Impact of COVID-19 lockdown and health risk modeling of polycyclic aromatic hydrocarbons in Onne, Nigeria

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Abstract The people living in Onne are highly vulnerable to PAH exposure due to constant exposure to black soot through oral, dermal, and inhalation routes. This work aims to determine the PAHs profile of selected soils in Onne, to determine the health risks associated with PAHs exposure through the soil, and to determine the impact of reduced industrial and other activities on the PAHs profile and associated public health risks. This study evaluated 16 priority polycyclic aromatic hydrocarbon (PAHs) pollutants in soil samples from the four (4) major clans in Onne using a gas chromatography flame ionization detector (GC-FID) during and after the COVID-19 lockdown. The results showed a differential presence of PAHs during and after the lockdown. Of the 16 priority PAHs, 10 and 8 PAHs were respectively detected during and after the COVID-19 lockdown. High molecular weight PAHs such as benzo(k)fluoranthene and benzo(a)anthracene were major contributors during the lockdown, while low molecular weight PAHs such as naphthalene, acenaphthylene, and fluorene were present at higher levels after the lockdown. An assessment of health risk by incremental lifetime cancer risks revealed that the entire population of Onne might be at risk of cancer development across periods, though a higher risk was presented during the lockdown. In addition, children under the age of 18 may be at greater risk. To the best of our knowledge, there is no previous report on the impact of the COVID-19 lockdown on soil PAH profile and health risks, with particular attention to the Onne industrial host community. Earlier work considered the ecological risks of heavy metals on dumpsites in Onne. Taken together, the PAH-contaminated soil in Onne poses an immediate health concern. Therefore, reduced anthropological activities, as evident during the COVID-19 lockdown, may play a role in exposure and cancer risk reduction. While there may not be another lockdown due to the challenging impacts associated with a physical lockdown, firmly controlled economic activity can be a solution if embraced by stakeholders. The COVID-19-lockdown was encumbered with restricted movements and security checks, which limited the number of samples collected. However, the Local Government Council (Department of the Environment) granted permission...
for the researchers to work with a minimal threat to their lives.

**Keywords**  PAHs · Toxic equivalent factor · Health risk modeling · Soil contamination

### Introduction

PAHs are ubiquitous and persistent organic compounds (Achten & Hofmann, 2009; Ni et al., 2019). PAHs are produced frequently due to partial incineration of plant and animal remains (Sun et al., 2020; Zhang et al., 2019), are poorly soluble in water, and do not disappear quickly from the environment (Vane et al., 2014; Zhang et al., 2019). They can accumulate in biological and ecological food chains and are, therefore, easily accessible to humans (Singh & Agarwal, 2018). About 16 PAHs are classified by the United States Environmental Protection Agency (USEPA) as priority pollutants owing to their importance naphthalene, acenaphthylene, fluorene, acenaphthene phenanthrene, anthracene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3 cd) pyrene, fluoranthene, dibenzo(ah)anthracene, and benzo (g, h, and i) perylene (Zhang et al., 2019; Zhu et al., 2019). Seven of the 16 priority PAHs are tagged as possible or probable human carcinogens (Santonicola et al., 2017). PAHs arise from a variety of sources, including biomass, volcanic eruptions, and fires (Keith, 2015; Mihankhah et al., 2020). However, many of these chemicals are after-effects of human activities, particularly in urbanized cities. Coal and wood burning, gasoline and diesel oil burning, and industrial plants are sources of PAHs. In addition, spilled liquid fuels can contribute to most of the PAHs in the environment (Farrington, 2020). The presence of PAHs in soils and sediments is frequently linked to pyrogenic non-point sources such as the incomplete burning of (fossil) organic matter (Hindersmann & Achten, 2018). Oil spills are one possible source of point sources (Zhang et al., 2019).

Several studies have confirmed the presence of PAHs in soil (Abdel-Shafy & Mansour, 2016; Achten & Hofmann, 2009; Emoyan et al., 2020), water (Adetunde et al., 2018; Nwaichi & Ntorgbo, 2016), air (Akinrinade et al., 2020; Munyeza et al., 2019), and sediments (Edokpayi et al., 2016). Oral intake, inhalation, and skin interaction are the three main routes of human exposure to PAHs (Ferguson et al., 2020). Exposure to PAHs is also associated with various diseases and bodily disorders (Adekunle et al., 2017; Santonicola et al., 2017), especially cancer (Falcó et al., 2003; Santonicola et al., 2017).

Urban soil represents a significant part of the environment contaminated by PAH chemicals, which are hazardous to ecological and human health (Tarafdar & Sinha, 2018). The soil framework seems to be the primary sink for PAHs and, therefore, a prominent indicator of PAH contamination (Chandra et al., 2018; Emoyan et al., 2020; Tarafdar & Sinha, 2018). There is confirmation that anthropogenic activities related to urbanization and industrialization significantly affect pollution levels in cities (Kumar et al., 2014; Oliveira et al., 2019). Moreover, the terrain and nearby wind and tide speeds and the plant canopy can affect the transmission and deposition of chemicals, including heavy metals and PAHs (Abderrahmane et al., 2021; Pal & Hogland, 2022). Other physical and chemical characteristics such as pH, temperature, total organic matter, and moisture content of the soil can affect the accumulation of PAHs in the soil. Environmental PAHs are generally carcinogenic to man and other animals, though some PAHs, such as dibenz[a, h] anthracene, benzo[a]pyrene, and benzo [g, h, i] perylene, are categorized as mutagenic (Anyanwu et al., 2020; Yost et al., 2021). Exposure evaluation is a critical step in determining health risks to circumvent the harmful impact of PAHs on the environment. The USEPA multi-pathway exposure model is the principal strategy for assessing health risks globally (Tarafdar & Sinha, 2018).

Onne, Eleme, Rivers State is situated in the Niger Delta part of Nigeria, where industrialization is commonplace. Several studies have detected PAHs in the soil of an oil-rich region (Orisakwe, 2021; Sojinu et al., 2010; Ugochukwu et al., 2018). The quality of soil affects vegetables and other food crops grown in an industrial region, and thus PAHs can disseminate across the food chain. (Kumar et al., 2014).

