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Original Research Article

Risk Assessment of Polycyclic Aromatic Hydrocarbons and Total Petroleum Hydrocarbons in Oilfield Produced Water and Sea Water at Gulf of Guinea Oilfield, Nigeria

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HIGHLIGHTS

- Petroleum spills has caused tremendous environmental issues to biodiversity and humans.
- These spills interact across all matrices leading chemical exposure to oil and gas workers in Nigeria.
- Health risk modelling shows that prolonged exposure has detrimental health impacts
- Regular medical test and monitoring health of workers will lead to timely diagnostics and treatment.

ABSTRACT

Physiochemical and health risk assessment was conducted on seawater and oilfield produced water collected at Gulf of Guinea Oilfield Location, Nigeria. Analytical parameters such as pH, conductivity, dissolved oxygen, salinity and total dissolved solids were determined, while polycyclic aromatic hydrocarbons (PAHs) and total petroleum was detected and evaluated concentration using gas chromatography-flame ionization detector (GIC-FID). Baseline assessment showed that pH was basic (alkaline), conductivity, salinity, and total dissolved was low indicating less reactive ions, dissolved oxygen was okay across water source. Concentration of PAHs and TPHs results showed that oilfield produced water was highest compared to seawater (seaboard and portside), which was low. Carbon preference index (CPI) conducted on TPHs showed that TPHs had phytoplankton and man-made contribution in chemical composition. Risk assessment conducted on PAHs showed that non-carcinogenic assessment was highest in causative impact compared to carcinogenic assessment, as inhalation exposure was a major contribution less than ingestion (oral) and dermal. Risk assessment conduced on aliphatic and aromatic TPHs showed that carcinogenic assessment had high impact via aromatic than aliphatic while non-carcinogenic assessment had high impact via aliphatic than aromatic. Exposure pathway from risk assessment of PAHs and TPHs showed that inhalation had high carcinogenic and non-carcinogenic health impact compared to dermal and ingestion pathways. Specific care must be taken into consideration when working in an offshore environment as inhalation of these pollutants can cause respiratory and tumours related health issues over a prolong period from oilfield produced water compared to seawater portside and starboard.

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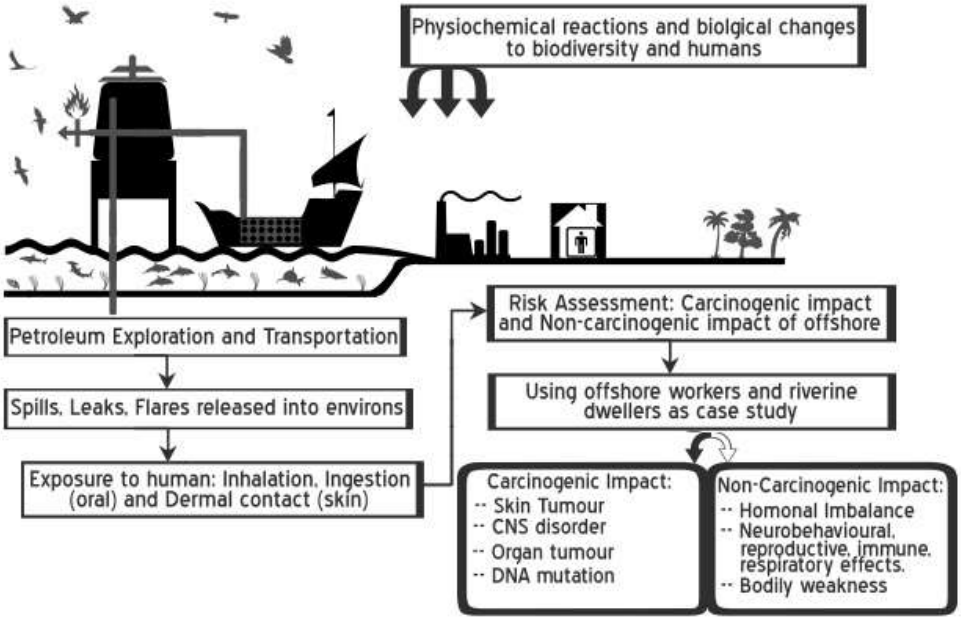
GRAPHICAL ABSTRACT



Introduction

Petroleum has continued to be Nigeria's major income earner since the relative reduction from agricultural sector to oil sector due to low sulphur content, high naphthenic hydrocarbons, dye additives, antioxidants, alkanes, alkenes, alkynes and heavy metals [1-4]. However, Significant chemical releases from petroleum operations (oil and gas drilling, transportation, mining and maritime) into environmental matrices has led to increased concentration of petroleum residues such as polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs), which have low degradation level, mobile and persistent to organisms. These pollutants result in environmental issues such as biological toxicity and chemical accumulation across biodiversity, which impacts on temperature, suspended solids, pressure, salinity, solar radiation, makes them readily reactive influencing seawater colour, dissolved oxygen and aquatic organisms [2]. Polycyclic aromatic hydrocarbons (PAHs) are group of aromatic hydrocarbons with two or more fused benzene rings in various structured configurations, which undergoes thermal decomposition before getting into environment by natural and anthropogenic sources [5,6]. PAHs is known to be highly hazardous, which negatively influences human health as well as the environment thus causing carcinogenesis, localized skin effects, pulmonary and respiratory problems, genetic reproductive and development effects, behavioral, neurotoxic, genotoxic and other organ system effects [7]. Total petroleum hydrocarbons (TPHs) are broad family of several hundred chemical compounds that originates from crude oil thus is a measure of concentration of petroleum hydrocarbon constituents such as mineral oil, hydrocarbons oils, extractable hydrocarbons oil and grease, which ranged between 1000 – 2000 mg/kg as mixtures characterized by low solubility, volatile and high persistent. [8-11]. During offshore petroleum exploration, seawater and oilfield produced water trapped in underground formation are removed during drilling processes, which are partially

treated or not treated leading to environmental interaction from chemical contaminants, thus deposited into sea or marine due to cost of drilling, treatment and deposition as regulatory standards are not adhered nor followed appropriately. As these chemical contaminants in seawater and oilfield produced water interacts with land, air and water matrices, it leads to increasing biological and physiochemical changes to biodiversity. Human exposure to these contaminants at higher dose occurs mainly by direct or indirect processes from inhalation, dermal (skin contact) and ingestion (oral) [12,13]. Offshore workers have been reported to have health related illnesses such as nervous disorders, respiratory, pulmonary, genetic and reproductive diseases from prolonged exposure to pollutants from salinity, heavy metal, petroleum hydrocarbons and naturally occurring radioactive materials, which is dependent of geographical nature of the oilfield [14]. The study seeks to investigate the physiochemical parameters of total petroleum hydrocarbon and polycyclic aromatic hydrocarbons in seawater and oilfield location in Gulf of Guinea, Nigeria to ascertain the level of contaminations on sea environment and conduct health risk assessment to offshore workers from exposure in the Niger Delta region of Nigeria.

Experimental

Sampling site and Methods

The sampling locations was Gulf of Guinea oilfield locations which has presence of International and Indigenous Oil and gas companies domiciled with oil mining license (OML) or oil prospecting license (OPL) for oil and gas exploration around Nigeria territorial water as shown in **figure 1**. Two (2) liters of Oilfield produced water and saltwater (portside and starboard) were collected into pre-treated glass jars from offshore production platform about 120 km of Rivers State, Nigeria. Parameters such as temperature, pH and conductivity, total dissolved solids, dissolved oxygen and salinity were determined in-situ during sampling phase using respective instruments in triplicate and mean taken. The samples were well labelled, packaged in a black cellophane and taken to the lab within 24 h of collection and kept in a refrigerator until analyzed.

Fig. 1. Map of Nigeria Gulf of Guinea and Coastal Countries showing sampling location. (Sourced from http://www.researchgate.net, 2013).

