

## Crude Oil Contaminated River Fishes arising from the Activities of Illegal Petroleum Refining in Oshika and Egbalor Communities in the Niger Delta Region of Nigeria

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### Abstract

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This study evaluated catfish from the impact of crude oil as contaminants on catfish caught from the surrounding streams of two selected sites of illegal petroleum refineries which have been abandoned as a result of its destruction by the government Task Force against illegal refineries. Laboratory analysis was carried out on the samples from the two sites at Oshika and Egbalor communities and a control, all in Rivers State, Nigeria. Tests for Heavy metals (Cd, Ni, As, Zn, Cu, Co, Cr, Pb), Polycyclic Aromatic Hydrocarbon (PAH), Benzene, Toluene, Ethyl benzene and Xylene (BTEX) and Total Hydrocarbon Content (THC) were carried out with Atomic Absorption Spectrophotometer (AAS) and Gas Chromatograph-Flame Ionization Detector (GC-FID). Duncan's New Multiple Range Test Statistical method was used in the analysis. This study showed that the concentrations of heavy metal pollutants in Fish followed distribution patterns of Cu>Pb>As>Co>Ni>Zn>Cr>Cd in Oshika site while that of Egbalor site is Zn> Cu> As> Ni> Cr> Co> Cd> Pb Which are all higher than WHO recommended permissible limits and control except Zn. This makes the fish contaminated from the illegal refinery activities. The result showed high concentrations of Polycyclic Aromatic Hydrocarbons (PAH)s in the sampled fish which are higher than the WHO recommended permissible limits and USEPA regulatory standard values for PAHs with a corresponding 30.09% and 11.64% of carcinogenic PAHs for Oshika and Egbalor sites respectively, thereby making the fish toxic. Recommendations were made for possible mitigation for illegal refineries.

### Introduction

The environmental degradation being experienced in the Niger Delta region has now reached an alarming proportion as a result of the activities of illegal petroleum crude oil refining. These activities led to oil spillage, gas flaring, contamination of farmlands, fishing ponds, streams and complete destruction of the aquatic habitat. It could also be said that the main cause of adverse environmental degradation emanates from crude oil pipeline and well head vandalism, spillages, gas flaring and production activities caused by these Illegal refineries [1]. These adverse effects culminated into loss of fishing and farmlands which are predominantly the primary indigenous vocations, leading to indigenes inability to fend for the basic needs of life. The pollution also arises from the illegal refining method of production processes in which the residue from the refinery is dumped indiscriminately into the neighbouring surface water, streams, ponds and rivers thereby

contaminating these water bodies and its aquatic life in general with fish inclusive, ultimately endangering the lives of humans when such contaminated aquatic animal is ingested [2]. Aquatic life and food chains within the ecosystems of mangrove forest, streams, rivers and fishponds are being polluted and contaminated whenever there is oil spillage thereby creating major problems for the livelihood, sustenance and general wellbeing of the community members [3].

There are over 142 illegal refineries in Rivers State and the State government has destroyed 128 so far while those of Bayelsa, Delta, Abia, Imo and Akwa Ibom States are left with an estimated total number of over 250 illegal refineries dotted across the Niger Delta region [4]. The Oshika and Egbalor illegal refinery sites are among the ones destroyed by the Rivers State Government.

### Statement of the Problem:

The fundamental issue is the environmental impact on the water resources, aquatic life (fish) within the operating areas of the illegal refineries. With the rapid expansion in the number of the illegal refinery sites across the Niger Delta region of Nigeria, the contamination of the ecosystems would greatly be increased. Therefore, studies of how these illegal crude oil refining activities affect the ecosystem in terms of crude oil hydrocarbon contaminations have become inevitable.

### Aim and Objectives:

The aim of this study is to investigate the environmental impact at Oshika and Egbalor communities' sites of crude oil contamination emanating from two abandoned illegal refinery activities on fish within the adjoining rivers where residues from production is channeled into.

The objectives include:

- 1) Investigate the extent of heavy metals (Cd, Ni, As, Zn, Cu, Co, Cr, Pb) and Polycyclic Aromatic Hydrocarbon (PAH) contaminants in the fish from two different streams adjoining the two illegal refinery sites at Oshika and Egbalor communities.
- 2) To determine Benzene, Toluene, Ethylbenzene and Xylene (BTEX) hydrocarbon contaminants in the sampled fish.
- 3) Determine the Total Hydrocarbon Content (THC) in the sampled fish.
- 4) Fish at sites, to be investigated with control fish sample taken from 45km away to check for specified heavy metals, BTEX, THC and PAH in the control.

