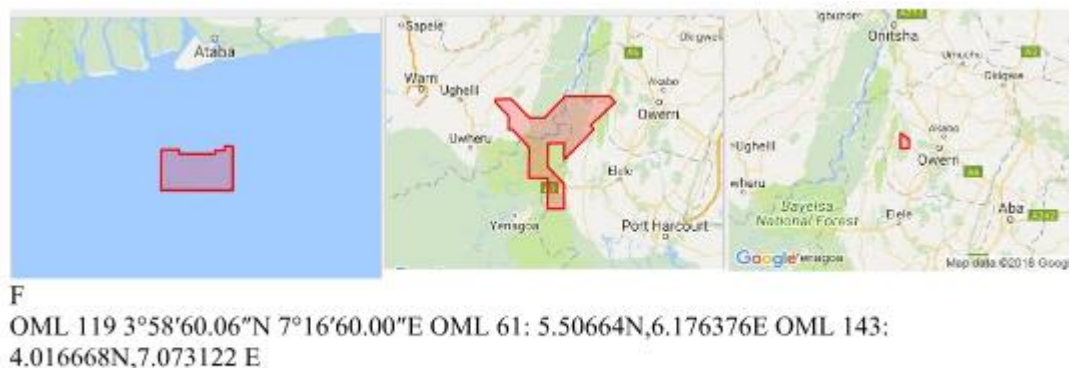

F
OML 119 3°58'60.06"N 7°16'60.00"E OML 61: 5.50664N,6.176376E OML 143: 4.016668N,7.073122 E

Figure 1: Satellite imagery location maps of the mining leases

II. Materials and Methods

Experimental Design

Two mini-aquarium measuring 65cm x 25cm x 40cm each was fabricated with glass material to act as water tanks. The tops were half covered to provide a platform for the installation of an energy bulb and an anchor for a portable submersible pump and air pump. The submersible was adjusted to a suitable horsepower required to generate a corresponding flow rate to provide to an ambient turbulence (>4000 Reynolds) while the air pump supplied air through the accessories to produce aeration similar to that in a natural environment.

Three water matrices were used for the study namely: groundwater, freshwater and sea water with the groundwater as the control.

Sample Collection and Preparation

Crude oil samples were collected with sampling thief from the ship composites during loading from the storage tanks of the two different oil fields. The collected samples were placed in metal cans and transported to the laboratory.

Analytical methods

PAHs concentration was determined using standard protocol (USEPA, 610).Sample detection and identification was by FID by taking advantage of the differences in retention time of the components while quantification was obtained from the corresponding areas of the respective chromatograms. Solvent blank was analysed and quantified with no PAHs found in these blanks. The GC was calibrated using dichloromethane-based standards. The coefficient of determination values (R^2) was greater than 0.95. Surrogate standards were introduced to the sample to attenuate abnormal matrix effect.

III. Results and Discussion

The properties of the fresh water and the saline water used for this study are shown in Table 2. Apart from the pH values that are within the neutral range, other quality parameters indicated typical distinguishing features.

TABLE 2: Properties Measured in Fresh and Saline Water Matrices

Property	Unit	Fresh Water	Saline water (Brackish)
Density	g/ml	0.9998	1.024
pH	-	7.5	7.1

TDS	mg/l	14	10,650
Conductivity	µS/cm	28	21,300
Salinity	mg/l	9.2	7,455

The distribution of PAHs concentrations in the water column at different depths was investigated. The variation of concentration with time at 10cm is shown Table 3 with the graphic representation in Figure 2 while the variation of concentration with time at 5cm and 20cm are shown in Table 4.

Table 3: PAHs distribution at 10cm for the two water matrices

Time, min	SW, ppm	FW, ppm
30	25.02	16.81
60	17.18	41.05
90	13.45	20.82
120	19.11	7.5

SW=saline water;FW=fresh water

TABLE 4: Distribution of PAHs Concentrations in Saline and Fresh Waters at Three Depths: 5cm (D1), 10cm (MIDDLE) and 20cm (D2)

Code/Depth	Time (min)						
	30	45	60	75	90	105	120
SWD1(5cm)	17.4389	19.0331	20.6272	20.1386	19.65	18.45	17.25
FWD1(5cm)	1.7851	1.7535	1.7219	1.7365	1.7511	2.5306	3.31
SWDM(10cm)	25.02	21.1	24.510	15.315	22.311	32.56	19.11
FWDM(10cm)	16.81	28.635	40.46	30.64	20.82	14.16	7.5
SWD2(20cm)	1.3389	1.3451	1.3513	2.3279	3.3010	3.3020	3.3045
FWD2(20cm)	17.3076	18.1068	18.9059	22.2946	25.6832	24.8031	23.923
	Concentration (ppm)						

The profile of the array of PAHs in a saline sample collected at 5cm depth is shown in Figure 5. All the sixteen (16) PAHs normally monitored in environmental samples were present.

