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Scientific Research

Spatial Variations of Particle-Bound Trace Metals in Ambient Air of Selected Niger Delta Communities of Rivers State, Nigeria

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ABSTRACT

The objective of this study was to determine the spatial variation of particle-bound heavy metals in two communities with different industrial status in Nigeria's Niger Delta Area. Fourteen ambient respirable particulate matter (PM_{10}) samples 7 each from Eleme (highly industrialized) and Ahoada East (less industrialized) communities were collected according to standard methods using Anderson High volume sampler. Samples were analyzed for trace metals including Fe, Zn, Ni, Cd, and Pb using Atomic Absorption Spectrophotometer. Data were analyzed using descriptive statistics, Man Whitney U test and Spearman Rank Correlation all at $P < 0.05$. PM_{10} levels were 1.83 times higher at Eleme than Ahoada East ($P < 0.05$) and all the values were higher than both the USEPA and WHO limits. At Eleme spatial variation of PM_{10} was in the following order: APE5 > APE3 > APE7 > APE1 > APE4 > APE6 > APE2. Fe, Zn and Cd were higher at Eleme than Ahoada East and the EC/WHO values. Pb was poorly correlated with PM_{10} ($r^2 = 0.0819$, $P > 0.05$) at Eleme. Communities with higher industrial presence in the Niger Delta are more exposed to particulate burden. Routine monitoring and strict adherence to regulatory limits must be enforced.

Keywords: Industrial Pollution; Particulate Matter; Trace Metals; Spatial Variation; Niger Delta Communities

1. Introduction

Particulate matter (PM) one of the major contributors of air pollution remains a big threat to human health. The WHO indicates that 4% - 6% of the world population die annually due to air pollution related morbidities [1]. PM_{10} is particularly considered to be a reliable indicator for possible health effects [2,3].

The airborne PM is usually composed of and or adsorbed by organic and inorganic toxic pollutants and studies [4] have established links between high levels of PM and health effects including respiratory and cardiac diseases [5,6]. Current studies have revealed that the mortality and morbidity rate is directly related to concentration and number of particles in the aerosol [7-12].

The nature of PM can be organic, inorganic or a mixture with the organic compounds contributing 10% to 40% of the mass of PM. Heavy metals are among the inorganic elements constituting the PM [13]. Some of these elements, such as As, Pb, Cd, Hg, Zn, Ni, Cu, Mn and Cr are of major concern due to their toxic nature while others, such as Fe, Ca, Ba, and Mn are mainly linked to the earth's crust or resuspended soil.

Overall, the effect of PMs depends on its shape, size, composition, mass and number concentrations and the receptor cells. The fine particles provoke lung inflammation and are responsible for cardiovascular diseases [14] and are potentially toxic to human health because of their large surface areas, which are coated with different chemical constituents and carcinogens [15]. The chemical characteristics of atmospheric PM are important for both particle toxicity and its role in climate change [16-18].

The source of toxic trace metals in ambient PM is de-

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pendent on the various anthropogenic processes in a particular area. These include industrial emissions, power plants, urban traffic and combustion by-products. Combustion from automobiles constitutes one of the major sources of particulate emissions, especially the respirable fraction and is directly related to human health [19]. According to Kisku *et al*. [20] and Sharma *et al*. [21] vehicle related emissions is the main source of particulate pollution in Lucknow. Except for storage batteries, paint and gasoline additives were the two major high-volume products containing Pb; about the same quantity of Pb, 5 to 6 million metric tons, was used to manufacture each [22]. Pb is associated with the smallest particles, the clay grain size fraction in urban soils [23], therefore the concentration of Pb in dust originating from urban soils [24] is higher than that from simple measurements of the Pb content of the soil [25].

Several reports show that Pb induces severe neurological and hematological effects on the exposed population especially children [26]. Cd and Ni are known for inducing carcinogenic effects in humans through inhalation. Occupational level of Cd exposure is a risk factor for chronic lung diseases [27]. Cr is known for its toxic and carcinogenic effect on the bronchial tree [28,29]. Mn exposure leads to increased neurotoxic impairments [30]. The increased level of Cu can lead to respiratory irritancy [23,31].