Analytical Method

100 ml of oilfield-produced water were collected and extracted with 50ml of dichloromethane (DCM) using separating funnel while another extracted was done with aqueous layer using anhydrous sodium sulphate to remove water content. Each extract was combined together with DCM interchanged with n-hexane and re-concentrate to 2ml. The extract was fractionated using a fractionating column to extract aliphatic and PAHs components by adding dichloromethane (40ml) and concentrate each fraction into 2ml vials. Fractions of PAHs and TPHs was analyzed using Gas Chromatography Flame Ionization Detector. The procedure was replicated for seawater (seaboard and portside) respectively.

Carbon Preference Index

Carbon Preference index (CPI) is the total on *n*-alkanes with odd carbon number divided by total of *n*-alkanes with even carbon number in the range of C_8 – C_{40} to estimate the relative input from natural or manmade contribution to petroleum as shown in **equation (1)**.

$$\text{CPI} = (\text{sum of odd } n\text{-alkanes})/\ (\text{sum of even } n\text{-alkanes}) \quad (1)$$

CPI is used as environmental forensic indication for source of petroleum products as CPI value greater than 1 are due to natural contribution from biogenic sources (e.g.: phytoplankton, plant waxes) while CPI value less than 1 are manmade contribution in the presence of ubiquitous contribution from natural sources [15].

Risk Assessment

Risk assessment is a tool used in apportioning liability or impact to number of factors such as health and exposure to injury or other causatives. The basic analogy to analyse risk assessment is combination of toxicity or exposure to the dose (amount), risk = toxicity × dose, using USEPA models to evaluate the carcinogenic or non-carcinogenic impact usually at a period [16-18]. Risk assessment conducted on PAHs and TPHs was used by determining the average daily intake (ADI); thereafter evaluate the carcinogenic and non-carcinogenic impact to adults through dermal, inhalation and ingestion as shown in equation (2 – 4) [19,20].

$$\text{Dermal ADI (mg/kg/day)} = \left(\frac{CS \times SA \times AF \times ABS_{sk} \times ET_W \times EF \times ED \times CF}{BW \times AT}\right) \quad (2)$$

$$\text{Ingestion ADI (mg/kg/day)} = \left(\frac{CS \times IR_{ig} \times EF \times ED \times CF}{BW \times AT}\right) \quad (3)$$

$$\text{Inhalation ADI (mg/m}^3\text{)} = \left(\frac{CS \times K \times IR_{ih} \times EF \times ET_{ih} \times ED}{BW \times AT}\right) \quad (4)$$

Where: CS is concentration in water (mg/L), SA: skin surface area (19652cm^2 for adults), AF: water adherence: (0.2mgcm^{-2}for adults), ABS_{sk} is fraction of chemical absorbed through the skin (unit-less) (0.001 for adults). ET_w is exposure time during work event (1.42h/event for adults), IR_{gi} is daily water ingestion rate (L/day) (2.5L/day for adults), EF is exposure frequency (350-day year^{-1}), ED is exposure duration (26 years for adults), CF is conversion factor (1×10^{-6} kg/mg), K is volatilization factor (unit-less) (0.5 L/m^3 for adults). IR_{ih} is daily inhalation rate (15 m^3/day for adults), ET_{ih} is Exposure time – Shift work (12 hours/day), BW is body weight (80kg for adults), AT is average time (non-carcinogens = ED ×365 days), (carcinogen =70×365).

After assessing average daily intake (ADI), carcinogenic and non-carcinogenic assessment was conducted from different exposure pathways:

Carcinogenic risk assessment

Carcinogenic risk assessment was determined using ADI of dermal, ingestion and inhalation as shown in **equation (5)** [19].

$$\begin{aligned}\text{Risk}_{total} &= \text{Risk}_{dermal} + \text{Risk}_{ingestion} + \text{Risk}_{inhalation} \\ &= ([\text{ADI(Dermal)} \times \text{CSF}\,] \\ &+ [\text{ADI(Ingestion)} \times \text{CSF}\,] \\ &+ [\text{ADI(Inhalation)} \times \text{CSF}\,]) \qquad (5)\end{aligned}$$

Where Risk is a unit-less probability of an individual developing cancer over a lifetime, ADI (E) is average daily intake (exposure), CSF is Cancer slope factor of PAHs and TPHs (mg/kg/day), Risk $_{\text{total}}$ is the total excess lifetime cancer calculated from risk pathway.

Non-carcinogenic risk assessment

Non-carcinogenic risk assessment was performed using ADI of dermal, ingestion and inhalation as shown in **equation (6)** [19].

$$\begin{aligned}\text{HI} &= \text{HQ}_{dermal} + \text{HQ}_{ingestion} + \text{HQ}_{inhalation} \\ &= \left(\left[\frac{\text{ADI(Dermal)}}{\text{RfD}}\right] + \left[\frac{\text{ADI(ingestion)}}{\text{RfD}}\right]\right. \\ &\left. + \left[\frac{\text{ADI(inhalation)}}{\text{RfD}}\right]\right) \quad (6)\end{aligned}$$

Where HI is sum total of more than one hazard quotient of multiple exposure pathway, HQ is hazard quotient is a unit-less number for expressing the probability of an adverse health effect, ADI (E) is average daily intake (exposure), RfD is reference dose of PAHs and TPHs (mg/kg/day).

The reference table for polycyclic aromatic hydrocarbons (PAHs) carcinogenic and non-carcinogenic risk assessment are presented in **table 1**.

The reference table for total petroleum hydrocarbons (TPHs) carcinogenic and non-carcinogenic risk assessment with are presented in **Table 2**.

Table 1. Reference value for polycyclic aromatic hydrocarbons (PAHs)

TPHs	**Dermal**			**Ingestion**			**Inhalation**		
	CSF	RfD	Source	OSF	RfD	Source	IUR	RfC	Source
Naphthalene (Nap)	NA	NA		NA	0.3	PPRTV	NA	0.003	IRIS
Acenaphthene (Acy)	0.01*	0.16**		0.01*	0.2	PPRTV	6E-06*	0.16**	
Acenaphthylene (Ace)	0.001*	0.16**		0.001*	0.6	PPRTV	6E-07*	0.16**	
Fluorene (Flu)	NA	NA		NA	0.4	ATSDR	NA	NA	
Phenanthrene (PA)	NA	NA		NA	0.4	PPRTV	NA	NA	
Anthracene (Ant)	NA	NA		NA	3.0	PPRTV	NA	NA	
Fluoranthene (Flt)	0.01*	0.16**		0.01*	0.1	PPRTV	6E-06*	0.16**	
Pyrene (Py)	0.1*	0.16**		0.1*	0.3	PPRTV	6E-05*	0.16**	
Benzo[a]anthracene (BaA)	0.1*	0.16**		0.1*	0.16**		6E-05*	0.16**	
Chrysene (Cry)	0.001*	0.16**		0.001*	0.16**		6E-07*	0.16**	
Benzo[b]fluoranthene (BbF)	0.1*	0.16**		0.1*	0.16**		6E-05*	0.16**	
Benzo[k]fluoranthene (BkF)	0.01*	0.16**		0.01*	0.16**		6E-06*	0.16**	
Benzo[a]pyrene (BaP)	1.0*	0.16**		1.0*	0.16**		6E-04*	0.16**	
Dibenzo[a,h]anthracene (DBA)	1.0*	0.16**		1.0*	0.16**		6E-04*	0.16**	
Indeno[1,2,3-cd]pyrene (IND)	0.1*	0.16**		0.1*	0.16**		6E-05*	0.16**	
Benzo[ghi]perylene (BghiP)	0.01*	0.16**		0.01*	0.16**		6E-06*	0.16**	

Where: *[17,18], **[21]. IRIS: Integrated Risk Information System, PPRTV: Provisional Peer-Reviewed Toxicity Value, ATSDR: Agency for Toxic Substances and Disease Registry, CSF: cancer slope factor (mg/kg/day), OSF: oral slope factor (mg/kg/day), IUR: inhalation unit risk (mg/m^3), RfD: reference dose RfC: reference concentration

Table 2. Reference value for Total petroleum hydrocarbons (TPHs)