Table 5: List of PAHs in saline water sample at 5cm depth

| Peak No	Peak Name	Ret Time (min)	Result (ppm)	Peak Area (counts)
1	Naphthalene	6.426	8.9819	21289
2	Acenapthene	6.826	2.7658	7041
3	Acenaphthylene	7.234	0.3020	452
4	Fluorene	7.843	0.5111	1073
5	Phenanthrene	9.075	0.8024	1505
6	Anthracene	9.830	1.6458	2157
7	Fluoranthene	12.292	0.4646	804
8	Pyrene	12.443	0.0379	63
9	Benzo[a]anthracene	14.162	0.2970	391
10	Chrysene	14.212	0.3861	547
11	Benzo[b]fluoranthene	14.357	0.9694	1071
12	Benzo[k]fluoranthene	14.433	0.4114	427
13	Benzo[a]pyrene	14.464	0.9986	892
14	Indeno[1,2,3-cd]pyrene	14.846	0.9943	878
15	Dibenzo[a,h]anthracene	15.204	0.5287	403
16	Benzo[ghi]perylene	15.689	0.5302	469
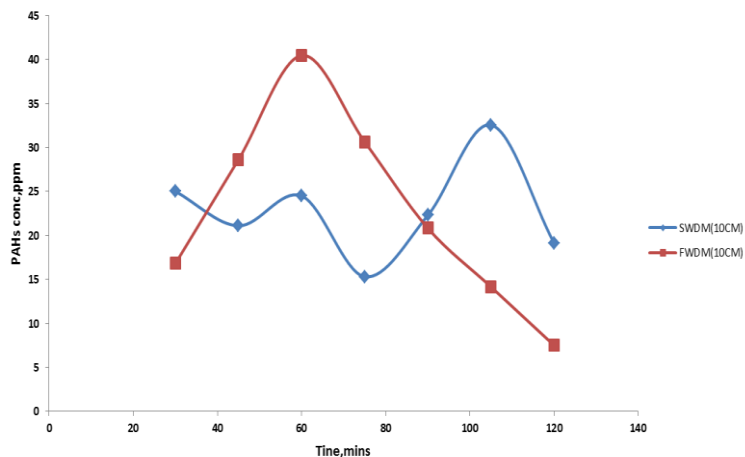
Figure 2: Variation of PAHs concentration with time at 10cm depth

The graphic representations of the variation of concentration with time at the various depths investigated are depicted in Figure 3, while the separation of the graphs for clarity purposes are shown in Figures 4 and 5.
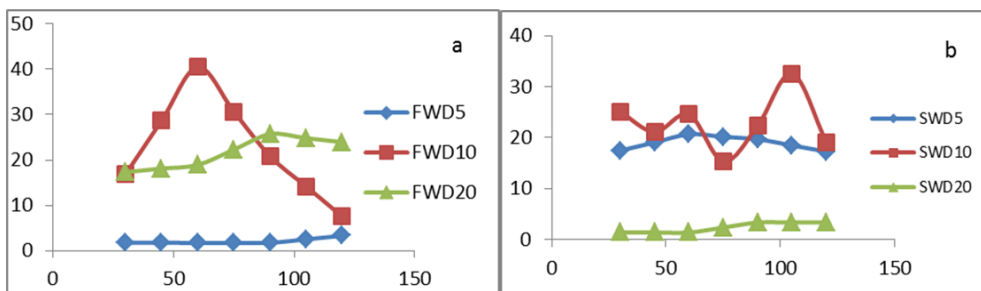

Figure 3: PAHs concentration profiles at three depths for freshwater (a) and saline water (b)
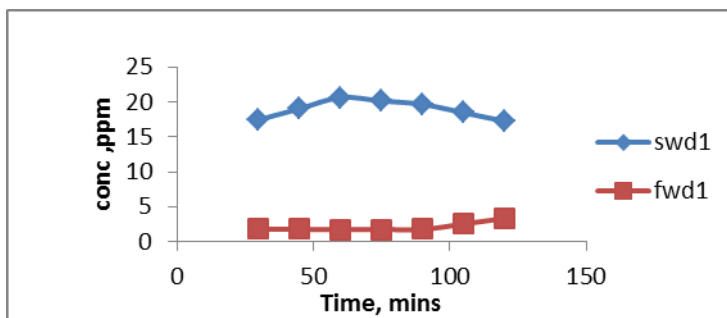The pictures become clearer when Figure 3 is separated into figures 4 and 5