### Related Literatures:

The activities of illegal refinery operations have recently been brought to the fore with its adverse and devastating environmental impact in the Niger Delta region. There are reports that the activities of the illegal refineries impacted negatively on the habitat, as there was an increased concentration of heavy metals content in water bodies and the environment in general [5]. The report continued, that petroleum, and its refined products have the ability of increasing heavy metals concentration content above the World Health Organization (WHO) [6] recommended permissible maximum limits. Some researchers in their various studies also stated that there was an exceedingly high rise of toxic heavy metals concentration contents for Nickel (Ni), Cadmium (Cd), Cobalt (Co) etc in water bodies affecting aquatic animals like fish when polluted with crude oil [7][8].

It has been reported that over 250 toxins [9] have been detected from crude oil and flared gases, whose constituents contribute to environmental problems, and this is easily associated with illegal refinery operations where there is no safety checks on gas flares and general oil spillages. The toxins are listed as follows: Benzene, Toluene, Ethylbenzene, Xylene, Polycyclic Aromatic Hydrocarbons (PAHs), Sulphur Dioxide, Hydrogen Sulphide, etc.

Crude oil hydrocarbons have been reported to have negative impact on aquatic species like Eastern oyster (*Crassostrea virginica*), Nile tilapia (*Oreochromis niloticus*), rainbow trout (*Oncorhynchus mykiss*) when the aquatic environment is polluted [10][11][12]. Also (*Achirus lineatus*) fish when exposed to polluted water with crude oil alters its gut bacteria composition in short period and on severe exposure leads to possible oxygen depletion in the gastrointestinal [13][14]

Fish vision impairment is reported to be caused by Polycyclic Aromatic Hydrocarbons (PAHs) in petroleum crude oil [15] with the retina of zebra fish when exposed to crude oil exhibited cell death and also the cardiovascular performance was reduced in the Gulf killfish (*Fundulus grandis*) with its eggs hatching reduced when they were exposed to crude oil [16]

Other researchers [17] reiterated that refineries produced gas, liquid and solid wastes and contaminants which end up within the habitat with a good number of these contaminants being naturally toxic compounds. Polycyclic Aromatic Hydrocarbons (PAHs) are reported to be the most abundant toxic compounds found in crude oil and get readily stabilized once introduced into the habitat especially in the soil and sediments (stream and riverbanks). Its stabilization could be between 48hours to 400days depending on the environmental conditions and are not easily degradable and remain in the sediments from rivers, streams, and ponds for a long time. It could bio-accumulate in tissues of organisms which can easily be assimilated into the food chain especially when fish is ingested.

### Materials and Methods

#### Area of Study:

The study was carried out in Rivers State in the Niger Delta region which is bounded by the Atlantic Ocean with swampy mangrove terrain. This difficult terrain contributes to the entire area being difficult to police thereby creating an easy avenue for criminals to vandalize crude oil pipes and facilities to steal crude oil for illegal refinery activities.

Two major sites of non-active Illegal refineries are selected for evaluation which are located in Oshika community in Ahoada West Local Government Area and Egbalor Community, Ebube in Eleme Local Government Area of the State.

The Oshika community has coordinates, latitude 5.04 North (5.073665) and longitude 6.51(6.562638) East of the State. The site and host community is situated in between SPDC pipeline (Right of Way) and the Agip Oil Company pipeline (Right of Way) that make up the Ebocha- Brass Pipeline (14" Okordia-Rumuekpe Trunk, Osika). Unfortunately, this unique situation makes the place attractive for illegal petroleum refiners as they tap from both lines with the surrounding stream into which waste products are emptied and also make them prone to oil spillages. The Illegal refinery was destroyed in February 2022.

The second site is located at about 20 kilometers away from the Egbalor community, covering vast hectares of devastated land and water bodies. Its coordinates are latitude 4°46' North (4.782922) and longitude 7°09' (7.154665) East. The site is within the Egbalor mangrove forest hosting the SPDC 24-inch Nkpoku-Bomu Trunk pipeline Right of Way. The illegal refinery was destroyed in January 2022.

