

GEOSPATIAL QUANTIFICATION OF THE POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN THE WETLANDS OF KOLOKOLO AND ENVIRONS (OIL BEARING COMMUNITIES), WARRI NORTH, DELTA, NIGERIA

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ABSTRACT

This study was an ex-port factor research that investigated the content of PAHs in the wetlands in Kolokolo and environs. The study answered 5 research questions and tested a hypothesis. To achieve these, the wetlands in the 5 settlements were mapped into 5 sampling grids of 50 meters apart and water samples were collected from 5 spots with 125mL plastic sampling bottles at 10cm depth and covered sub surface. The samples from each grid were bulked, composites drawn and fixed with HNO₃ and stored in ice cooled flasks for analysis. The analytical standard adopted was EU 1881/2014 while the instrument of determination deployed was Agilent GC/MS Triple Quadruple model 7000. The mean result obtained were; pyrene 1.02 ± 0.01µg/l, chrysene, 1.02±0.01 µg/l, BaP; 1.03 ± 0.01µg/l BaA; 1.02 ±0.02ug/l and BbF, 1.03 ± 0.02µg/l. The mean results were subjected to test of significance with ANOVA using SPSS IBM model 29 at 0.05 level of significance and the *p* value was 0.042 thus rejecting H₀. The study concluded that the wetlands are contaminated with PAHs above EU 1881/2014 MPC for wetlands thus the produce are not fit for human and animal consumption. They are equally not exportable. The study recommended that the oil companies should be compelled to adopt world best practices in their operational activities, the monitoring agencies NESREA and NOSDRA should scale up their surveillance and the impacted ecosystem should be remediated and restored.

Keywords: aromatic hydrocarbons (PAHs), Wetlands, Oil production, polycyclic contamination.

INTRODUCTION

Wetlands are complex, delicate and highly valuable ecosystem that exist in varying degrees in virtually all countries on the planet earth. It is an ecosystem that is saturated or flooded with water permanently or partially for decades, or years (Sabastine 2021, Cole 2022, Ogwu *et al.*, 2022) Wetlands are areas where water is present near the surface of the soil in most period of the year (Thompson 2016, Dell 2018, Sodiq 2023). They are transitional lands between aquatic and terrestrial lands with high water table usually near the surface and in most times covered by shallow water (Shingle 2019, Doff 2021, Spence 2018) Wetlands are areas of land covered by swamp, bog, fen or mash (Benson 2015 Betrand 2018). They are low lying lands with soil spongy in nature with high moisture content all year round. (Onwuka 2017, Ogwu *et al.*, 2022,

Ogwu *et al.*, 2021).

Wetland ecosystem is the habitat for numerous species of fauna and flora (Ogwu 2021, Bangboye 2022, Adeeko 2021), they provide shore protection, prevent coastal erosion and purify run off water (Surrel 2019, Maxwell 2018, Afocabi 2020). Wetlands provide breeding place for fish and wetland animals (Osodeke 2019), and provide recreation and tourists destination (Duru 2018, Odili 2020), they recharge the rivers, cool the higher grounds and balance redox reaction. (Ogwu *et al.*, 2023 Okpako 2023, Maduka 2024).

Wetlands globally have been subjected to various abuses from industrial effluents discharges containing heavy metals, pesticides, detergents, styroforms, (Ogwu *et al.*, 2022, Ogwu *et al.*, 2021), micro plastics, polycyclic aromatic hydrocarbons (PAHs) Benson *et al.*, 2014, Beriro *et al.*, 2016, Chen *et al.*, 2015, Chang *et al.*, 2016). Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds that are composed of simple to complex benzene rings (Canozzi *et al.*, 2016, Caruso *et al.*, 2015, Celeiro *et al.*, 2014). PAHs occur naturally in coal, gasoline and crude oil (Cili *et al.*, 2014, Dela-Rosa *et al.*, 2016, Chropenova *et al.*, 2016). Oil spillage into and wetland occur via pipelines rupture; well head blow out, tank wash equipment failure (Ogwu *et al.*, 2022, Abubakar 2020, Nurudeen 2022). Bioavailability of PAHs in wetland ecosystem results in bioaccumulation and biomultiplication in wetland fauna and flora (Coronas *et al.*, 2016, Corrotea *et al.*, 2014, Dellarulle *et al.*, 2016, Deng *et al.*, 2014) and PAHs have been fingered in cataracts, liver problems, renal complications, cancer of the gastrointestinal tract. (El-Saeid *et al.*, 2015).