In Nigeria, Ana *et al*. [32] showed varying concentrations of particulate matter in selected Niger Delta communities. However, other researchers [33-35] reported suspended particulates and their elemental concentrations within and around industrial complexes, road side dust, and its effect on soil, vegetation and crops in other parts of the country. Efe [36] reported on spatial distribution of particulate air pollution in Nigerian cities and their implication for human health. The study showed that over 70% of Nigerian urban environments have mean annual ambient PM10 value of over 120 $\mu g/m^3$. Okuo and Ndiokwere [37] studied elemental concentration of Total Suspended Particles with levels as high as 1332.75 $\mu g/m^3$ in Warri and elemental concentrations range ($\mu g/m^3$) for metals including As (3.01 - 5.21), Cd (0.02 - 0.23), Pb (1.01 - 1.04) and Fe (1.13 - 1.38). Also Akeredolu *et al*., [38] and Asubiojo *et al*. [39] reported levels of particulate matter 40,000 $\mu g/m^3$ in industrial sites and 1033 $\mu g/m^3$ in ambient air. But in all these studies there were no indications on the varying pollution levels arising from different sources.

Our study therefore elucidated the spatial variations of the particle-bound trace metals between two communities of different urban and industrial status in Nigeria's Niger Delta Area.

2. Material and Methods

2.1. Description of the Study Area

The study was carried out in two local government areas (LGAs): Eleme a highly industrialized LGA located about 20 km away from Port Harcourt city, the Rivers state capital and Ahoada East a less industrialized LGA located about 80 km from the state capital. The major industries at Eleme include Shell Petroleum Development Corporation (SPDC) oil wells at Ebubu, Petrochemicals at Akpajo/Agbonjia, Refinery at Alesa/Okirika and a fertilizer complex at Onne. Both LGAs share a similar tropical climate. Their vegetation is a mixture of rainforest and mangrove/swamp forest. In addition, the aquatic resources are equally a mixture of fresh and brackish water.

2.2. Sampling Locations and Conditions

Particle-bound heavy metal samples from outdoor ambient air were collected systematically from 14 locations: 7 from Eleme and 7 from Ahoada East communities respectively (see **Figure 1**). Samples were collected during late dry season conditions (February-March).The average meteorological conditions recorded showed temperature range of 28˚C - 31˚C. Average windy conditions with wind speed hardly exceeding 3.5 $m \cdot s^{-1}$ at the sample locations with no cloud cover. A low relative humidity of less than 12 - 33 mm was recorded throughout the period of sampling.

2.3. Determination of Respirable Particulate Matter (PM_{10})

The respirable particulate matter (PM_{10}) samples were obtained using a high volume sampler Anderson model reference method No RFPS-1287-063 with 10 µm cut off inlet at a flow rate of 1 - 1.2 m^3 for 4 hr. Preweighed glass fibre filter papers with dimension 20.3 × 25.4 cm (8 × 10 in) (eCat No: 1882 866) EPM 2000 were used and reweighed after sampling in order to determine the mass of the particles collected. The concentration of the particulate matter ($\mu g/m^3$) was computed on the basis of the net mass collected divided by the volume of air sampled.

2.4. Trace Metals Analysis

The concentration of heavy metals in air was determined with slight modifications using methods described by Dorn *et al*. [40]. The filter papers shredded into tiny fractions were carefully digested with 10 ml of concentrated HNO_3 inside a Teflon beaker and heated at about 120˚C until solution became clear. The content was filtered through a Whatman filter (No. 42) and final volume was