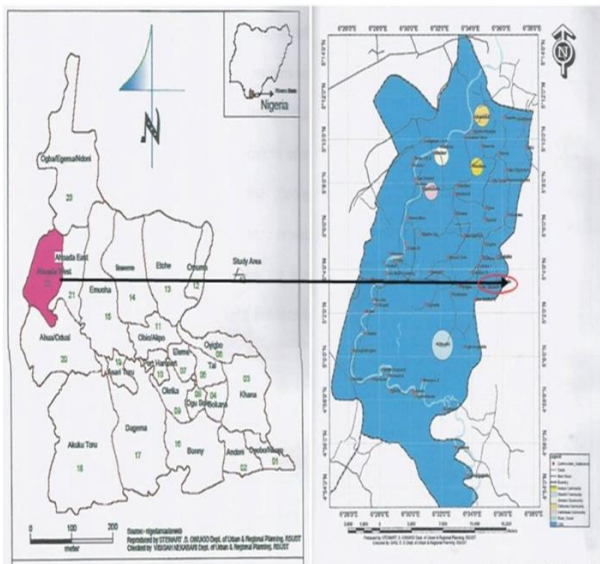


Figure 1 Ahoda West LGA, Oshika Village Map [18]

### Experimental Research

Catfish sample was collected from the streams adjoining the illegal refinery sites after several attempts and analyzed in the laboratory where some parameters like; heavy metal content (Cd, Ni, As, Zn, Cu, Co, Cr, Pb), Polycyclic Aromatic Hydrocarbons (PAHs), Benzene, Toluene, Ethyl-benzene and Xylene (BTEX) and Total Petroleum Hydrocarbon (TPH) contents were determined. The sites were abandoned artisan refinery sites with visual assessment showed that the environment was heavily polluted with petroleum products with little or no clean-up of the environment.

Oshika community site is named Site A while Egbalor community site is named Site B for this study.

### Fish Sample Preparation

The Catfish got from the polluted sites and a control were dissected and digested to extract the desired chemical elements from their body by cutting 10gms each of the fish into two different 250ml conical flasks and subjecting it to chemical extraction processes. The solution was then analyzed according to American Public Health Association (APHA) 3111B test method with the Atomic Absorption Spectrophotometer (AAS) for heavy metal content (Cd, Ni, As, Zn, Cu, Co, Cr, Pb).

**Determination of Benzene, Toluene, Ethyl benzene and Xylene (BTEX), Total Hydrocarbon Content (THC) and Poly Aromatic Hydrocarbon (PAH) by Gas Chromatograph-Flame Ionization Detector (GC-FID) Equipment.**

### Sample Extraction:

10grams of anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) was added into an amber glass bottle containing 10g of soil sample for removing moisture after being stirred. 300 $\mu\text{g}/\text{ml}$  of surrogate (1-chloro-octadecane) standard was added and 30ml of dichloromethane (DCM) was also added extraction purposes. The sample bottle placed in a shaker was capped properly in order to avoid any leak when vigorously agitated in the laboratory shaker for about 6hr at room temperature and given about 1hr to settle and stabilize, after which 110mm filter paper was used for filtration into a clean beaker. The filtrate was evaporated and concentrated to 1ml overnight in a fume cupboard.

### Sample Clean-up

A glass column was used for preparation by placing glass cotton into it and 10g silica gel was dissolved with 50ml (DCM) forming a slurry in the column with 10g anhydrous  $\text{Na}_2\text{SO}_4$  added with pentane. 20ml of cyclohexane was added to the sample extract, then placed in a beaker and take to the prepared and cleaned column which is then eluted using 30ml pentane as solvent and collected in a beaker below the column. The sample extract was eluted further by adding more 20ml pentane into the column, thereafter, rinsed with 20ml DCM. The eluted sample was kept overnight at ambient temperature in a fume cupboard to allow evaporation to occur.

### Sample Separation and Detection

The Agilent 6890N Gas Chromatograph – Flame Ionization Detector (GC-FID) equipment was used for this process. 3 $\mu\text{l}$  of the concentrated prepared sample was introduced into the GC vial. The blank DCM was equally introduced into the micro-syringe of GC for cleaning 3 times before analysis. The prepared sample was used to clean again the micro-syringe and injected into the column for full compound separation analysis. After separation, the compounds were passed through a flame ionization detector which detects the compounds in the sample. The various quantities of BTEX were determined at a particular chromatogram in mg/kg for sample. The same procedure was used to resolve THC and PAH in all the various samples from the sites.