In addition, there is a general concern about the impact of environmental pollutants from black soot deposits in the Niger Delta in Nigeria, mainly due to illegal petroleum exploration. This problem creates dissatisfaction among local people and other stakeholders (Orisakwe, 2021; Zabbe et al., 2017). Although a large body of work on PAHs’ contamination in the Nigerian Niger Delta is available, the COVID-19 lockdown provided a departure from the usual human lifestyle. After the outbreak of the COVID-19 virus in 2020, a total lockdown became
necessary in many countries (Mboera et al., 2020). The COVID-19 lockdown was accompanied by a decline in physical business, academic, and tourist activities around the world (Oyewola et al., 2022; Pahrudin et al., 2021). Consequently, it is important to explore whether the reduced human activities evident during the COVID-19 lockdown are affecting the concentration, distribution, sources, and potential health risks of PAHs across all areas in Onne, Nigeria. Therefore, this study sought to:

1. Determine the concentration of PAHs in soil samples in Onne
2. Assess the major sources and distribution of PAHs in Onne using already established diagnostic ratios.
3. Use the toxic equivalency factor and incremental lifetime cancer risk to assess the potential health risks associated with PAH-contaminated soils from Onne.
4. To evaluate the impact of the COVID-19 lockdown on concentrations, distribution, source attribution, and health risks of PAHs in Onne, Nigeria, by assessing changes in concentrations, sources, and distribution of PAHs during and after the lockdown.

At the time of writing this manuscript, the authors are not aware of any written works specifically about Onne, with particular emphasis on the ongoing decades of exposure of the population to black soot due to illegal bunkering activities and multidimensional industrial and human activities in Onne, Nigeria. This research will improve our understanding of the general properties of PAHs in the soil samples in Onne and the attendant health risks. This will assist stakeholders to adopt efficient pollution mitigation approaches in Onne, Nigeria.

Materials and methods

Study area

Onne is among the ten communities in Eleme Local Government of Rivers State. It is located at longitudes and latitudes of 4.723816 and 7.151618° east. Alejor, Ekara, Agbeta, and Ogoloma are the four main clans that makeup Onne. It is situated between Okrika and Ogu in Rivers State (Fig. 1). The Nigerian Ports Authority

Fig. 1 Map depicting the different locations of Onne
(NPA), the Oil and Gas Free Zone (OGFZA), the Nigerian Navy Basic Training School, the Nigerian Naval College (officers), Integrated Logistics (intels), and Notore Chemicals (formerly the National Fertilizer Company of Nigeria) are located in Onne, thereby positioning the community as a key industrial hub of Rivers State. It is a semi-urban dwelling place for both indigenes and foreigners. The NPA is a center of attraction in Onne because it is one of the largest oil and gas-free zones supporting exploration and production in Nigeria. This port is responsible for 65% of all exported cargo via the Nigerian seaports. In addition to the oil and gas business, the port also operates several other businesses. Consequently, the port serves a variety of cargo needs. Onne settlement is about 1–2 km from the port. In the midst of heavy industries, natives use their land for agriculture, mechanical workshops, and residential areas, among other things.

Collection and pretreatment of soil samples

Multiple evenly spaced sampling sites utilized for mechanical workshops, farmland, NPA schools, churches, mosques, boundaries, and fertilizer company vicinities were used to collect soil samples. Four (4) different areas of Onne, namely Alejor, Ekara, Agbeta, and Ogoloma, were chosen, and the position of each location was recorded using a handheld Garmin GPS device. Using a soil auger at 0–25 cm depth, 5 sub-samples were collected 5 m apart in a triangular shape and mixed appropriately to prepare a composite sample for each site based on a previously established method (Tarafdar & Sinha, 2018; Wu et al., 2019). After the manual removal of non-soil particles, the samples were stored in an ice-filled cooler and then shipped to the International Energy Services Laboratory in Port Harcourt, Nigeria, for analysis. The soil samples were air dried in the lab for 3 days to maintain a constant weight throughout the test. A 2 mm stainless steel screen was used to sift the soil into uniform sizes and articles and to remove unwanted particles. Two composites, which consisted of five sub-soil samples, were collected from each of the communities, Alejor, Ekara, Agbeta, and Ogoloma, in July 2020 during the COVID-19 lockdown and in March 2021 after the lockdown.

Analytical procedures

All chemicals, including anhydrous sodium sulfate, dichloromethane, and activated silica gel, were analytical grade. Physicochemical properties of soil such as pH, temperature, electrical conductivity, moisture content, total organic matter content, and total organic matter were determined by established methods as reported (Emoyan et al., 2020). For PAH determination, 10 g of the sample was weighed into a clean 50-mL extraction bottle; 30 mL of dichloromethane (DCM, the extraction solvent) was added to the flask. The mixture was agitated by shaking for 2 min and allowed to settle. The extracted mixture was then passed through 42-size Whatman paper containing 5 g of activated silica gel and 5 g of the sodium sulfate into a vial and held ready for injection into the GC-FID.

Sample dilution

An aliquot (5 mL) of sample extract was diluted with 10 mL of dichloromethane.

Instrumentation

The carrier gas utilized was nitrogen (30 mL/min). The hydrogen and compressed air pressures were each 27.8 pounds per square inch (psi) at 35 mL per minute and 250 mL per minute, respectively. The results were scored using the sixteen (16) standard PAHs for the analysis. To rank the compounds, the retention times based on the standards were compared to those of a sample extract, while quantification incorporated individual PAH analysis. To ensure that all calculated PAHs are accurate, a blank analyte verification and an initial or trial demonstration were used to verify the method. The standards used for the analysis included naphthalene, 2-methyl naphthalene, acenaphthylene, fluorene, acenaphthene, phenanthrene, anthracene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indenol(1,2,3 cd) pyrene, fluoranthene, dibenzo(ah) anthracene, and benzo (g, h, and i) perylene.