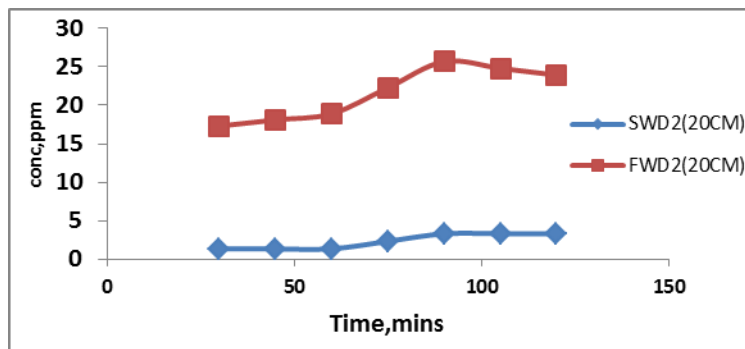**FIG 4:** Distribution of PAHs Concentrations in Saline and Fresh Waters at 5cm

FIG 5: Distribution of PAHs Concentrations in Saline and Fresh Waters at20cm

The profile of PAHs as indicated by the chromatogram of saline sample from 20cm at 60mins is shown in Figure 6. Presence of fewer PAHs at 20cm corresponding to lower concentration is clearly evident.
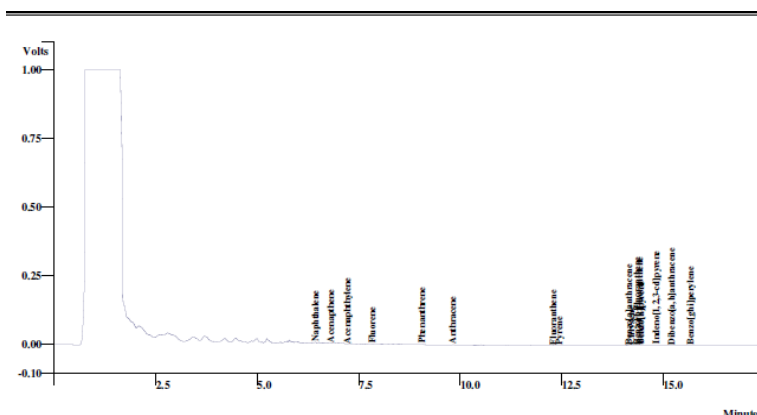

Figure 6: Chromatogram of PAHs in saline sample from 5cm at 60mins

Table 6: List of PAHs in saline water sample at 20cm depth at 60mins

| Peak No	Peak Name	Ret Time (min)	Result (ppm)	Peak Area (counts)
1	Naphthalene	6.059	0.0331	78
2	Acenapthene	6.940	0.0539	137
3	Acenaphthylene	7.250	0.0822	123
4	Fluorene	7.815	0.0952	200
5	Phenanthrene	8.986	0.0367	69
6	Anthracene	9.832	0.1793	235
7	Fluoranthene	12.275	0.0559	97
8	Pyrene	12.786	0.1536	254
9	Benzo[a]anthracene	14.090	0.1220	161
10	Benzo[k]fluoranthene	14.431	0.2926	304
11	Dibenzo[a,h]anthracene	15.216	0.0712	54
12	Benzo[ghi]perylene	15.589	0.1756	155
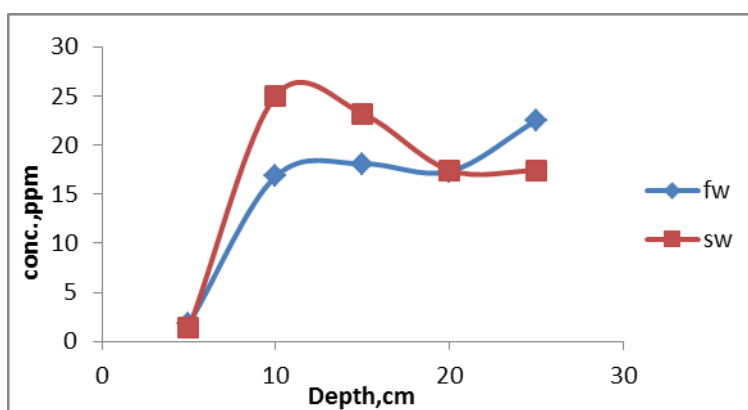
Figure 7: Concentration-Depth profiles of PAHs in the two water matrices

Analysis results indicate that the pH values of the samples are 7.5 and 7.1 respectively for the fresh and saline water (Table 2). These two values fall within neutral range of 6.5-8.5 (WHO, 1996, Werner *et al.*, 2012). The density of the fresh water is 0.9998g/ml while that of the sea water is 1.024g/ml. Similar results have been reported by Wood (2016) and Powell (2018) as one of the major differences between fresh water and saline water.