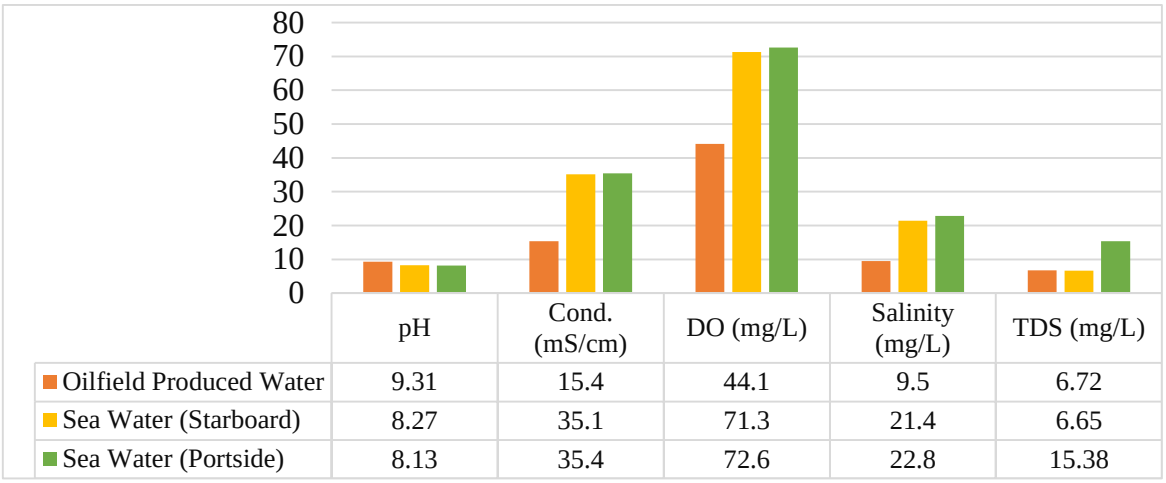
Aliphatic	**Dermal**			**Ingestion**			**Inhalation**		
	CSF	RfD	Source	CSF	RfD	Source	CSF	RfC	Source
Low carbon range (C5-C8)	NA	5.00	PPRTV	NA	0.3	PPRTV	1.9E-04	2.0	PPRTV
Medium carbon range (C9-C18)	NA	0.10	PPRTV	NA	0.1	PPRTV	4.5E-03	0.1	PPRTV
High carbon range (C19-C32)	NA	0.10	PPRTV	NA	30.0	PPRTV	NA	NA	
High carbon range (C33-C40)	NA	2.00	PPRTV	NA	30.0	PPRTV	NA	NA	
Aromatic	**Dermal**			**Ingestion**			**Inhalation**		
	CSF	RfD	Source	CSF	RfD	Source	CSF	CSF	Source
Low carbon range (C6-C8)	NA	0.04	PPRTV	0.055	0.01	IRIS/ PPRTV	7.8E-03	0.08	IRIS/ PPRTV
Medium carbon range (C9-C16)	NA	0.04	PPRTV	NA	0.3	PPRTV	NA	1	PPRTV
High carbon range (C17-C32)	NA	0.03	PPRTV	NA	0.4	HEAST	NA	NA	
High carbon range (C33-C40)	NA	0.03	PPRTV	NA	0.4	HEAST	NA	NA	

Where: PPRTV: Provisional Peer-Reviewed Toxicity Value, HEAST: Health Effect Assessment Summary Table, IRIS: Integrated Risk Information System.

Results and Discussion

Physiochemical parameter of Oilfield PW, Seawater (SB and PS)

Figure 2 shows the physiochemical parameters sampled from petroleum exploration area shows that pH was alkaline across different sampling points thus associated from dissolved alkaline rock minerals such as carbonate and bicarbonate components which increases pH of oilfield produced water, seawater (starboard and portside). Conductivity was relatively okay across the three-sampling point thus, showing less reactive anions or cations. Dissolved oxygen is influenced by temperature, biological and chemical process, which reduces chemical component via versa for oxidation increasing corrosion of metallic materials. Salinity content was relatively low which can be attributed to salts content such as chloride, sulphates, carbonates etc. Total dissolved solid impacts on palatability of water, as there are little health-based issues associated but can impacts on conductivity, turbidity, reactivity potential and dissolved oxygen [22, 23].



	pH	Cond. (mS/cm)	DO (mg/L)	Salinity (mg/L)	TDS (mg/L)
Oilfield Produced Water	9.31	15.4	44.1	9.5	6.72
Sea Water (Starboard)	8.27	35.1	71.3	21.4	6.65
Sea Water (Portside)	8.13	35.4	72.6	22.8	15.38

Fig. 2. Physiochemical parameters.

Polycyclic Aromatic Hydrocarbons of Oilfield PW, Seawater (SB and PS)

Fig. 3 shows the concentrations of polycyclic aromatic hydrocarbon with sum total of 266.7534 mg/L, 36.4268mg/L and 45.3311mg/L for oilfield produced water, seawater seaboard and seawater portside. Oilfield produced water had high PAHs content compared to the seawater samples, which can impact on offshore or petroleum exploration officers from inhalation, skin contact or ingestion thus leading to cancer risk such as CNS disruption, reproductive issues, enzyme disruption, kidney and liver issues. [22, 24].