Source allocation studies

Knowing the sources of PAHs makes it easier to determine how they are distributed in the environment. Commonly, the diagnostic ratio method is used to discriminate between different PAHs sources in the ecosystem (Edokpayi et al., 2016; Tobiszewski and Namieśnik (2012). Ratios include LPAHs/HPAHs (low molecular weight PAHs), Fla/(Fla + Pyr) (fluoranthene + pyrene), BaA/(BaA + PAHs)
+ Chr(chrysene), and Ant(anthracene)/(Ant + Phe) (phenanthrene). For instance, a ratio of LPAHs/HPAHs < 1 indicates pyrogenic origin, whereas a ratio > 1 point to a petrogenic source. A ratio of Fla/(Fla + Pyr) < 0.4 specifies a petrogenic source, a ratio between 0.4 and 0.5 indicates a coal, wood, or grass incineration source. For BaA/(BaA + CHR), a ratio < 0.2 signifies a petroleum source, a ratio between 0.2 and 0.35 indicates a mixed source, and a ratio > 0.35 shows a combustion source. Values of the Ant/(Ant + Phe) ratio are classified as either <0.1 or >0.1, representing petroleum and combustion sources, respectively (Brändli et al., 2007).

Soil pollution scales

To assess soil pollution levels, Maliszewska-Kordybach (1996) proposed that soil contaminated by PAHs could be classified into four levels: non-contaminated, weakly contaminated, contaminated, and heavily contaminated. Soil PAH concentrations less than 0.2 mg/kg are considered non-contaminated; concentrations between 0.2 and 0.6 mg/kg are considered weakly contaminated; concentrations between 0.6 and 1.0 mg/kg are considered contaminated; and concentrations greater than 1.0 mg/kg are considered heavily contaminated (Maliszewska-Kordybach, 1996).

Health risk assessment

Toxic equivalent concentration \( (BaPeq) \) and incremental lifetime cancer risk

The health risk assessment model for carcinogenic risk was evaluated by the benzo(a)pyrene equivalent \( (BaPeq) \) concentration and the incremental lifetime cancer risk \( (ILCR) \) for carcinogenic risks. The \( BaPeq \) concentration with a toxic equivalent factor of one (1) is normally used as a basis for toxicity and carcinogenicity. This is because benzo(a)pyrene is the most extensively researched congener of PAHs. To appraise the hazardousness of soil samples, toxic equivalency factors \( (TEFs) \) were adopted to produce toxic equivalent concentrations, i.e., \( BaPeq \), as reported earlier (Nisbet & LaGoy, 1992). To assess the potential toxicity of a PAH congener, its concentration was multiplied by the estimated TEF value (Appendix 1).

\[
\Sigma BaP_{eq} = \Sigma C_i \times TEF_i
\]

where \( BaP_{eq} \) is the equivalent concentration of benzo(a)pyrene, \( C_i \) is the concentration of PAH congener in soil, and \( TEF_i \) is the toxic equivalency factor of PAH congener relative to benzo(a)pyrene \( (BaP) \). The carcinogenic potencies of PAHs were estimated by adding their \( BaPeq \) values and comparing them with a reference value (Canadian Council of Ministers of the Environment-CCME, 2010). Environmental PAHs pose a significant health risk. The USEPA (United States Environmental Protection Agency) model of the incremental lifetime cancer risks \( (ILCR) \) model, as reported by Qu et al. (2020), was used for the cancer risks in soil samples. Cancer risk modeling considered three pathways of exposure, viz., oral, dermal, and inhalation. The risk evaluation considered four exposure populations: children (0–18 years), young adults (20–44 years), middle-aged (45–59 years), and the elderly (>60 years). Furthermore, the following equation was used:

\[
ILCR_{\text{ingestion}} = \frac{CS \times IR_{soil} \times EF \times ED \times CSF_{\text{ingestion}}}{BW \times AT \times 10^6}
\]

\[
ILCR_{\text{dermal}} = \frac{CS \times SA \times AF \times ABS \times EF \times CSF_{\text{dermal}}}{BW \times AT \times 10^6}
\]

\[
ILCR_{\text{inhalation}} = \frac{CS \times IR_{\text{air}} \times EF \times ED \times CSF_{\text{inhalation}}}{BW \times AT \times 10^6}
\]

The equation terms are defined as follows:

\( CS = \) toxic equivalent PAHs compound concentration in soil \( (\text{mg/kg}) \).

\( CSF = \) carcinogenic slope factors (in milligrams of \( BaP \) per kilogram or milligrams per liter) for the three major pathways (oral, dermal, and inhalation): CSF ingestion, CSF dermal, and CSF inhalation. They are, respectively, 1.0–25.0 and 3.85 mg.kg.day\(^{-1}\) (Tarfad & Sinha, 2018).

\( IR_{soil} = \) soil ingestion rate in milligrams per day.

\( AF_{soil} = \) dermal adherence factor in milligrams per square centimeter.

\( IR_{air} = \) inhalation rate in cubic meters per day.

\( ED = \) exposure duration in years.

\( EF = \) exposure frequency in days per year (365 days per year).

\( BW = \) body weight \( (\text{kg}) \).

\( AT = \) average life span in days.
PEF = particle emission factor in cubic meters per kilogram of soil.
SA = exposed skin surface area.
ABS = dermal absorption factor.

Since children are most vulnerable to environmental pollutants, the main issue was to identify the risks associated with this population (Wirnkor et al., 2019).

According to USEPA cancer risk classifying standards, an ILCR of less than $10^{-6}$ is considered practically safe, a value between $10^{-6}$ and $10^{-4}$ is considered low risk, and above $10^{-4}$ indicates a potentially high risk for significant health concerns (Qu et al., 2020; USEPA, 1996). The parameters imputed and used for the calculation are explained in Appendix 2.