Kolokolo and the adjoining villages are wetland oil bearing communities whose wetlands are the recipients of the spills that occur during oil extraction and loading. The focus of this study is the analysis of the wetlands water in Kolokolo, Ayogboro, Daghele, Eghoro and Dudu Town for the contents of polycyclic aromatic hydrocarbons as concomitant effect of oil production in the area.

The PAHs investigated are pyrene, chrysene, Benzo(a)pyrene (BaP), benzo(a) anthracene (BaA), and benzo(a) fluorathene (BbF)

Research Questions

The study was guided by research questions as:

1. what are the concentrations of pyrene, chrysene BaP, BaA and BbF in the wetlands of Kolokolo and environs?
2. are the concentrations of the PAHs in the wetlands within the maximum Permissible Concentration(MPC) of 1.00µg/l as espoused by EU code1881/2014?
3. are the produce from the wetlands fit for human consumption?
4. will the produce be fit for animal feeds formulation?
5. will the produce be exportable considering Codex 1963 commission standards for produce export?

Hypothesis

The study was guided by a null hypothesis at 0.05 level of significance as thus;

H₀: there is no significant difference between the concentrations of PAHs in the wetlands in Kolokolo and environs and EU 1881/2014 MPC for PAHs in wetlands.

Study Area

Kolokolo, Ayogboro, Daghele, Egboro and Dudu Town are oil bearing Itsekiri settlements in Warri North local government area Delta state Nigeria. They are within latitude 6° 45' 31"N and longitude 5° 4" E. The inhabitants of these wetlands settlement are predominantly fishermen and farmers. Some are artisans while some are petty traders. A very few are public servants teaching in public primary and secondary schools and some work in the oil companies operating in the area.

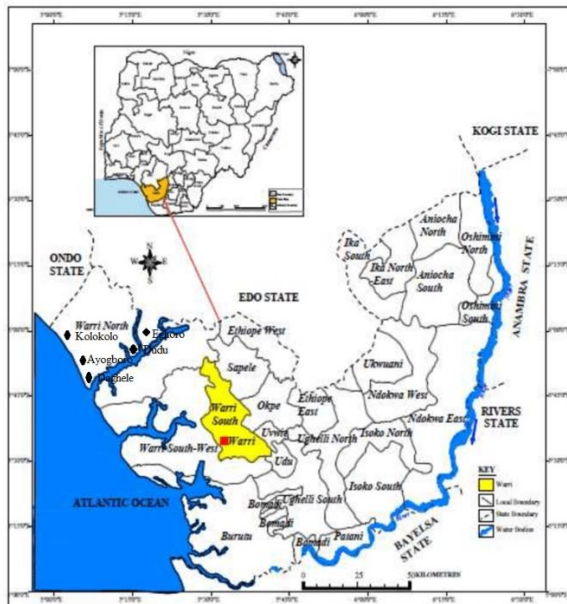


Figure 1: Map of Warri North Showing Kolokolo and environs) Adapted from: Ogeleka et al. (2016)

MATERIALS AND METHODS

This study was conducted within a period of six (6) months spanning from October 2023 to march 2024. Five (5) research assistants were enlisted for the samples collection, one in each of the 5 settlements. Grab hydrological sampling technique was adopted, and the wetlands were mapped out into 5 sampling grids

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and Samples were collected from 5 spots in each grid using 125mL plastic sampling bottle at 10cm depth, bulked and composites taken fixed with nitric acid and stored in ice cooled sample boxes for analysis. 125 samples were collected for the study.