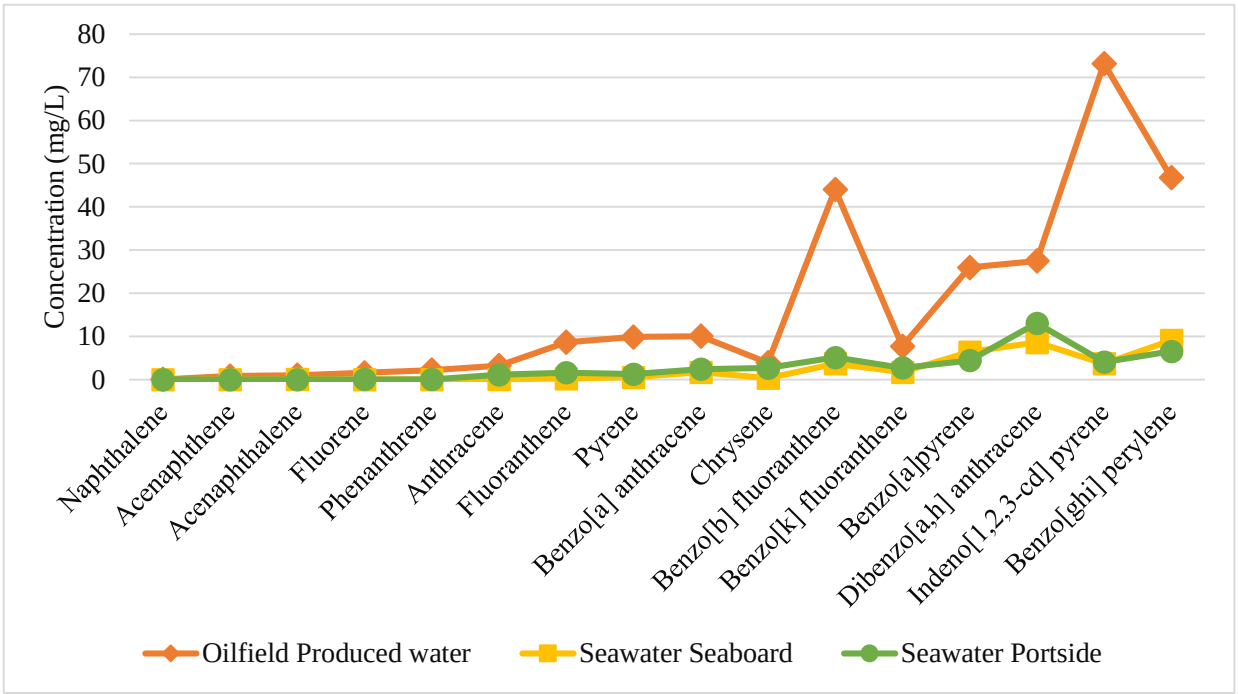


Fig. 3. PAHs concentration

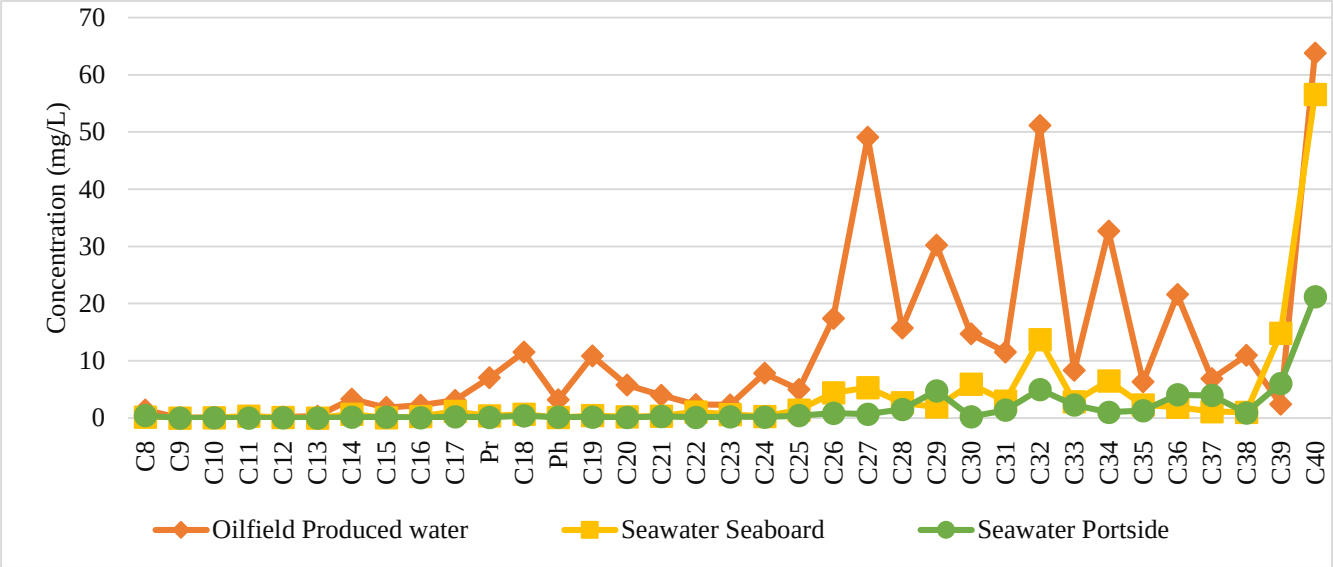


Fig. 4. TPHs concentration

Total Petroleum Hydrocarbons of Oilfield PW, Seawater (SB and PS).

Fig. 4 shows the concentration of total petroleum hydrocarbons with sum total of 414.9637mg/L, 132.0674mg/L and 58.1939mg/L for oilfield produced water, seawater seaboard and seawater portside. TPH is a combination of aliphatic and aromatic petroleum hydrocarbons which has being associated to form toxic product in the presence of free chlorine and high temperature forming polychlorinated – n – alkanes (PCAs) and polychlorinated biphenyls PCBs) across water sources causing mutagenic and carcinogenic human risk [25].

Carbon Preference Index

Carbon preference index (CPI) conducted on total petroleum hydrocarbons for oilfield-produced water, seawater seaboard and seawater portside respectively. Different TPH segmentation done as shown in **fig. 5** indicates that C8 – C11 and C33-C40 was below 1 indicating man-made contribution while C12 – C17, C18 – C25, and C26 – C33 for Seawater SB and PS were above 1 indicating presence of biogenic source. CPI has been used for forensic science but other studies indicates that CPI is unrelated to petroleum contamination but source identification process [26-28].

Risk Assessment for Polycyclic Aromatic Hydrocarbons

Risk assessment conducted for polycyclic aromatic hydrocarbons (PAHs) using carcinogenic and non-carcinogenic average daily intake (ADI) for dermal, ingestion and inhalation as shown in **figure 6a - c.** The cumulative sum of ADI – Dermal for Oilfield produced water, Seawater Seaboard and Portside was (6.36E-06, 9.05E-07, 1.13E-06), (1.78E-05, 2.44E-06, 3.03E-06) respectively. For ADI – Ingestion was (2.97E-06, 4.05E-07, 5.05E-07), (7.99E-06, 1.09E-06, 1.36E-06) respectively while ADI – Inhalation was (107, 14.6, 18.2), (288, 39.3, 48.9) respectively. Having assess the ADI for dermal, ingestion and inhalation pathways shows that non-carcinogenic ADI was highest for oilfield produced water compared to sweater portside and seaboard, which were relatively low in term of concentration compared to carcinogenic ADI values. Inhalation pathway shows that non-carcinogenic ADI was highest compared to carcinogenic ADI due to human contact of a long period has detrimental impact to health of offshore workers.