Statistical analysis

Statistical analysis was performed using GraphPad Prism Software 9.00 (San Diego, CA, USA). Values are expressed as the mean ± SEM of 2 replicates. $P < 0.05$ was considered to be statistically significant. The student’s $t$-test was used to determine the difference between PAH concentrations during and after confinement, while Pearson’s correlation coefficient was used to determine the relationship between other physicochemical parameters and PAHs.

Results and discussions

Physicochemical parameters and PAHs in soil samples

The physicochemical parameters of the soil samples were assessed. The results of the mean values of the physicochemical parameters are summarized in Table 1. There was no consistency in the way the physicochemical properties changed, apart from temperature and conductivity, which showed a consistent increase in the four communities post-lockdown. The temperature ranged between 24.45 and 25.15 °C during the lockdown but increased to between 28 and 29 °C after the lockdown across the periods. Conductance range values were 17–19 during the lockdown and 20–36 after the lockdown. Tables 2 and 3 showed that Pearson correlation values were statistically not significant ($p > 0.05$).

Correlation studies by Pearson show that pH, conductance, moisture content, and total organic matter were positively associated with PAHs during lockdown (Table 2), whereas conductance and moisture content were the only parameters in positive association with PAHs after the lockdown (Table 3).

Table 4 illustrates the concentrations of individual PAHs in selected soil samples. Of the 16 priority PAHs assessed in this study, 10 PAHs were detected in Onne soils during the lockdown, while eight (8) PAHs were detected in post-lockdown soil samples. Student’s $t$-test analysis shows significant differences in mean total PAH concentrations in Alejor ($p < 0.0001$), Agbeta (1$p < 0.0001$), and Ogoloma (1$p < 0.005$), but not in Ekara. In summary, 75% of the soil samples tested showed significant changes in concentrations after the lockdown. Both low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAHs) were detected, but the LPAHs predominated over the HPAHs in both periods. However, HPAHs were in higher concentrations during the lockdown than after the lockdown. For example, BaA and BKF recorded mean values of 0.41 ± 0.02 and 0.95 ± 0.05, respectively, during the lockdown but were absent after the lockdown (Table 4). In general, naphthalene was present in all samples from all four

| Table 1 | Physicochemical properties of soil during (1) and after (2) COVID-19 lockdown |
|---------|---------------------------------------------------------------|
|         | Al¹ | Al² | Ek¹ | EK² | Aγ¹ | Aγ₂ | Oγ¹ | Oγ₂ |
| PAHs    | 2.02 ± 0.1 | 0.85 ± 0.25 | 1.14 ± 1.07 | 1.63 ± 0.32 | 2.03 ± 0.37 | 1.30 ± 0.32 | 1.82 ± 0.25 | 1.35 ± 0.10 |
| pH      | 7.45 ± 1.35 | 6.1 ± 0.35 | 5.65 ± 0.45 | 6.1 ± 0.35 | 5.90 ± 0.0 | 6.0 ± 0.40 | 6.50 ± 0.60 | 6.1 ± 0.40 |
| Temp °C | 24.85 ± 0.35 | 29 ± 0.65 | 25.15 ± 0.05 | 28 ± 0.40 | 25.15 ± 0.05 | 28 ± 0.10 | 24.45 ± 1.05 | 28 ± 0.20 |
| Cond    | 15.0 ± 1 | 20 ± 2.5 | 19.0 ± 5 | 23 ± 0.50 | 17.00 ± 1 | 20 ± 0.050 | 18.00 ± 10 | 36 ± 13 |
| MC      | 12.50 ± 0.65 | 18 ± 1.9 | 13.80 ± 0.7 | 18 ± 1.6 | 12.37 ± 3.23 | 19 ± 1.5 | 13.80 ± 0.20 | 16 ± 2.5 |
| TOC     | 2.27 ± 0.42 | 2.5 ± 0.63 | 2.71 ± 0.86 | 1.7 ± 0.090 | 4.07 ± 1.52 | 2.5 ± 0.035 | 1.61 ± 0.22 | 1.9 ± 0.86 |
| TOM     | 6.86 ± 1.25 | 7.5 ± 1.9 | 8.21 ± 2.56 | 5.1 ± 0.29 | 12.31 ± 4.60 | 7.6 ± 0.095 | 4.86 ± 0.64 | 5.8 ± 2.6 |

¹ Alejor, Ek Ekara, Ag Agbeta, Og Ogoloma, Temp temperature, Cond conductivity, MC moisture content, TOM total organic matter
communities: Alejor, Ekara, Agbeta, and Ogoloma. During the lockdown, seven (7) PAHs were detected in all samples: naphthalene, fluorene, fluoranthene, acenaphthene, anthracene, benzo(a)anthracene, and benzo(k)fluoranthene. Pyrene was detected in Alejor, Agbeta, and Ogoloma but not in Ekara. On the other hand, phenanthrene was not detected in Ogoloma but was present in Alejor, Ekara, and Agbeta. Acenaphthylene was only detected in Ogoloma. In all, eight (8) PAHs were detected in Ekara, whereas nine (9) PAHs were detected in Alejor, Agbeta, and Ogoloma. In contrast, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene were detected in the four communities, whereas fluorene was detected in Ogoloma, and pyrene was detected in Alejor and Ogoloma. Pyrene was the only HPAH detected in a low quantity after the lockdown.