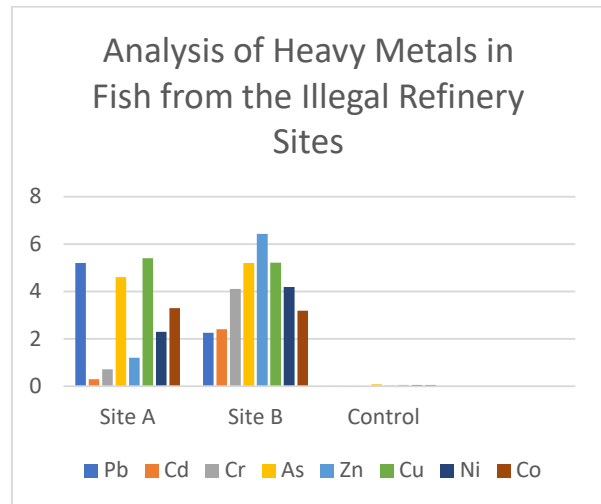
### Statistical Analysis

Statistical analysis was carried out using Statistical Package for Social Statistics (SPSS) software for the data got from the field work for heavy metals, PAH, BTEX and THC in fish. The various means and standard deviations were separated with the aid of The Duncan's New Multiple Range (DNMR) Test ( $p \leq 0.05$ ).

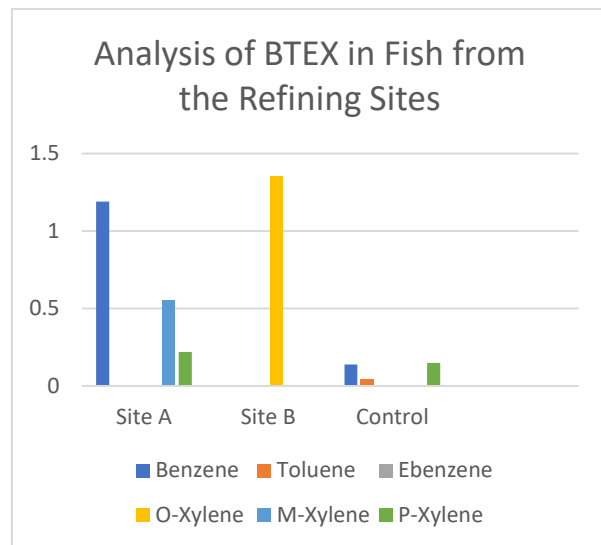
## Results

**TABLE 1** (Heavy Metals and BTEX) Result of Fish Analysis for Sites A and B.

Heavy Metal Content				
Heavy Metals (mg/kg)	Site A	Site B	Control	Standard (WHO)[4]
Pb	5.2±0.001	2.25±0.12	0.01±0.000	2
Cd	0.3±0.00	2.4±0.23	0.02±0.00	0.005
Cr	0.71±0.004	4.1±0.06	0.013±0.006	0.15
As	4.6±0.02	5.2±0.12	0.082±0.01	0.01
Zn	1.2±0.01	6.43±0.02	0.034±0.002	10.75
Cu	5.4±0.03	5.21±0.12	0.061±0.01	1.3
Ni	2.3±0.00	4.18±0.06	0.061±0.004	0.5
Co	3.3±0.01	3.19±0.01	0.06±0.001	0.11
Hydrocarbon Content: Benzene, Toluene, Ethylbenzene and Xylene (BTEX)				
Hydrocarbon	Site A	Site B	Control	Standard (mg/l) *
Benzene	1.19±0.10	-	0.14±0.002	0.1 – 0.3
Toluene	-	-	0.04±0.002	0.18 – 0.6
O-Xylene	-	1.35±0.20	-	0.1 – 0.3
M-Xylene	0.55±0.03	-	-	0.1 – 0.3
P-Xylene	0.22±0.12	-	0.15±0.001	0.1 - 0.3
Ethylbenzene	-	-	-	0.1 – 0.3



**Figure 2** Analysis of Heavy Metals in Fish from the Sites



**Figure 3** BTEX Content in Fish from the Refining Sites

Values represent Mean ± S.E.M at n= 3 and p≤ 0.05.