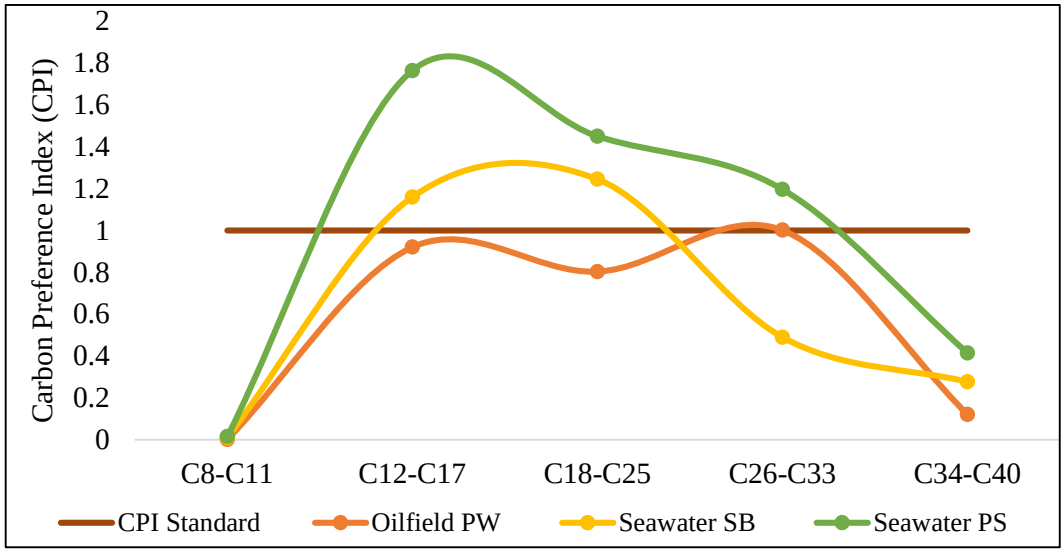


Fig. 5. Carbon Preference Index of TPHs

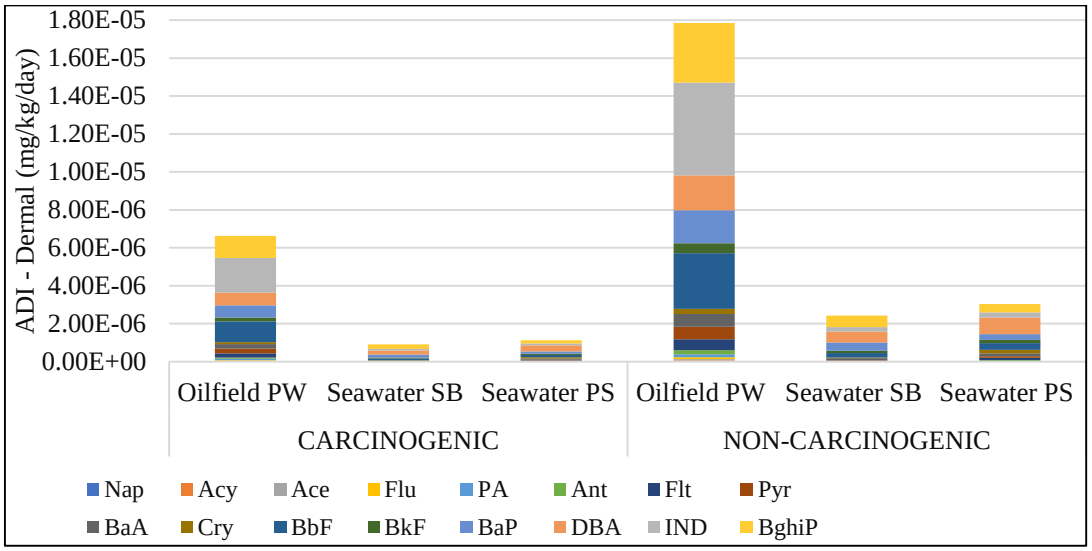


Fig 6a. PAHs average daily intake for dermal pathway

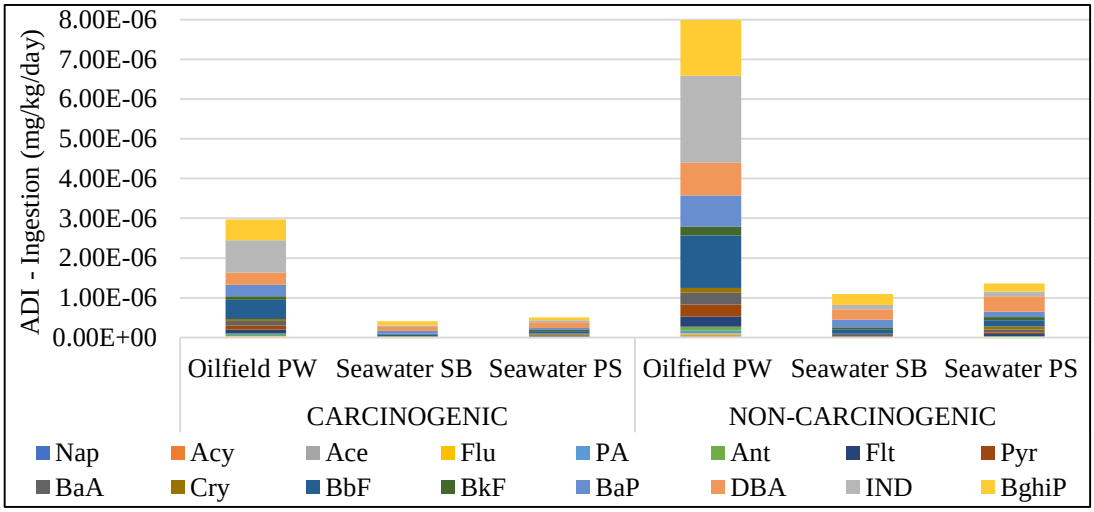


Fig. 6b. PAHs average daily intake for ingestion pathway

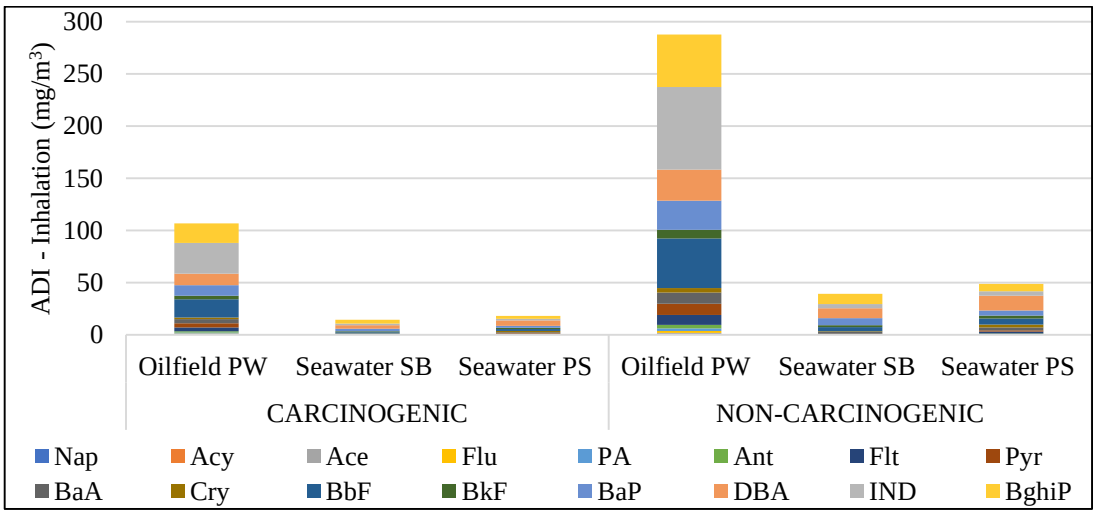


Fig. 6c. PAHs average daily intake for inhalation pathway

Carcinogenic risk assessment of PAHs

Carcinogenic Risk assessment presented in **Table 3** and **fig. 7** shows the cancer risk of dermal, ingestion and inhalation of polycyclic aromatic hydrocarbons (PAHs). The USEPA considers acceptable cancer risk in range of 1.0E-06 to 1.0E-04 (USEPA, 2018). Results assessed showed that dermal and ingestion pathways was within safe range, while inhalation was below range across the different sampling points with cumulative PAHs inhaled was 27.2, 6.45, and 7.45. Benzo[a]pyrene (BaP) used as reference value for conducting PAH assessment indicates that it has detrimental impact to health of offshore employee of a long period from multiple agents acting at an offshore location. In combination with dermal and ingestion pathways, the carcinogenic risk is organ and system failure from sub-chronic and chronic exposure leading to toxicokinetic and carcinogenencity [29-31].

Non-carcinogenic risk assessment of PAHs

Non-carcinogenic risk assessment was conducted on different exposure pathway: dermal, ingestion and inhalation of polycyclic aromatic hydrocarbons.

Table 3. Cancer risk of PAHs from different risk pathways

PAHs	Dermal			Ingestion			Inhalation		
	Oilfield PW	Oilfield PW	Seawater SB	Oilfield PW	Seawater SB	Oilfield PW	Seawater SB	Seawater SB	Seawater PS
Nap	NA	NA	NA	NA	NA	NA	NA	NA	NA
Acy	2.12E-10	6.86E-12	3.01E-12	9.48E-11	3.07E-12	9.48E-11	3.41E-03	1.11E-04	4.85E-05
Ace	2.59E-11	1.22E-12	5.74E-13	1.16E-11	5.49E-13	1.16E-11	4.18E-04	1.98E-05	9.26E-06
Flu	NA	NA	NA	NA	NA	NA	NA	NA	NA
PA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ant	NA	NA	NA	NA	NA	NA	NA	NA	NA
Flt	2.15E-09	6.57E-11	4.04E-10	9.65E-10	2.94E-11	9.65E-10	3.47E-02	1.06E-03	6.52E-03
Pyr	2.46E-08	1.33E-09	3.19E-09	1.10E-08	5.94E-10	1.10E-08	3.96E-01	2.14E-02	5.15E-02
BaA	2.50E-08	4.32E-09	6.06E-09	1.12E-08	1.94E-09	1.12E-08	4.04E-01	6.97E-02	9.77E-02
Cry	9.69E-11	9.25E-12	6.72E-11	4.34E-11	4.14E-12	4.34E-11	1.56E-03	1.49E-04	1.08E-03
BbF	1.10E-07	9.21E-09	1.28E-08	4.91E-08	4.12E-09	4.91E-08	1.77E+00	1.48E-01	2.07E-01
BkF	1.92E-09	4.34E-10	6.74E-10	8.61E-10	1.94E-10	8.61E-10	3.10E-02	7.00E-03	1.09E-02
BaP	6.45E-07	1.59E-07	1.10E-07	2.89E-07	7.12E-08	2.89E-07	1.04E+01	2.56E+00	1.78E+00
DBA	6.83E-07	2.14E-07	3.25E-07	3.06E-07	9.61E-08	3.06E-07	1.10E+01	3.46E+00	5.23E+00
IND	1.82E-07	9.19E-09	1.01E-08	8.15E-08	4.11E-09	8.15E-08	2.93E+00	1.48E-01	1.62E-01
BghiP	1.16E-08	2.26E-09	1.63E-09	5.21E-09	1.01E-09	5.21E-09	1.87E-01	3.64E-02	2.63E-02
ΣPAHs	1.68E-06	4.00E-07	4.7E-07	7.55E-07	1.79E-07	7.55E-07	2.72E+01	6.45E+00	7.57E+00