Analysis

The samples were analyzed using gas chromatography with mass spectrometry adopting EU 1881/2014 as describe in (Dudghagara et al., 2016, Dong et al., 2015 Ganna et al., 2014) 5ml of the wetlands water samples were measured into beakers into which 2g of sodium sulphate (anhydrous) were added. They were agitated vigorously for good mixing. The mixtures were then transferred into extraction beakers with tight lids and allowed to settle for 30minutes. Dicafluorabiphenyl were added and also sodium hydrosulphate and the beakers were again vigorously agitated until free flowing flurry appears. The beakers were allowed to settle again for about 30 minutes to 1 hour. The mixtures produced were aspirated into gas chromatography and mass spectrometry (GC/MS) chambers of Agilent Triple Quadruple 7000 model for the reading of the concentrations of PAHs under investigation.

RESULTS

The results of the PAHs content in the wetlands in Kolokolo and environs were as in Figures 2 to 6 and comparative means result in Figure 7.

The values obtained from Kolokolo were as in Figure 2.

Table 1: results of the PAHs content in Kolokolo and EU 1881/2014 MPC for PAHs in wetlands in µg/l

	A	B	C	D	E	Mea n	EU 1881/2014 MPC µg/l
Pyrene	1.0	1.0	1.0	1.0	1.0	1.03	1
Chrysene	1.0	1.0	1.0	0.9	1.0	1.01	1
Benzo(a)pyrene	2	3	2	8	4	1.02	1
Benzo(a)anthracene	1	8	3	2	2	1.01	1
Benzo(b)fluorathene	1.0	0.9	1.0	1.0	1.0	1.02	1

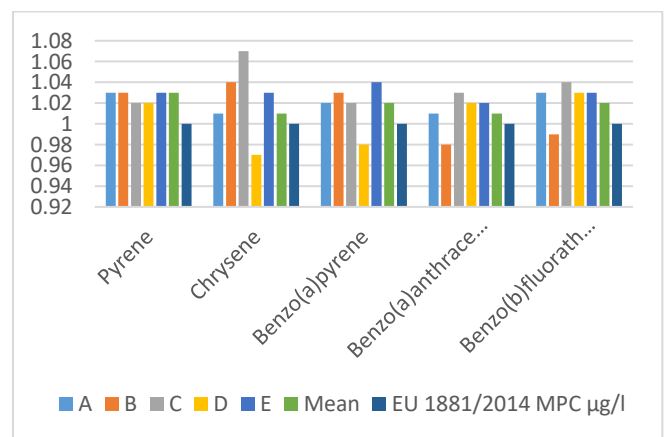


Figure 2: results of the PAHs content in Kolokolo and EU 1881/2014 MPC for PAHs in wetlands in µg/l

The values obtained from Ayogboro were as in Figure 3.

Table 2: results of the PAHs content of the wetland in Ayogboro and EU 1881/2014 MPC for PAHs in wetland in µg/l

	A	B	C	D	E	Mea n	EU 1881/2014 MPC
Pyrene	0.9	1.0	1.0	1.0	1.0	1.01	1
Chrysene	3	2	2	2	4	1.03	1
Benzo(a)pyrene	3	3	4	3	1	1.03	1
Benzo(a)anthracene	1.0	1.0	1.0	1.0	1.0	1.02	1
Benzo(b)fluorathene	1.0	1.0	1.0	1.0	1.0	1.03	1

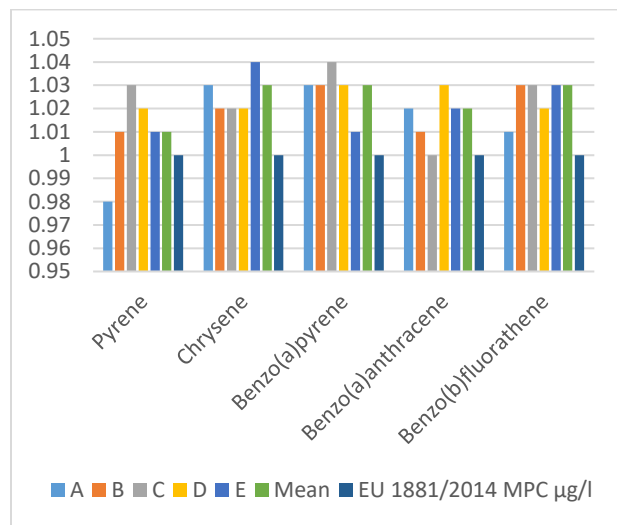


Figure 3: results of the PAHs content of the wetland in Ayogboro and EU 1881/2014 MPC for PAHs in wetland in µg/l. The values obtained from Daghele were as in Figure 4.