**TABLE 2:** Result of Fish analysis for Site A and B

\*USEPA Regulatory Standards for Polycyclic Aromatic Hydrocarbons (PAH) in water, fish and plants [19]

**TABLE 3** (THC levels) Result of Fish analysis for Site A and B

Total Hydrocarbon Content (THC) (mg/l)			
Hydrocarbon	Site A	Site B	Control
C8	-	-	-
C9	-	-	-
C10	-	2.5±0.29	-
C11	-	-	-
C12	28.62±0.01	-	-
C13	-	-	-
C14	-	-	-
C15	13.44±0.25	9.1±0.06	0.001±0.06
C16	-	-	-
PRISTON	-	-	-
C17	-	-	-
C18	49.14±0.08	-	-
Ph	-	-	-
C19	-	-	-
C20	-	5.94±0.01	-
C21	-	-	-
C22	-	-	-
C23	-	-	-
C24	-	-	-
C25	-	-	-
C26	-	-	-
C27	-	-	-
C28	-	-	-
C29	-	-	-
C30	-	-	-
C31	-	-	-
C32	-	-	-
C33	-	-	-
TOTAL	91.19	17.54	0.001

It shows the THC levels in the Fish samples from Sites A, B and control.

The mean values are as follows 91.19, 17.54 and 0.001 respectively.

## Discussions

Table 1 shows that the highest mean values for heavy metals were in Cu and Zn with  $5.4\pm 0.03$  and  $6.43\pm 0.02$  for sites A and B respectively, followed by Pb and Cu at  $5.2\pm 0.001$  and  $5.21\pm 0.12$  for respective sites. Arsenic (As) was next for sites A and B with its mean values  $4.6\pm 0.02$  and  $5.2\pm 0.12$ , while Co and Ni mean values are  $3.3\pm 0.01$  and  $4.18\pm 0.06$  respectively. Sites A and B results continued with Ni and Cr with mean values at  $2.3\pm 0.00$  and  $4.1\pm 0.06$ , while the mean concentration of Zn and Co in the fish were  $1.2\pm 0.01$  and  $3.19\pm 0.01$  respectively. Cr and Cd have mean values of  $0.71\pm 0.004$  and  $2.4\pm 0.23$ , while Cd and Pb have the least value of heavy metal concentration of  $0.3\pm 0.00$  and  $2.25\pm 0.12$  for sites A and B respectively.

The distribution and pattern of heavy metals in the fish got from site A is as follows; Cu>Pb>As>Co>Ni>Zn>Cr>Cd while that of site B is Zn>Cu>As>Ni>Cr>Co>Cd>Pb. The DNMR with ANOVA tests and results indicate that all the mean values for heavy metals from both Sites are significant at  $p<0.05$  which show tendency of bioaccumulation in plants and aquatic animals and conforms to the studies of other researchers [7], [20], [8],

Polycyclic Aromatic Hydrocarbons (PAH) (mg/l)				
Parameter	Site A	Site B	Control	Standard*
Naphthalene	-	4.42±0.24	2.14±0.08	
Acenaphthylene	5.64±0.02	2.35±0.20	1.04±0.02	
Acenaphthene	9.21±0.01	-	-	
Fluorene	2.38±0.219	-	-	
Phenanthrene	-	1.13±0.069	0.85±0.029	
Anthracene	-	2.95±0.027	-	
Fluoranthene	1.94±0.023	-	-	
Pyrene	-	-	-	
Benzo(g,h,i)perylene	-	1.43±0.019	-	
Benz(a)anthracene	-	-	-	0.1mg/l
Chrysene	8.25±0.029	-	-	0.2mg/l
Benzo(b)fluoranthene	-	-	-	0.2mg/l
Benzo(k)fluoranthene	-	-	-	0.2mg/l
Benzo(a)pyrene	-	-	-	0.2mg/l
Indeno(1,2,3cd)pyrene	-	-	-	0.4mg/l
Dibenz(a,h)anthracene	-	-	-	0.3mg/l
TOTAL	27.42	12.28	4.03	
Σ Carcinogenic PAHS	8.25	1.43	0	
% Carcinogenic	30.09	11.64	0	

[21]. All the values are higher and above that of the control values and the WHO permissible limit in fish except Zn that is within the standard. This is definitely so as a result of the crude oil spillages and constant discharge of the illegal refinery residues and waste into the adjoining streams as seen in plates 1 and 2. Although Zinc is known to be non-toxic but its excess intake via food chain like fish (as a result of bioaccumulation) over a period of time have been implicated in nausea, vomiting, epigastric pain, diarrhea, loss of appetite etc to humans [22].