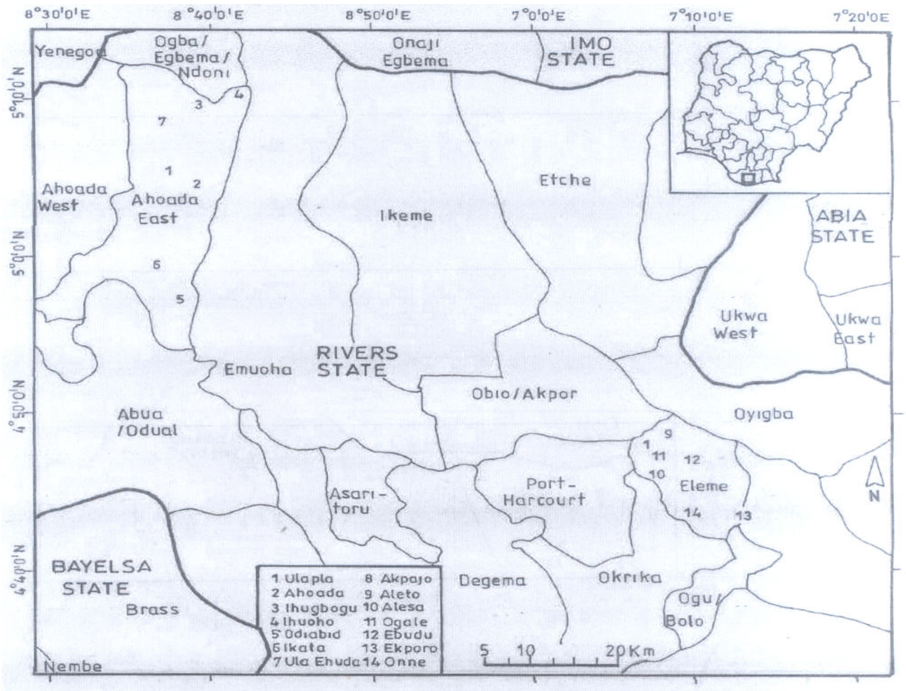


Figure 1. Air sampling locations in study communities.

made up to 50 ml with Milli Q water. The concentrations of heavy metals (mg/m^3) Fe, Zn, Ni, Cd, and Pb were determined using Perkin Elmer AAS model 929 with double beam background corrector. Air-acetylene flame and graphite furnace with appropriate cathode lamps were used.

2.5. Statistical Analysis

Data obtained from the field and laboratory were processed statistically using SPSS version 15. Data were analyzed using descriptive statistics, Mann-Whitney test and Spearman correlation for quantitative variables all at 5% level of significance.

3. Results

3.1. Concentration of Respirable Particulate Matter (PM_{10})

The PM_{10} and trace metals: Fe, Zn, Pb, Cd and Ni concentration were determined in the ambient air at Eleme. **Table 1** indicates that the highest PM_{10} levels were recorded at Alesa (232.5 ± 23.2 $\mu g/m^3$) and Ebubu (260.6 ± 47.7 $\mu g/m^3$) compared to all other sampling locations and the mean PM_{10} levels recorded at Eleme was observed to be higher than Nigeria's minimum (100 $\mu g/m^3$) but lower than maximum (250 $\mu g/m^3$) guideline limits (**Figure 2**) respectively. The spatial variation in the concentration of PM_{10} in the ambient air at Eleme is in the following order: APE5 > APE3 > APE7 > APE1 > APE4 > APE6 > APE2.

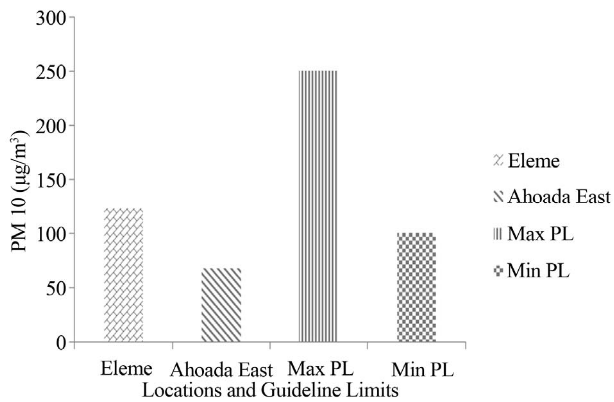


Figure 2. PM_{10} levels at study locations in comparison with guideline limits.

At Ahoada East **Table 2** shows that the highest PM_{10} concentrations were recorded at Ahoada (161.4 ± 10.2 $\mu g/m^3$) and Ula Ehuda (141.9 ± 7.92 $\mu g/m^3$) as compared to other sampling locations. The mean PM_{10} levels were both lower than Nigeria's Minimum guideline limit of 100 $\mu g/m^3$ and the maximum guideline limit of (250 $\mu g/m^3$) (**Figure 2**).The spatial variation in the PM_{10} concentration in descending order is as follows APA2 > APA3 > APA4 > APA1 > APA5 > APA7 > APA6 with the most prominent urban communities of Ahoada (APA2) and Ula Ehuda (APA3) recording the highest concentrations.

Table 1. PM_{10} and trace metal concentrations in ambient air at Eleme.