Comparison with soil pollution criteria

The summation of PAH concentrations in the four communities in Onne revealed that the mean level of PAHs was 1.75 mg/kg and ranged between 1.14 and 2.04 mg/kg (Table 1) during the lockdown, while the mean value was 1.28 mg/kg and ranged between 0.85 and 1.35 mg/kg after the lockdown. Therefore, 100% of the soil’s concentrations in Alejor (2.02±0.1; 0.85±0.25 mg/kg), Ekara (1.14±1.07; 1.63±0.32 mg/kg), Agbeta (2.03±0.37; 1.30±0.32 mg/kg), and Ogoloma (1.82±0.25; 1.35±0.10 mg/kg) might be termed highly contaminated by PAHs based on the soil pollution scale (Maliszewska-Kordybach, 1996). Reduced industrial, commercial, and physical activity might have resulted in lower PAH after the COVID-19 lockdown. This work is in accordance with the report by Inam et al. (2016), which recorded 1.77 mg/kg PAHs in a mechanic shop at Uyo in the Niger Delta area of Nigeria. Other reports by Daniel et al. (2020) found a range of PAH concentrations between 214.83 and 537.22 mg/kg in urban soil samples used for mechanic work, and Onyedikachi et al. (2019) confirm the presence of PAHs above the WHO acceptable limit in the Niger Delta region of Nigeria. Separate studies on PAH concentrations in urban soils outside Nigeria showed that Greater London had values between 4 and 66 mg/kg (Vane et al., 2014), industrial areas of the Yangtze River Delta region in China had intermediate values of PAHs between 341.40 and 471.30 µg/kg and Moscow had <1 to 1 mg/kg (Vane et al., 2014). However, all of these values are within the acceptable WHO standard of 1 mg/kg.

The percentage composition of PAHs is illustrated (Figs. 2, 3, 4, and 5).

The fraction of low molecular weight PAHs significantly increased as NaP rose from 16.08% during lockdown to 22.65% after lockdown. Similarly, Acy and Ant

### Table 2 COVID-19 lockdown Pearson correlation

|                | PAHs   | pH     | Temp | Cond | MC    | TOC   | TOM  |
|----------------|--------|--------|------|------|-------|-------|------|
| PAHs           | 1      | 0.30   | −0.19| 0.36 | 0.02  | −0.08 | 0.20 |
| pH             | 1      | −0.77  | 0.04 | −0.33| −0.06 | −0.05 |
| Temp           | 1      | 0.24   | 0.21 | −0.15| −0.14 |
| Cond           | 1      | −0.01  | −0.10| 0.13 |
| Moisture C     | 1      | 0.47   | 0.47 |
| TOC            | 1      |        |      | 0.96 |
| TOM            | 1      |        |      | 1    |

### Table 3 Post COVID-19 lockdown Pearson correlation

|                | PAHs   | pH     | Temp | Cond | MC    | TOC   | TOM  |
|----------------|--------|--------|------|------|-------|-------|------|
| PAHs           | 1      | −0.28  | −0.83| 0.28 | 0.18  | −0.31 | −0.45|
| pH             | 1      | 0.52   | −0.41| −0.74| −0.21 | 0.45 |
| Temp           | 1      | −0.07  | −0.55| 0.23 | 0.41 |
| Cond           | 1      | 0.01   | 0.31 | −0.61|
| MC             | 1      | 0.30   | −0.42|
| TOC            | 1      |        | 0.10 |
| TOM            | 1      |        | 1    |
increased from 9.05 and 3.52% to 17.88 and 28.61% in Alejor. In Ekara, NaP showed a positive percentage increase from 11.63 to 25.83% after the COVID-19 lockdown. Flu also increased from 4.65 to 16.61%. However, Ant increased (2.33–20.30%) during and after the COVID-19 lockdown. This trend holds for Agbeta and Ogoloma, except for Phe and Ant, which showed a decrease in percentage composition in Agbeta after the lockdown.

### Table 4
Concentration of PAHs congeners (mg/kg) during (1) and after (2) COVID-19 lockdown

| PAHs (mg/kg)/ring no | AI1 (mg/kg) | AI2 (mg/kg) | EK1 (mg/kg) | EK2 (mg/kg) | Ag1 (mg/kg) | Ag2 (mg/kg) | Og1 (mg/kg) | Og2 (mg/kg) |
|----------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Nap2                 | 0.32±0.03   | 0.19±0.19   | 0.20±0.20   | 0.42±0.08   | 0.46±0.19   | 0.411±0.016 | 0.20±0.04   | 0.49±0.02   |
| Acy3                 | -           | 0.15±0.08   | -           | 0.28±0.06   | -           | -           | 0.27±0.00   | 0.02±0.02   | 0.29±0.02   |
| Ace3                 | 0.02±0.00   | 0.15±0.02   | 0.02±0.00   | 0.23±0.08   | 0.01±0.00   | 0.21±0.03   | 0.01±0.01   | 0.19±0.02   |
| Flu3                 | 0.18±0.01   | 0.24±0.03   | 0.08±0.09   | 0.27±0.06   | 0.07±01     | 0.29±0.02   | 0.08±0.06   | 0.27±0.02   |
| Phe3                 | 0.01±0.00   | 0.10±0.02   | 0.01±0.01   | 0.33±0.30   | 0.01±0.01   | 0.09±0.01   | -           | 0.01±0.00   |
| Ant3                 | 0.07±0.00   | 0.10±0.00   | 0.04±0.00   | 0.33±0.30   | 0.08±0.02   | 0.02±0.02   | 0.04±0.02   | 0.01±0.00   |
| Fla3                 | 0.02±0.00   | -           | 0.01±0.01   | -           | 0.02±0.00   | -           | 0.01±0.01   | -           |
| Pyr/4                | 0.01±0.01   | 0.002±0.00  | -           | 0.01±0.01   | -           | 0.02±0.02   | -           | -           |
| BaA/4                | 0.41±0.02   | -           | 0.21±0.17   | 0.17±0.15   | 1.06±0.75   | -           | -           | -           |
| Total PAHs           | 2.02±0.1    | 0.85±0.25   | 1.14±1.07   | 1.63±0.32   | 2.03±0.37   | 1.30±0.32   | 1.82±0.25   | 1.35±0.10   |
| Total LPAHs          | 1.06±0.06   | 0.84±0.33   | 0.58±0.01   | 1.63±0.02   | 0.99±0.00   | 1.30±0.12   | 1.44±0.10   | 1.35±0.10   |
| Total HPAHs          | 0.95±0.01   | 0.002±0.00  | 0.56±0.01   | 0           | 1.03±0.00   | 0           | 0.38±0.00   | 0.003±0.00  |
| LPAHs/HPAHs          | 0           | 351         | 0.07        | 1.63        | 0           | 1.30        | 1.04        | 450         |
| WHO (mg/kg)          | 1           | 1           | 1           | 1           | 1           | 1           | 1           | 1           |