Table 3: results of the PAHs content in wetlands in Daghele and EU 1881/2014 MPC for PAHs in wetlands in µg/l.

	A	B	C	D	E	Mea n	EU 1881/2014 MPC
Pyrene	1.0	1.0	1.0	1.0	1.0	1.02	1
Chrysene	3	1	1	2	3	1.02	1
Benzo(a)pyrene	3	2	4	3	3	1.03	1
Benzo(a)anthracene	1.0	1.0	1.0	1.0	1.0	1.02	1
Benzo(b)fluorathene	1.0	1.0	1.0	1.0	1.0	1.03	1

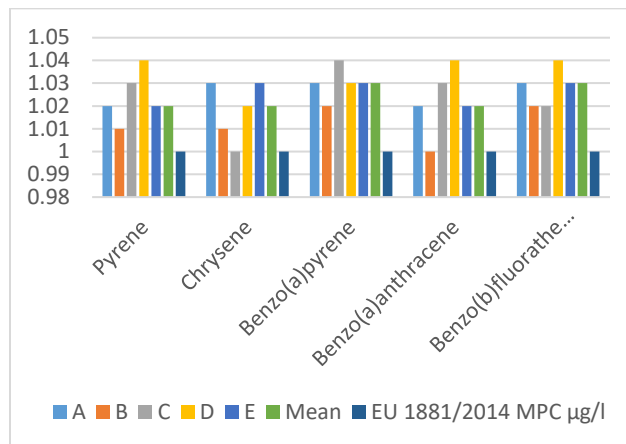


Figure 4: results of the PAHs content in wetlands in Daghele and EU 1881/2014 MPC for PAHs in wetlands in µg/l.

The values obtained from Egboro were as in Figure 5.

Table 4: results of the PAHs content in wetland in Egboro and EU 1881/2014 MPC for PAHs in wetlands in µg/l

	A	B	C	D	E	Mea n	EU 1881/2014 MPC
Pyrene	1.0	1.0	1.0	1.0	1.0	1.01	1
Chrysene	2	3	1	1	2	1.03	1
Benzo(a)pyrene	2	2	3	3	4	1.03	1
Benzo(a)anthracene	1.0	1.0	1.0	1.0	1.0	1.03	1
Benzo(b)fluorathene	1.0	1.0	1.0	0.9	1.0	1.02	1

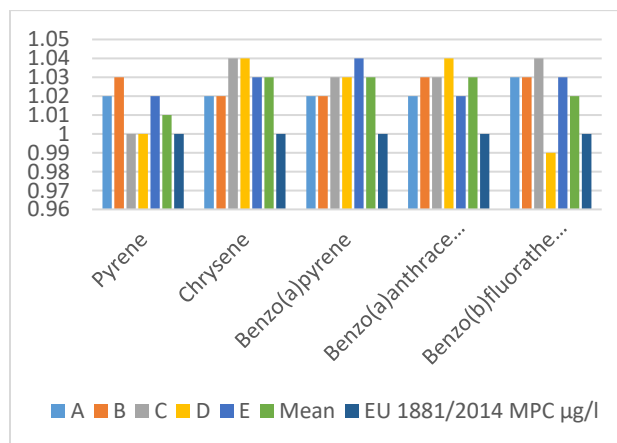


Figure 5: results of the PAHs content in wetland in Egboro and EU 1881/2014 MPC for PAHs in wetlands in µg/l

The values obtained from Dudu Town were as in Figure 6.

Table 5: results of the PAHs content in wetland in Dudu Town and EU 1881/2014 MPC for PAHs in wetlands in $\mu\text{g/l}$.