The total dissolved solids (TDS) for the fresh water is 14mg/l while that of the sea water is 10,650mg/l. These values are in agreement with ranges reported by Sharma (2008) and Mishra *et al.* (2011). The electrical conductivity values for the two water samples are 28μS/cm and 21,300μS/cm. These values are consistent with those reported by Werner, (2012). The salinity values of the water are 9.2mg/l and 7,455mg/l respectively for

the fresh and saline water. Mayer et al., (2005) reported similar values for fresh and saline water bodies in Australia.

The PAHs concentrations in the saline water ranged from 13.45ppm-25.02ppm, while that of the fresh water ranged from 7.5ppm-41.05ppm (Table 3). The results show that there was rapid mobilization or spread of the PAHs in the fresh water that resulted to a low PAHs concentration of 7.5ppm after 120mins at 10cm depth compared to that of the saline water

The PAHs concentrations of the saline water did not indicate a strong or clear spatial disparity with time at this depth (Figure 2).

This observed trend is in line with values that ranged from 170.7 ± 70.8 ng/g- 908.5 ± 78.1 ng/g dry weights; 31.2 to 51.2 ng/L (mean = 40.3 ± 6.0ng/L) and 24.2 to 58.0 ng/L (mean = 35.5 ± 9.0 ng/L) reported by He *et al*., (2014) and Adhikari (2015) respectively; and Diercks (2010) in the DWH incident.

Samples collected at different depths for the two water matriceswithin the same time intervals showed that PAHs concentrations ranged from 1.34ppm-1.79 ppm (5cm) and 11.91ppm-25.68ppm (5cm) for fresh water and 2.05ppm-20.63ppm (5cm) and 1.11ppm-3.31ppm (20cm) for saline water respectively (Table 4).The profiles indicate that while higher concentrations of PAHs were found in the upper water column for the saline water, higher concentrations were found in the lower 20cm column for the fresh water for the same time period (Figures 3 a and b).

The reason for this characteristic PAHs distribution is not very clear but the higher density and dissolved solids of the saline water compared to that of fresh water may be responsible. Such interactions of the PAHs with the dissolved solids and other exotic materials and activities associated with the sea water had been reported by Joye (2015). Oil viscosity may not be a factor since the two water matrices were exposed to the same crude oil type. The longer resident time observed in this study that is associated with the PAHs in the saline water is probably due to formation of PAHs-particulate moieties. NRC (1999) and Omotosho *et al*., (2002) reported that. incorporation of minerals in the form of dissolved solids is a likely scenario that could explain the longer resident time for PAHs in saline water.

This trend in the distribution of PAHs concentration isalso consistent with values that ranged from 170.7 ± 70.8 ng/g- 908.5 ± 1878.1 ng/g dry weights obtained by He *et al*.,(2014) for sea water. There were no comparable results with that obtained in this study for fresh water as most studies on vertical PAHs fluxes in water had been on some sea/ocean waters; not even in the waters of Northern Gulf of Mexico as reported by Adhikari (2015).The PAHs profile in fresh water, as a function of time, shows a spike in concentration in the upper column, about 1hr after the introduction of crude oil in water and a rapid decline in the next 1hr. This is unlike the saline water where there was no substantial change in PAHs levels within the same period but a concentration oscillation about an average. Longer resident time as a result of PAHs-solute-particulate interactions has been reported byLee (2002). This can account for the wide disparities in the distribution of PAHs in the two water matrices; a typical difference that is in agreement with that reported by Powell (2018).

The result from sample collected at 5cm from the saline water at 60minutes indicated that all the members of the EPA 16 were present (Table 5 and Fig. 6). In other words, there was abundance of low molecular weight and medium molecular weight PAHs in the sample to the tune of more than 80% of the total PAHs.