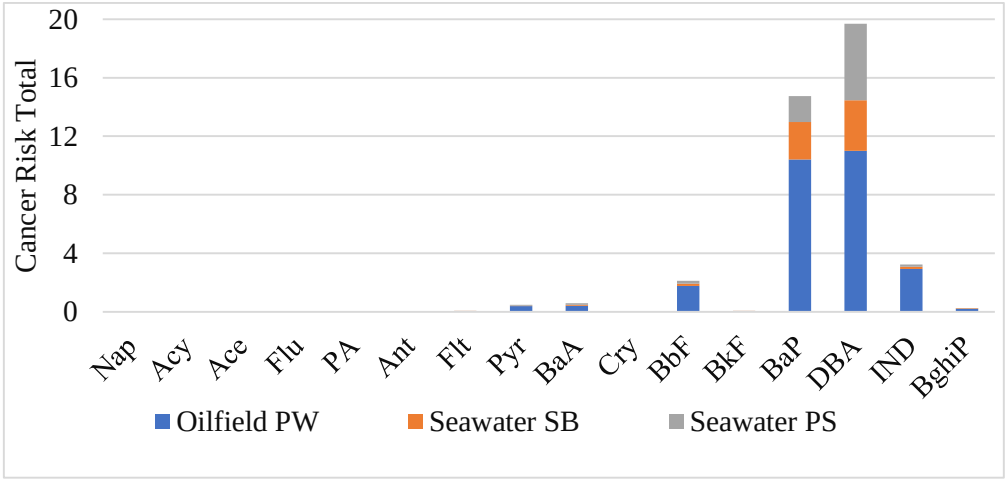


Fig. 7. Cancer risk total of PAHs

Table 4 shows the hazard quotient while the cumulative PAHs is the Hazard Index as presented in **fig. 8**. Hazard Index for dermal and ingestion pathways was below 1 indication no health risk to populace from skin interaction or possible ingestion of these PAHs. Inhalation pathway indicates that HQ was greater than 1, which has health risk to offshore workers. Several assessments showed that prolonged exposure leads to neurobehavioral, developmental, skin tumour, reproductive, and immune effects from PAHs exposure in the liver, kidney, respiratory tract, pharynx and skin of a human [29]. In addition, exposure to PAHs has capacity to activate biochemical metabolism leading to genetic changes tumor sites (DNA mutations) in humans [31]. According USEPA assessment, PAHs is classified as probable human carcinogen (B2) which has genotoxic capacity that influence human DNA over a long period from dermal, inhalation and ingestion [32].

Table 4. Hazard quotient of PAHs from exposure pathways

PAHs	Dermal			Ingestion			Inhalation		
	Oilfield PW	Oilfield PW	Seawater SB	Oilfield PW	Seawater SB	Oilfield PW	Seawater SB	Seawater SB	Seawater PS
Nap	2.68E-08	1.17E-09	7.48E-09	6.39E-09	2.80E-10	1.79E-09	23.01E+00	1.01E+00	6.44E+00
Acy	3.56E-07	1.15E-08	5.06E-09	1.28E-07	4.14E-09	1.81E-09	5.74E+00	1.86E-01	8.16E-02
Ace	4.36E-07	2.06E-08	9.66E-09	5.21E-08	2.46E-09	1.15E-09	7.03E+00	3.32E-01	1.56E-01
Flu	NA	NA	NA	1.19E-07	2.96E-09	4.26E-09	NA	NA	NA
PA	NA	NA	NA	1.65E-07	1.29E-09	3.68E-09	NA	NA	NA
Ant	NA	NA	NA	3.24E-08	1.07E-09	1.13E-08	NA	NA	NA
Flt	3.62E-06	1.11E-07	6.80E-07	2.60E-06	7.92E-08	4.87E-07	5.85E+01	1.78E+00	1.10E+01
Pyr	4.14E-06	2.23E-07	5.38E-07	9.88E-07	5.33E-08	1.28E-07	6.67E+01	3.60E+00	8.67E+00
BaA	4.21E-06	7.28E-07	1.02E-06	1.89E-06	3.26E-07	4.57E-07	6.80E+01	11.73E+00	1.64E+01
Cry	1.63E-06	1.56E-07	1.13E-06	7.30E-07	6.97E-08	5.06E-07	2.63E+01	2.51E+00	1.82E+01
BbF	1.84E-05	1.55E-06	2.16E-06	8.25E-06	6.94E-07	9.65E-07	2.97E+02	24.98E+00	3.48E+01
BkF	3.23E-06	7.30E-07	1.13E-06	1.45E-06	3.27E-07	5.08E-07	5.22E+01	11.78E+00	1.83E+01
BaP	1.09E-05	2.68E-06	1.86E-06	4.86E-06	1.20E-06	8.32E-07	1.75E+02	43.15E+00	3.00E+01
DBA	1.15E-05	3.61E-06	5.46E-06	5.15E-06	1.62E-06	2.45E-06	1.85E+02	58.20E+00	8.81E+01
IND	3.06E-05	1.55E-06	1.70E-06	1.37E-05	6.92E-07	7.59E-07	4.93E+02	24.92E+00	2.73E+01
BghiP	1.96E-05	3.80E-06	2.74E-06	8.76E-06	1.70E-06	1.23E-06	3.15E+02	61.29E+00	4.42E+01
ΣPAHs	1.09E-04	1.52E-05	1.84E-05	4.89E-05	6.77E-06	8.34E-06	1.77E+03	2.45E+02	3.04E+02

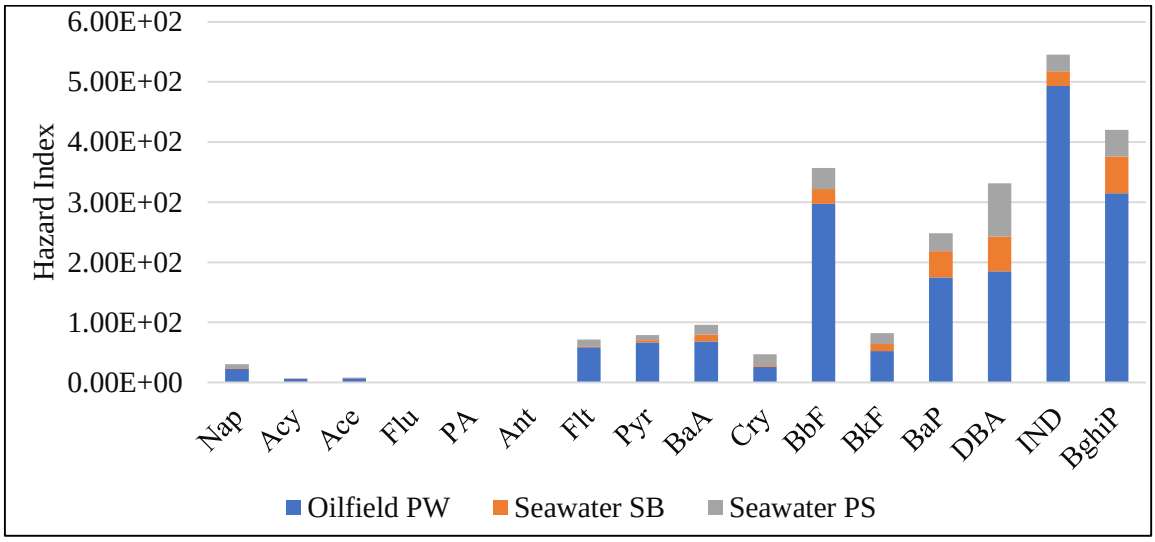


Fig. 8. Hazard Index of PAHs

Risk Assessment of Total Petroleum Hydrocarbons

Risk assessment conducted on total petroleum hydrocarbons from carcinogenic and non-carcinogenic average daily intake (ADI) across different exposure pathway (dermal, ingestion and inhalation as shown in **figure 9a - c**. Looking at the cumulative ADI for dermal, ingestion and inhalation pathways, shows that ADI was highest for oilfield produced water compared to sweater seaboard and least to seawater portside, which were relatively low in term of concentration for both carcinogenic and non-carcinogenic ADI assessment. Inhalation pathway shows non-carcinogenic risk was higher in ADI concentration compared to carcinogenic risk, which shows that it has inherent health impact to offshore workers.