	A	B	C	D	E	Mea n	EU 1881/2014 MPC $\mu\text{g/l}$
Pyrene	1.0	1.0	0.9	1.0	1.0	1.03	1
Chrysene	9	3	3	2	2	1.02	1
Benzo(a)pyrene	2	3	2	3	1	1.02	1
Benzo(a)anthracene	3	2	1	3	3	1.02	1
Benzo(b)fluorathene	4	3	4	3	3	1.03	1

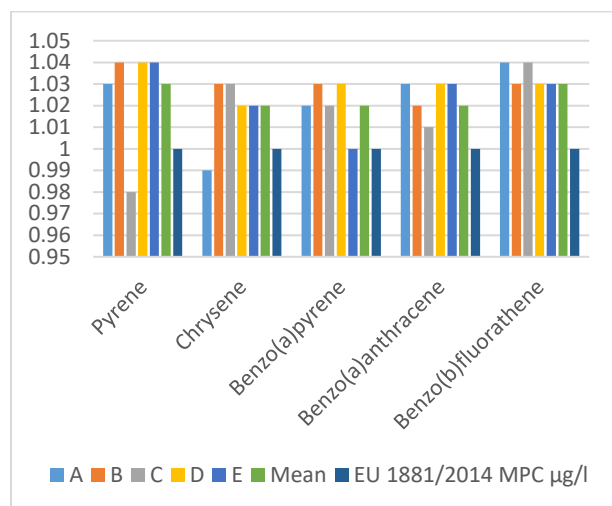


Figure 6: results of the PAHs content in wetland in Dudu Town and EU 1881/2014 MPC for PAHs in wetlands in $\mu\text{g/l}$.

The comparative mean results are as in Table 7 and Figure 7

Table 6: mean results of the PAHs content of the wetlands in Kolokolo and environ and EU 1881/2014 MPC for PAHs in wetlands in $\mu\text{g/l}$.

	A	B	C	D	E	Mea n	EU 1881/2014 MPC $\mu\text{g/l}$
Pyrene	1.0	1.0	1.0	1.0	1.0	1.02	1
Chrysene	1	3	2	3	2	1.02	1
Benzo(a)pyrene	2	3	3	3	2	1.03	1
Benzo(a)anthracene	1	2	2	3	2	1.02	1
Benzo(b)fluorathene	2	3	3	2	3	1.03	1

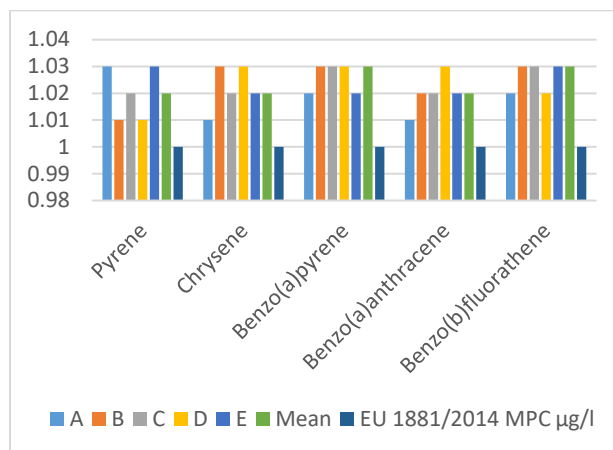


Figure 7: mean results of the PAHs content of the wetlands in Kolokolo and environ and EU 1881/2014 MPC for PAHs in wetlands in $\mu\text{g/l}$.

The mean results of the PAHs in the wetlands in Kolokolo and environs were subjected to test of significance with analysis of variance using special package for social science (SPSS) IBM model 29 at 0.05 level of significance. The p value was 0.042 thus rejecting H_0 .

DISCUSSION OF FINDINGS

PAHs contamination of wetlands occasioned by industrial activities is replete in literature but studies of PAHs contamination of wetlands in Kolokolo and surrounding settlements remain unavailable and this underscored the study. The investigation of the PAHs content in Kolokolo and environ presented varying results.