The BTEX result indicates that Benzene is present in fish from Site A but absent in Site B with a mean value of  $1.19\pm 0.10$ . Toluene is absent in the fish from both sites but O-Xylene  $1.35\pm 0.20$  present in Site B and absent in Site A. M-Xylene is present in Site A but absent in Site B with its mean value of  $0.55\pm 0.03$ . P-Xylene is present in Site A with its mean value as  $0.22\pm 0.12$  and within the WHO permissible Limit but absent from Site B. Ethylbenzene is not present in the fish from both Sites. If Xylene bioaccumulates in the fish over a period of time and ingested, could lead to stomach irritation, nausea, vomiting, liver

damage, diarrhea with acute systemic toxicity in humans [23]. The results were highlighted in Figures 2 and 3 which show clearly that Site B has more concentration spread of heavy metals but less carcinogenic hydrocarbons.

The total PAH present in the Fish is 27.42 and 12.28 for Sites A and B with the control being 4.03. The summation of carcinogenic PAHs found comprising Chrysene and Benzo(g,h,i)perylene with mean values as 8.25 and 1.43 for Sites A and B respectively. The carcinogenic PAH mean values are more when compared with WHO standard permissible limits for fish.

From the tables it could be observed that lots of heavy metal is being accumulated by the fish from both Sites A and B. Generally, it could be deduced that the fish found at the Egbalor refinery site has more metal heavy metal pollutant spread but has less carcinogenic PAH. The difference in carcinogenic PAH might not be unconnected with the present cleanup and remediation taking place at Ogoniland which includes the Egbalor polluted community. The possible total hydrocarbon content (THC) that were detected from the tests in the fish were C10, C12, C15, C18 and C20 from both sites and control with total values 91.19, 17.54 and 0.001 respectively which have health risks when ingested by human. Although the control value is insignificant but is connected with the air pollution in form of soot caused by the activities of illegal refinery that settled in the various private fishponds during the destruction and burning of illegal refinery sites by the State government.

However, it has been reported that fish bio-accumulate heavy metals in considerably amount and since the metals are non-biodegradable, they remain in the tissue of the fish over a long time and on consumption the pollutant gets transferred to human causing heavy metal poisoning at high concentration [24]. Plants and animals are known to take up these heavy metal pollutants and could bio-accumulate and no matter how low level they are, might increase and slip into the food chain and affect the health of human.

Apart from the heavy metals in the fish, the fish are also contaminated by PAH which makes it toxic with its high concentration of carcinogenic PAHs and not fit for human consumption. The control fish had no carcinogens.

## Conclusions

The environmental destruction and degradation associated with illegal oil refineries are most visible in the pictures taken at the study sites of Oshika community in Ahoada West Local Government Area and Egbalor, Ebube, Eleme Local Government Area of Rivers State as indicated in Plates 1 and 2. It shows terrible devastation of the farm lands and surface water with visual assessment showing that the environment was heavily polluted with petroleum products with little or no clean-up of the environment even after about nine months the illegal refineries were destroyed.

This study showed that the Fish found on both sites contain high concentration of heavy metals and carcinogenic PAHs thereby making the fish toxic and

unfit for human consumption because of illegal petroleum crude oil refining activities.

## Recommendations

The problems of illegal refining could be eliminated if:

- a) Government could reactivate the existing moribund refineries to eliminate the supply gap as this will definitely diminish the demand for illegal refinery petroleum products with its safety and production attendant problems.
- b) More investors should be encouraged into the refining sector with adequate enabling business policies.
- c) Integration of these illegal refineries into modular refinery scheme that will evolve by setting up Corporate societies and associations with adequate financial and technical support with safety and standard of operation put in place.
- d) Proper remediation and complete cleanup to be carried out at inactive illegal refinery sites to mitigate the adverse impact of the illegal refining activities on the contamination and degradation of the environment and the surrounding water bodies in order to safeguard both aquatic and human lives.

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## Conflicts of interest

There are no conflicts to declare.

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