Source allocation studies

The possible sources of PAHs were predicted using PAH diagnostic ratio indices. Inferences show that soil PAHs were a combination of several sources during the COVID-19 lockdown but were majorly petrogenic after the lockdown (Tables 5, 6, 7, and 8). The predominance of low molecular weight PAHs against high molecular weight PAHs indicates more petrogenic

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**Fig. 2** Percentage composition of PAHs in soil samples during and after the COVID-19 lockdown in Alejor. Legend: Nap = naphthalene, Acy = acenaphthylene, Ace = acenaphthene, Flu = fluorne, Phe = phenanthrene, Ant = anthracene, Fla = fluoranthene, Pyr = pyrene, BaA = benz(a)anthracene, and BKF = benzo(k)fluoranthene.
sources rather than pyrogenic sources. LPAHs are common in petroleum mixtures. This work is in conformity with similar studies in the Niger Delta, Nigeria (Emoyan et al., 2020; Osu & Asuoha, 2010). The Niger Delta part of Nigeria is well known for its oil exploration, heavy traffic movement, and other industrial activities (Orisakwe, 2021; Ugochukwu et al., 2018). This undoubtedly leads to oil spillage and pollution by spent petroleum products. The continuous vehicular movements in and out of the seaport combined with ongoing bunkering activities and diesel combustion in the industrial plants could also explain the fact that pyrogenic activities were common prior to lockdown, leading to HPAHs accumulation, which was evident in the higher percentage contribution of BaA and BKF in Alejor (20.60 and 47.74%); Ekara (23.84 and 52.23%); Agbeta (9.12 and 55.5%); Ogoloma (58.24 and 20.88%) (Figs. 2, 3, 4, and 5).

Although USEPA identified 16 PAHs as priority pollutants, 7 compounds, namely benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(ah)anthracene, and indeno(1,2,3-cd) pyrene are classified as probable human carcinogens (Abdel-Shafy & Mansour, 2016). The presence of benzo(a)anthracene and benzo(k)fluoranthene are pointers to higher health risks during the lockdown than after the lockdown.

PAH diagnostic ratios are routinely used to analyze soil samples, but they give no information about the stability of soil PAHs. The primary fate of PAHs in soils is atmospheric desorption (Feng et al., 2019; Liu et al., 2016), and diagnostic ratios can vary depending on the altitude of the soil sampling site (Jiang et al., 2009). PAHs may desorb: fluoranthene and pyrene desorb at comparable rates, although Phe desorbs more rapidly than Ant (Enell et al., 2005). LPAHs can be metabolized...
by endogenous bacteria and fungi, resulting in a (potentially selective) drop in concentration over time based on soil type, organic carbon and nutrient content, humidity, and aeration (Gerhardt et al., 2009).

Health risk assessment

The health risks posed by PAH exposure are well researched (Abdel Shafy & Mansour, 2016; Canadian Council of the Ministers of the Environment-CCME, 2010; Adekunle et al., 2017; Santonicola et al., 2017). The health risk assessment model for carcinogenic risk was evaluated by the BaPeq concentration and the ILCR for carcinogenic risks. Toxic equivalent factors are used in the calculation (Appendix 1), while the details on how BaPeq concentration was calculated are provided in Supplementary information (1).

Health risk assessment

BaPeq concentration with a toxic equivalent factor of one (1) could be used as a basis for toxicity and carcinogenicity. To evaluate the hazardous potency of soil samples, toxic equivalency factors (TEFs) (Appendix 1) was used to produce toxic equivalent concentrations (BaPeq) for evaluation and quantification. BaPeq concentrations ranged from 0.01 to 0.02 mg/kg across Alejor, Ekara, Agbeta, and Ogoloma (Table 8). These values were below the 0.6 mg/standard allowed for PAH concentrations in soils (Canadian Council of the Ministers of the Environment-CCME, 2010). Based on these values, the soil likely does not pose any health risk due to BaPeq concentration.

The computed values of the ILCR of soil PAHs within the specified period are presented in Table 9. The order of the risk is children > middle aged > elderly > young adults during the lockdown and children > middle aged = elderly > young adults (Table 10). Children may have a greater risk of developing cancer later in their lifetime. The inhalation route is the most effective route of exposure across all ages of life. The oral route was the weakest means of cancer risk exposure, whereas the dermal route showed a weak likelihood of cancer risk across all ages. The inhalation route is evident as inhaled black soot from colloids in the noses of individuals in Onne accumulates over

**Table 5** Computed source allocation of PAHs in Alejor soil samples during and after COVID-19 lockdown

| Diagnostic ratios | Alejor during COVID-19 lockdown | Possible source | Alejor after COVID-19 lockdown | Possible source |
|-------------------|---------------------------------|-----------------|-------------------------------|-----------------|
| LPAHs             | 0.001                           | Pyrogenic       | 351                           | Petrogenic      |
| HPAHs             | 0.885                           | Pyrogenic       | 0.09                          | Petrogenic      |
| LPAHs             | 0.65                            | Grass coal combustion | Not applicable | Not applicable |
| Hamme            | 1                               | Combustion      | Not applicable | Not applicable |

*Table 5* Computed source allocation of PAHs in Alejor soil samples during and after COVID-19 lockdown

**Fig. 5** Percentage composition of PAHs in soil samples during and after the COVID-19 lockdown in Ogoloma. Legend: Nap=naphthalene, Acy=acenaphthylene, Ace=acenaphthene, Flu=fluorene, Phe=phenanthrene, Ant=anthracene, Fla=fluoranthene, Pyr=pyrene, BaA=benz(a)anthracene, and BKF=benzo(k)fluoranthene.
time, hence gaining access to the systemic circulation of exposed people (Abdel-Shafy & Mansour, 2016). This present work contradicts the reports of Onyedikachi et al. (2019), where oral ingestion was the most effective exposure route in cancer risk assessment among other routes, such as inhalation and dermal routes of exposure. In addition, Parra et al. (2020) reported the dermal route as the most effective route of PAH exposure and that the elderly were more at risk, whereas our present study found that children are at higher risk. Some factors affect the mechanisms by which PAHs are absorbed in humans. For instance, the age and metabolism of the subject, routes of exposure, and environmental circumstances such as temperature, humidity, solar radiation, wind speed, and precipitation rates can influence PAH metabolism (Kim et al., 2013; Ma & Harrad, 2015).