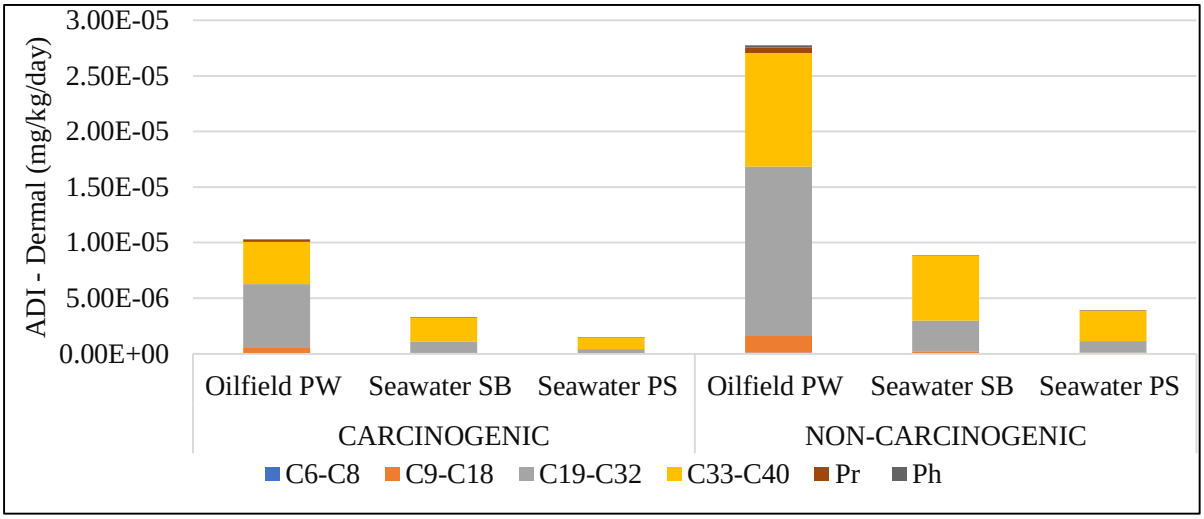


Fig. 9a. TPHs average daily intake for dermal pathway

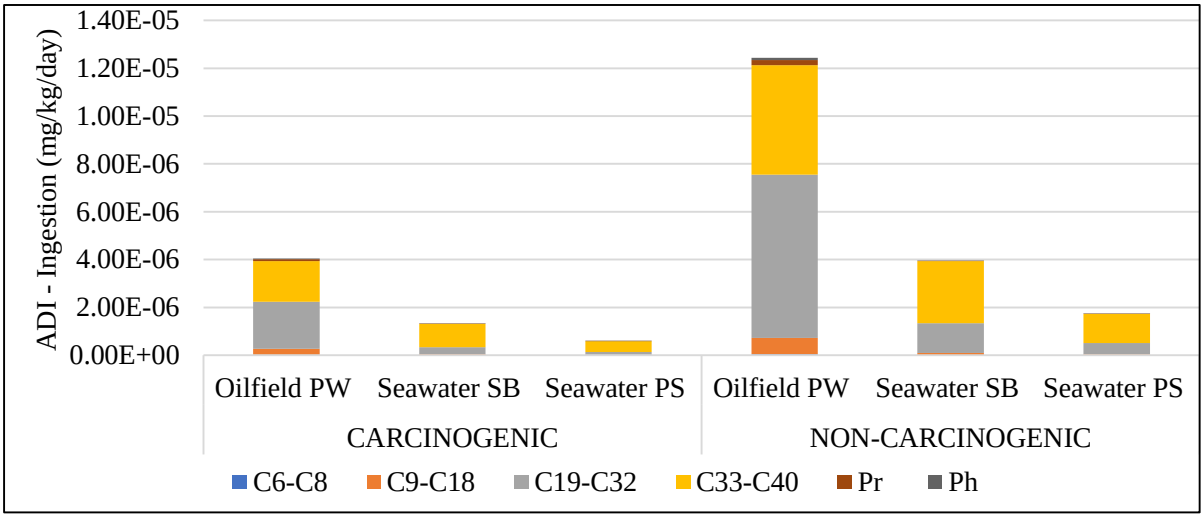


Fig. 9b. TPHs average daily intake for ingestion pathway

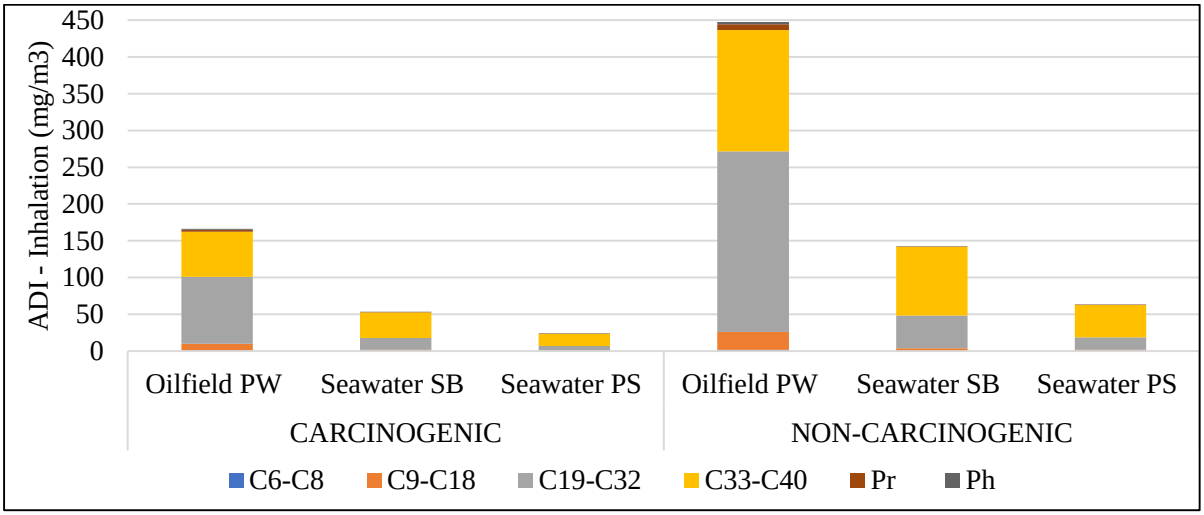


Fig. 9c. TPHs average daily intake for inhalation pathway

Carcinogenic risk assessment of TPHs

Carcinogenic risk assessment was conducted using average daily intake (ADI) for offshore workers as presented in **table 5** and **fig. 10** shows that inhalation has high impact compared to other exposure pathway (dermal and ingestion) from lack of usage cancer slope factors. The USEPA considers acceptable cancer risk in range of 1.0E-06 to 1.0E-04, thus inhalation of aliphatic and (or) aromatic petroleum hydrocarbon for a prolong period has devastating consequences from biological toxicity leading to respiratory related issues from cancer of the lungs and pharynx and tumour of different bodily organs [32,33].