The concentration of pyrene in the wetlands in the Kolokolo and environs showed a range of $1.01\mu\text{g/l}$ in Ayogbero, and Egboro to $1.03\mu\text{g/l}$ in Kolokolo and Dudu Town with a group mean of $1.02\mu\text{g/l}$. This increased pyrene is anthropogenic. A similar report was in (Ogwu *et al.*, 2022, Fan *et al.*, 2014, Gao *et al.*, 2015). Ingestion of food contaminated by pyrene has been implicated in cancer of the gastro intestinal tract (Goa *et al.*, 2015) skin irritation, osteoporosis (Garrido *et al.*, 2014, Garcia-London *et al.*, 2015).

The wetland water analysis of Kolokolo and environs for the content of chrysene revealed the concentrations to be between $1.01\mu\text{g/l}$ in Kolokolo to $1.03\mu\text{g/l}$ in Ayogboro and Egboro with a mean of $1.02\mu\text{g/l}$. The elevated concentration of chrysene is traceable to the oil production activities in the area. This report is similar to reports in (Ogwu *et al.*, 2021, Foan *et al.*, 2015, Feng *et al.*, 2015, Guo *et al.*, 2015). Chrysene contamination have been fingered in liver degeneration, kidney failure (Han *et al.*, 2015, Hallare *et al.*, 2016, Grossman *et al.*, 2016), gene mutation (Hashemi *et al.*, 2016, Ogwu *et al.*, 2022).

The analysis of the wetlands in Kolokolo for the content of BaP presented a concentration of $1.02\mu\text{g/l}$ in Kolokolo and Dudu Town to $1.03\mu\text{g/l}$ in Ayogboro, Dughele and Egboro with a group mean of $1.03\mu\text{g/l}$; This high content of BaP is the impact of oil production in the area. This report is a corroboration of the reports in (Hassanwand *et al.*, 2015). The effect of BaP in human health include mutation, tetragenetic problems and lung cancer (Hussain *et al.*, 2015, Isaac *et al.* 2015) renal failure, cancer of the bone (Hu *et al.*, 2016).

BaA analysis in the wetlands of Kolokolo and environs presented

the concentrations of 1.01µg/l in Kolokolo to 1.03µg/l in Egboro with a mean of 1.02µg/l. This high content of BaA is as a result of man's interaction with the ecosystem via oil activities. High content of BaA was in the reports of (Auang *et al.*, 2015, Hung *et al.*, 2014, Heyderi *et al.*, 2014). BaA in man is associated with skin and lung cancer, eye irritation (Yang *et al.*, 2015, hang *et al.*, 2014, hang *et al.*, 2016).

The analysis of the wetland water in Kolokolo and environs for BbF showed that the concentrations of BbF varied from 1.02µg/l in Kolokolo and Egboro to 1.03µg/l in Ayogboro, Daghele and Dudu Town with a mean of 1.03µg/l. This increased content of BbF in the wetland is the effect of oil extraction activities. This result is in agreement with reports in (Kalwa *et al.*, 2014, Kamal *et al.*, 2015, Ogwu *et al.*, 2023). Health implications of human prolonged exposure to BbF include nephropathy, increases in liver enzymes (Ivshina *et al.*, 2016, Jin *et al.*, 2014, Jimenez *et al.*, 2014).

Conclusion and Recommendation

Contamination of wetlands through industrial activities is a global challenge that require concerted efforts from all concerned to ameliorate. The analysis of the wetlands in Kolokolo and environs has further reaffirmed reports in varying literature of industrial activities and wetlands contamination. The result of the analysis of the wetlands in Kolokolo and environs revealed the contamination of the ecosystems with PAHs above the maximum allowable concentration stipulated in EU 1881/2014 and thus the produce are not suitable for human and animal consumption. The produce will not be exportable for the failure to scale Codex Alimentarius hurdle for produce export.

Against this back drop, the study recommended thus;

The oil companies operating in Kolokolo and environs should be made to keep to standard global practice in oil industry; the monitoring agencies National Environmental Standards Regulation and Enforcement Agency (NESREA) and National Oil Spills Detection and Response Agency should be compelled to do their work efficiently to ensure oil companies compliance to set down standards and the impacted wetlands should be remediated and restored forthwith for continued ecosystem services.

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