However, according to the National Academy of Science, children are predisposed to PAH-associated health risks. The reasons can be both behavioral and physiological. Due to their young age, there can be a significant time lag between exposure to PAHs

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### Table 6  Computed source allocation of PAHs in Ekara soil samples during and after COVID-19 lockdown

| Diagnostic ratios | Ekara during COVID-19 lockdown | Possible source | Ekara after COVID-19 lockdown | Possible source |
|-------------------|-------------------------------|-----------------|-------------------------------|-----------------|
| LPAHs             | 0.069                         | Pyrogenic       | 1.63                          | Petrogenic      |
| HPAHs             |                               |                 |                               |                 |
| Ant               | 0.84                          | Pyrogenic       | 0.7                           | Pyrogenic       |
| Ant+Phe           |                               |                 |                               |                 |
| BaA               | 1                             | Combustion      | Not applicable                | Not applicable  |
| BaA+Chr           |                               |                 |                               |                 |
| Fla               | 1                             | Grass coal combustion | Not applicable | Not applicable |
| Fla+Pyr           |                               |                 |                               |                 |

*Ant anthracene, BaA benz(a)anthracene, Phe phenanthrene,Chr chrysene, Fla fluoreanthene, Pyr pyrene*

### Table 7  Computed source allocation of PAHs in Agbeta soil samples during and after COVID-19 lockdown

| Diagnostic ratios | Agbeta during COVID-19 lockdown | Possible source | Agbeta after COVID-19 lockdown | Possible source |
|-------------------|---------------------------------|-----------------|-------------------------------|-----------------|
| LPAHs             | 0.009                           | Pyrogenic       | 1.3                           | Petrogenic      |
| HPAHs             | 0.89                            | Pyrogenic       | 0.08                          | Petrogenic      |
| Ant               | 1                               | Combustion      | Not available                 | Not available   |
| Ant+Phe           |                                |                 |                               |                 |
| BaA               | 0.71                            | Grass coal combustion | Not available | Not available |
| BaA+Chr           |                                |                 |                               |                 |
| Fla               |                                |                 |                               |                 |
| Fla+Pyr           |                                |                 |                               |                 |

*Ant anthracene, BaA benz(a)anthracene, Phe phenanthrene, Chr chrysene, Fla fluoreanthene, Pyr pyrene*

### Table 8  Computed source allocation of PAHs in Ogoloma soil samples during and after COVID-19 lockdown

| Diagnostic ratios | Ogoloma during COVID-19 lockdown | Possible source | Ogoloma after COVID-19 lockdown | Possible source |
|-------------------|---------------------------------|-----------------|-------------------------------|-----------------|
| LPAHs             | 1.03                            | Petrogenic      | 408                           | Petrogenic      |
| HPAHs             |                                |                 |                               |                 |
| Ant               | 1                               | Pyrogenic       | 0.08                          | Petrogenic      |
| Ant+Phe           |                                |                 |                               |                 |
| BaA               | 1                               | Combustion      | Not applicable                | Not applicable  |
| BaA+Chr           |                                |                 |                               |                 |
| Fla               | 1                               | Grass coal combustion | Not applicable | Not applicable |
| Fla+Pyr           |                                |                 |                               |                 |

*Ant anthracene, BaA benz(a)anthracene, Phe phenanthrene, Chr chrysene, Fla fluoreanthene, Pyr pyrene*

### Table 9  Computed benzo(a)pyrene equivalent concentration of soil samples during and after COVID-19 lockdown

| Soil media | Calculated BaPeq1(mg/kg) | Calculated BaPeq2(mg/kg) |
|------------|--------------------------|--------------------------|
| Alejor     | 0.02                     | 0.002                    |
| Ekara      | 0.01                     | 0.005                    |
| Agbeta     | 0.01                     | 0.002                    |
| Ogoloma    | 0.02                     | 0.003                    |
| TBa(P)Eq   | 0.06                     | 0.012                    |

*BaPeq1 benzo(a)pyrene equivalent concentration during COVID-19 lockdown, BaPeq2 benzo(a)pyrene equivalent concentration after COVID-19 lockdown*
and the point at which toxic manifestations appear (Oliveira et al., 2019). Children also spend more time playing on the field, both at school and at home. Similarly, the poor electricity supply in Onne prevents the closure of windows, which would otherwise provide ventilation, in most classrooms in Onne, exposing young pupils and school children to polluted air. Again, their reduced body weight can allow PAHs to accumulate and have dangerous effects (Wang et al., 2011) Taken together, the present study supports the findings of Miller et al. (2010), which indicated that exposure to PAHs is more likely in children. To further substantiate the at-risk population, Perera et al. (2009) discovered a similar adverse relationship between intellect and PAH exposure during prenatal assessments up to 5 years of age.

Furthermore, the lack of adequately developed cytochrome P450 metabolizing enzymes in children could be a contributing factor (Björkman, 2006), while greater exposure to domestic and occupational PAHs is likely to increase the risk of toxicity in the working population. The senior population may be least in danger because the majority of them are no longer extremely active, whereas young adults’ higher level of exercise likely explains why they are at less risk than the other age groups.