Table 5. Cancer Risk of TPHs from exposure pathways

Aliphatic	**Dermal**			**Ingestion**			**Inhalation**		
	Oilfield PW	Seawater SB	Oilfield PW	Oilfield PW	Oilfield PW	Seawater PS	Oilfield PW	Seawater SB	Seawater PS
C6-C8	NA	NA	NA	NA	NA	NA	1.06E-04	1.27E-05	3.14E-05
C9-C18	NA	NA	NA	NA	NA	NA	4.10E-02	5.87E-03	1.85E-03
C19-C32	NA	NA	NA	NA	NA	NA	NA	NA	NA
C33-C40	NA	NA	NA	NA	NA	NA	NA	NA	NA
ΣTPHs	NA	NA	NA	NA	NA	NA	4.11E-02	5.89E-03	1.88E-03
Aromatic	**Dermal**			**Ingestion**			**Inhalation**		
C6-C8	NA	NA	NA	2.29E-09	2.74E-10	6.79E-10	1.17E-02	1.40E-03	3.47E-03
C9-C18	NA	NA	NA	NA	NA	NA	1.10E-01	1.58E-02	5.00E-03
C19-C32	NA	NA	NA	NA	NA	NA	NA	NA	NA
C33-C40	NA	NA	NA	NA	NA	NA	NA	NA	NA
ΣTPHs	NA	NA	NA	2.29E-09	2.74E-10	6.79E-10	1.22E-01	1.72E-02	8.46E-03

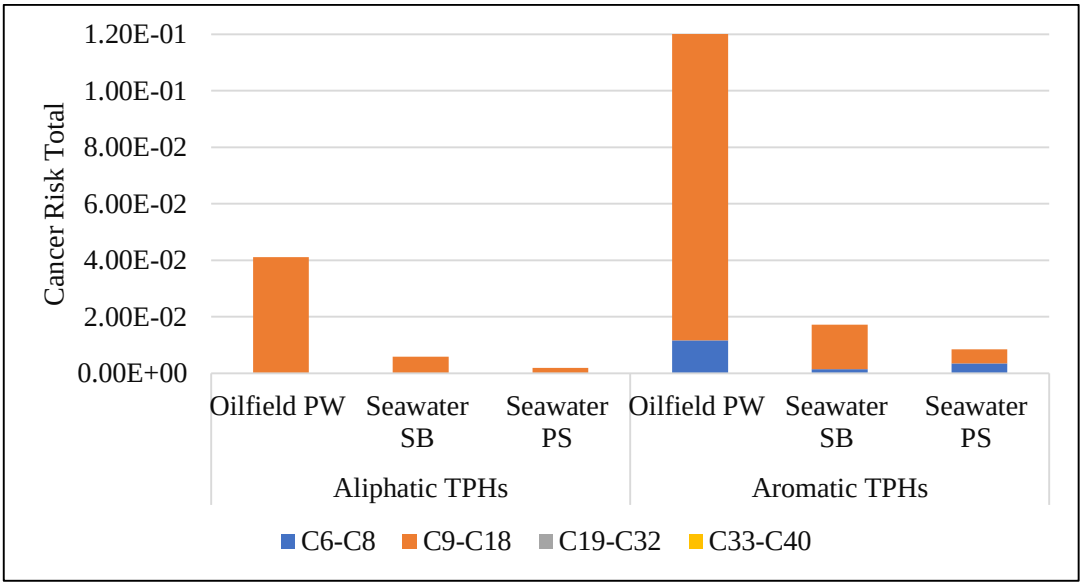


Fig. 10: Cancer risk total of TPHs

Non-carcinogenic risk assessment of TPHs

Non-carcinogenic risk assessment for offshore workers were conducted using ADI for aliphatic and aromatic TPHs by using average daily intake (ADI) as shown in **Fig. 9a-c**. Hazard quotient shows that inhalation, which influenced Hazard index graph as shown in Figure 11.

Table 6. Hazard quotient (HQ) for aliphatic and aromatic TPHs from exposure pathways

Aliphatic	**Dermal**			**Ingestion**			**Inhalation**		
	Oilfield PW	Seawater SB	Seawater PS	Oilfield PW	Seawater SB	Seawater PS	Oilfield PW	Seawater SB	Seawater PS
C6-C8	1.86E-08	2.23E-09	5.51E-09	5.15E-08	6.18E-09	1.53E-08	2.77E-01	3.30E-02	8.20E-01
C9-C18	1.52E-05	2.18E-06	6.88E-07	2.53E-06	3.63E-07	1.14E-07	9.11E+01	1.31E+01	4.12E+00
C19-C32	1.52E-04	2.76E-05	1.06E-05	6.55E-08	1.02E-08	4.01E-09	NA	NA	NA
C33-C40	5.11E-06	2.91E-06	1.36E-06	5.67E-08	3.23E-08	1.51E-08	NA	NA	NA
ΣTPHs	1.73E-04	3.27E-05	1.26E-05	2.70E-06	4.11E-07	1.49E-07	9.13E+01	1.31E+01	4.20E+00
Aromatic	Dermal			Ingestion			Inhalation		
C6-C8	2.32E-06	2.78E-07	6.89E-07	4.16E-06	4.99E-07	1.23E-06	1.87E+01	2.25E+00	5.56E+00
C9-C18	3.80E-05	5.45E-06	1.72E-06	2.27E-06	3.25E-07	1.03E-07	2.45E+01	3.51E+00	1.11E+00
C19-C32	5.08E-04	9.19E-05	3.52E-05	1.71E-05	3.09E-06	1.18E-06	NA	NA	NA
C33-C40	3.41E-04	1.94E-04	9.08E-05	1.15E-05	6.52E-06	3.05E-06	NA	NA	NA
ΣTPHs	8.89E-04	2.92E-04	1.28E-04	3.49E-05	1.04E-05	5.57E-06	4.32E+01	5.76E+00	6.66E+00

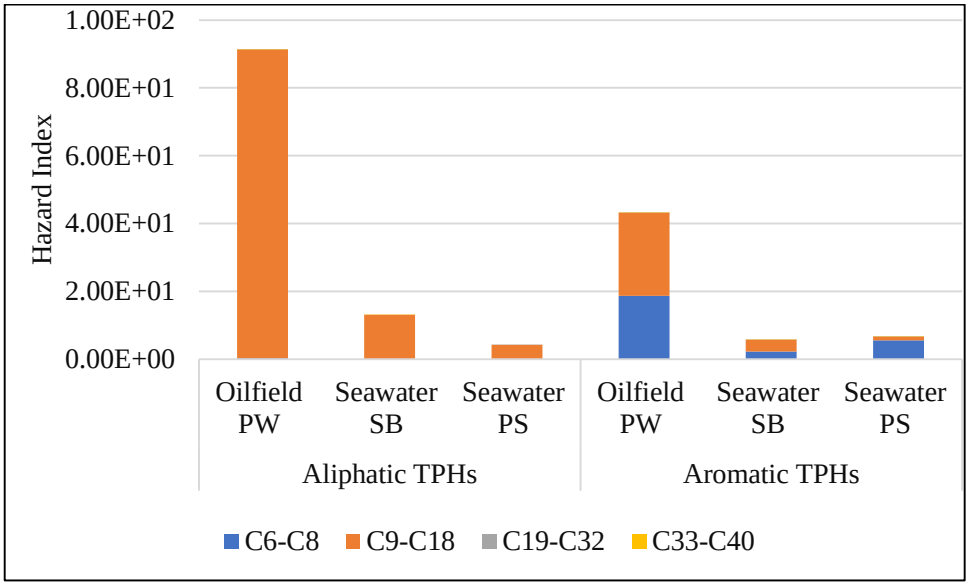


Fig. 11. Hazard Index of aliphatic and aromatic TPHs

Since Hazard Index (HI) is greater than one (1), there is high risk of respiratory issues (nasal lesions) from prolong bioaccumulation with cognisance to other exposure mechanism (dermal and ingestion) which is known to cause body weakness, weight loss, kidney and liver failure, skin rash and organ tumours [32,34,35].

Conclusion

The study assessed the physiochemical and risk assessment of seawater and oilfield produced water sampled from the Gulf of Guinea, Nigeria. Preliminary assessment showed that chemical releases has negative impact to biodiversity and humans attributed to release of spill and exploration in aquatic environment thereby causing adverse health effect from an array of exposure pathway to offshore workers and sea dwellers. Risk modelling studies conducted on polycyclic aromatic hydrocarbons and total petroleum hydrocarbon showed that prolonged exposure pathway from dermal, ingestion and

inhalation can lead to carcinogenic and tumour induction in humans. In addition, we showed that non-carcinogenic risk has more health impact compared to carcinogenic risk from bodily weakness, weight loss, kidney, liver and respiratory issues from inhalation pathway. Thus, we recommend that timely medical and toxicity assessment on offshore workers and sea dwellers before and after petroleum exploration to allow for proper health and environmental monitoring. Further regulations be set in place to prevent environmental pollution and protect residents who are susceptible to health-related illness and create sustainability.

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