This is consistent with the findings by Adhakari (2015) in his research within waters of Gulf of Northern Mexico following the DWH incident in which he listed the same group of PAHs as constituting more than 72 ± 11%.Comparable distributions of PAHs with preponderance of LMW and MMW compounds from different parts of the world have been reported by Allan *et al*., (2012); Colombo *et al*., (2006); Dachs *et al*., (1996, 1997); Deyme *et al*., (2011); Diercks *et al*., (2010); Lipiatou *et al*., (1993, 1997).

The result of the analysis of sample from 20cm depth at 60mins for saline water showed that some of the medium molecular weight and heavy molecular weight PAHs were present while some were missing(Table 6). While the PAHs concentration in fresh water is 20.6272ppm in sample from 5cm, it is 1.3513ppm in sample from 20cm at 60mins (1hr).

This may indicate that the some of the PAHs are still 'trapped' by the high viscosity and TDS associated with the saline water. Such interactions between oil and minerals in water has been reported by Omotosho *et al.,*(2002). Since this group of PAHs is generally less preponderant, lower concentrations were recorded. This finding is in tandem with the studies by Lee *et al*., (2016).

On the other hand, fresh water sample from 5cm and 20cm collected at 60 minutes had PAHs concentrations of 1.7219ppm and 11.9059ppm respectively (Table 4).

From the overall result it can be said that the distribution of PAHs concentration as a function of depth and time in a water body depends on the degree of oil-mineral interaction as well as the energy of the system as determined by other prevailing factors within the water column. This observation has been reported by Fingas, (2014b) and Lee *et al*. (2016) following the DWH incident which showed that most of the oil resides within the first 10m of the water column in deep waters and 1m in shallow waters.

The implication is that the thickness of the water column to which the oil spends most of the time (resides) is a function of the depth of the water body and hence the up thrust. This is in line with studies carried out by federal scientists (USEPA) and reported by Lee *et al.,* (2015).

The ultimate distribution in PAHs concentrations show increase with depth and time characterized by overall pattern of low concentrations at the upper 5cm water column trailed by increased concentrations at 10cm-15cm and then decreased or remained constant with increased depth as is the case with saline water. The same finding was reported by Adhikari (2015) in corresponding water columns in the Gulf of Mexico. The fresh water PAHs concentration-depth relationship indicated a similar but lagging profile to that of the saline water but having an elevated terminal concentration (Figure 7).

The implication of these observations is that the sensitive nature of fresh water as an environmental component/receptor could be ascribed to the rate of dispersion and unhindered spread of toxic substances introduced into it, This has been reported by Zhao *et al.(*2014). Any emergency response that cannot be activated within Ihr following a spill event may be not achieve the desired purpose.

From these observations, it is the properties of the water to be remediated that should be the major focus in designing a regime for PAHs removal. Other factors that should be taken into consideration may include the type of oil since this will determine the likely interactions between the oil slick and the water column. It is therefore important to note that though in situ remediation of PAHs in crude oil-exposed surface may be difficult; ex situ treatment is considered a viable option.

HWMPs tend to disperse faster in a fresh water environment than in sea water. The LMWPs, on the other hand, were more dominant in the upper column of the sea water. Dissolved solids/salinity might be a force to contend with in in situ removal of PAHs from water.Formation of oil-mineral particles as a result of abundance of dissolved solids as well as the associated high density and viscosity, may account for the higher PAHs concentration associated with the upper water column of the saline water due to longer resident time.

In order to appropriate these scientific insights to inform optimal strategies for PAHs removal and surface water remediation, we opine that the designation of a fresh water environment as 'sensitive' could be explained in terms of the ease of the dispersion/migration of PAHs and other toxic substances in a fresh water medium. The results of PAHs distribution in the water matrices show that each matrix requires a different strategy and a different treatment regime using in-situ treatment. So we recommend ex-situ batch process as a viable alternative since any type of water will be treated using this method.

Another inference that can be drawn from these observations is that any emergency response plan that cannot be activated and deployed within 1hr of any oil spill incident, especially in a fresh water environment, may not achieve the desired result.

IV. Conclusion

The concentrations of PAHs in the simulated aquatic environment indicated varying and non-uniform temporal and spatial distribution in the different water matrices; an indication that rate of distribution in fresh and saline water varies. This could be due to the different complexities and solubility of the PAHs on one hand, and the properties of the waters on the other hand.

It is recommended that studies aimed at developing a PAHs removal method and surface water remediation should focus on ex situapproach since the experimental conditions and design could be modulated or manipulated to achieve more reliable data compared to in situ.

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