**Conclusion**

Despite the extensive reports of pollution in the Niger Delta, the Nigerian government has yet to develop a plan to deal with PAH pollution. To our ultimate knowledge, this is the first study to examine the cancer risks of PAHs originating in the Onne community and the impact of the COVID-19 lockdown. Exposure to soil-borne PAHs via eating, ingestion, contact with the skin, and inhalation in the general population of Onne may present potential health risk concerns. This health risk warrants further investigation through biological monitoring to facilitate concerted efforts to mitigate the potential hazards. For this reason, anthropological activities such as uncontrolled bush burning and illegal oil refining should be prohibited in Onne and nearby communities. Since PAH exposure is literally unavoidable through the soil, concerted efforts should be made to engage researchers, nonprofit-making organizations, and other stakeholders to make policies that check PAH exposure in Onne. More research should be directed at the exposed population. People can be made aware of the public health risks associated with PAHs to enable them to embrace helpful lifestyle changes, such as the avoidance of cigarette smoking, which may increase exposure risks.

**Limitation of the study**

Although risk characterization is essential in health risk assessment studies, risk modeling is limited in predicting risk due to the possibility that risks may be overestimated or underestimated compared to the actual situation. In addition, soil sampling and laboratory experimentation are rigorous and require special expertise and skills.

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**Data availability** Data will be made available upon request.

**Declarations**

**Conflict of interest** The authors declare no competing interests.

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### Table 10: Comparison of ILCR of Onne population during (a) and immediately (b) after COVID-19 lockdown

| Population/route of exposure | Elderly       | Middle aged | Young adult | Children |
|-----------------------------|---------------|-------------|-------------|-----------|
| **Oral ingestion**<sup>a</sup> | 6.26E+02<sup>a</sup> | 6.26E−07<sup>a</sup> | 0.00000073<sup>a</sup> | 5.84E−06<sup>a</sup> |
| **Inhalation**<sup>b</sup> | 3.1E+08<sup>b</sup> | 3.1E+08<sup>b</sup> | 3.62E+08<sup>b</sup> | 8.6E+08<sup>b</sup> |
| **Dermal contact**<sup>b</sup> | 4.18E−07<sup>b</sup> | 3.88E−06<sup>b</sup> | 4.53E−06<sup>b</sup> | 2.99E−06<sup>b</sup> |
| **ILCR_Total<sub>a</sub>** | 3.88E+08<sup>a</sup> | 5.88E+08<sup>a</sup> | 3.62E+08<sup>a</sup> | 8.66E+08<sup>a</sup> |
| **ILCR_Total<sub>b</sub>** | 5.17E+07<sup>a</sup> | 5.17E+07<sup>b</sup> | 6.04E+06<sup>b</sup> | 1.43E+08<sup>b</sup> |
### Appendix

#### Appendix 1 Toxic equivalency factors of 16 priority PAHs by Nisbet & LaGoy, 1992

| PAHs/Code          | Toxic equivalency factor |
|--------------------|--------------------------|
| Naphthalene/Nap    | 0.001                    |
| Acenaphthylene/Acy | 0.001                    |
| Acenaphthene/Ace   | 0.001                    |
| Fluorene/Flu       | 0.001                    |
| Phenanthrene/Phe   | 0.001                    |
| Anthracene/Ant     | 0.01                     |
| Fluoreanthene/FluAn| 0.001                    |
| Pyrene/Pyr         | 0.001                    |
| Benz(a)anthracene, BaA | 0.1                     |
| Chrysene/Chr       | 0.01                     |
| Benzo(a)pyrene/BaP | 1                        |
| Benzo (b)fluoranthene/BbF | 0.1                  |
| Benzo(k)fluoranthene/BKF | 0.1                  |
| Benzo (g,h,I)perylene/BPy | 0.1                |
| Indenol(1,2,3−cd) pyrene/InP | 0.01                |
| Di benz (a,h) anthracene(DahA) | 1                |

#### Appendix 2 Values of parameter used for incremental cancer risk calculation

| Definition                          | Units                              | Children | Young adults | Middle age | Elderly | References               |
|-------------------------------------|------------------------------------|----------|--------------|------------|---------|--------------------------|
| Exposure frequency                  | (EF) days/year                     | 365      | 365          | 365        | 365     | Peng et al., 2011        |
| Exposure duration                   | (ED) year                          | 6        | 20           | 45         | 70      | USEPA, 2014              |
| Average body weight                 | kg                                 | 15       | 60           | 70         | 70      | Ohiozebau et al., 2016   |
| Average time                        | AT (days)                          | 2190     | 7300         | 25,550     | 25,550  | Soltani et al., 2015     |
| Inhalation rate IRi                 | M³/day                             | 10       | 20           | 20         | 10      | USEPA, 2011              |
| Ingestion rate for soil IrS         | Mg/day                             | 200      | 100          | 100        | 100     | USEPA, 2011              |
| Exposed skin surface area (SA)      | cm²                                | 1150     | 2145         | 2145       | 2145    | Qi et al., 2014          |
| Inhalation rate (InhR)              | M³/day                             | 7.6      | 12.8         | 12.8       | 12.8    | Qi et al., 2014          |
| Particle emission factor (PEF)      | M³/kg                              | 1.36×10⁻⁹| 1.36×10⁻⁹   | 1.36×10⁻⁹ | 1.36×10⁻⁹| USEPA, 2011              |
| Skin to skin adherence factor (AF)  | Mg/cm²-d                           | 0.2      | 0.65         | 0.65       | 0.07    | Wang et al., 2018; Qi et al., 2014 |
| Dermal absorption factor ABS        | Unitless                           | 0.13     | 0.13         | 0.13       | 0.13    | USEPA, 2011              |
Definition | Units | Children | Young adults | Middle age | Elderly | References
--- | --- | --- | --- | --- | --- | ---
Absorption factor for GIT water | Unitless | 1 | 1 | 1 | 1 | Qi et al., 2014
Carcinogenic slope factor (CSF) for ingestion, inhalation, and skin absorption | Mg/l/day | 7.3, 3.8, and 25 | 7.3, 3.8, and 25 | 7.3, 3.8, and 25 | Singh & Agarwal, 2018

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