Sample ID/Location/Parameter	APE1 Akpajo	APE2 Aleto	APE3 Alesa	APE4 Ogale	APE5 Ebubu	APE6 Ekporo	APE7 Onne
PM_{10} (μg/m^3)	75.0 ± 6.51	37.2 ± 0.35	232.5 ± 23.2	61.0 ± 2.26	260.6 ± 47.7	43.2 ± 7.49	154.4 ± 16.5
Fe (μg/m^3)	0.09 ± 0.02	0.09 ± 0.04	0.10 ± 0.07	0.10 ± 0.08	0.10 ± 0.09	0.10 ± 0.06	0.10 ± 0.08
Zn (μg/m^3)	0.04 ± 0.01	0.03 ± 0.02	0.05 ± 0.04	0.02 ± 0.01	0.05 ± 0.03	0.05 ± 0.02	0.10 ± 0.05
Pb (μg/m^3)	0.07 ± 0.02	0.10 ± 0.02	0.07 ± 0.03	0.02 ± 0.01	0.10 ± 0.05	0.05 ± 0.02	0.03 ± 0.03
Cd (μg/m^3)	0.02 ± 0.02	0.01 ± 0.01	0.02 ± 0.02	0.01 ± 0.03	0.002 ± 0.003	0.003 ± 0.002	0.004 ± 0.001
Ni (μg/m^3)	0.03 ± 0.02	0.03 ± 0.01	0.05 ± 0.03	0.02 ± 0.02	0.03 ± 0.04	0.04 ± 0.02	0.03 ± 0.02

Table 2. PM10 and trace metal concentrations in ambient air at Ahoada East.

Sample ID/Location/Parameter	APA1 Ulapata	APA2 Ahoada	APA3 Ula Ehuda	APA4 Ihubogu	APA5 Ihuoho	APA6 Ikata	APA7 Odiabidi
PM_{10} (μg/m^3)	25.9 ± 3.89	161.4 ± 10.2	141.9 ± 7.92	104.7 ± 8.41	20.4 ± 1.06	8.84 ± 0.50	10.4 ± 0.06
Fe (μg/m^3)	0.01 ± 0.01	0.03 ± 0.02	0.04 ± 0.02	0.04 ± 0.02	0.03 ± 0.01	0.03 ± 0.02	0.05 ± 0.04
Zn (μg/m^3)	0.08 ± 0.04	0.03 ± 0.01	0.05 ± 0.03	0.05 ± 0.03	0.04 ± 0.01	0.05 ± 0.03	0.42 ± 0.14
Pb (μg/m^3)	0.05 ± 0.02	0.04 ± 0.03	0.13 ± 0.08	0.03 ± 0.02	0.11 ± 0.10	0.11 ± 0.09	0.13 ± 0.07
Cd (μg/m^3)	0.01 ± 0.03	0.004 ± 0.002	0.01 ± 0.01	0.01 ± 0.03	0.002 ± 0.001	0.004 ± 0.002	0.01 ± 0.01
Ni (μg/m^3)	0.01 ± 0.01	0.02 ± 0.02	0.03 ± 0.02	0.03 ± 0.02	0.05 ± 0.03	0.03 ± 0.03	0.04 ± 0.02

3.2. Concentration of Trace Metals

Table 1 indicates that the highest Pb level was recorded at Ebubu (0.10 ± 0.05 μg/m^3) while the highest Cd levels was recorded at Akpajo (0.02 ± 0.02 μg/m^3) and Alesa (0.02 ± 0.02 μg/m^3) respectively. At Ahoada East the highest Pb levels were recorded at locations in Ula Ehuda (0.13 ± 0.08 μg/m^3) and Odiabidi (0.13 ± 0.07 μg/m^3) (**Table 2**). Of the five heavy metals assessed three viz Fe, Zn and Cd recorded higher concentrations at Eleme. Only Pb recorded a higher concentration at Ahoada East (**Figure 3**).

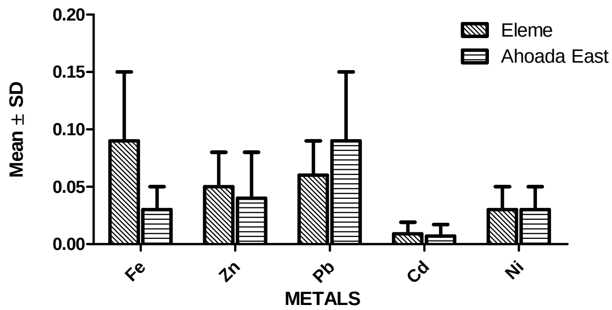


Figure 3. Comparison of mean values of heavy metals between Eleme and Ahoada East.

3.3. Relationship between PM_{10} and Trace Metals

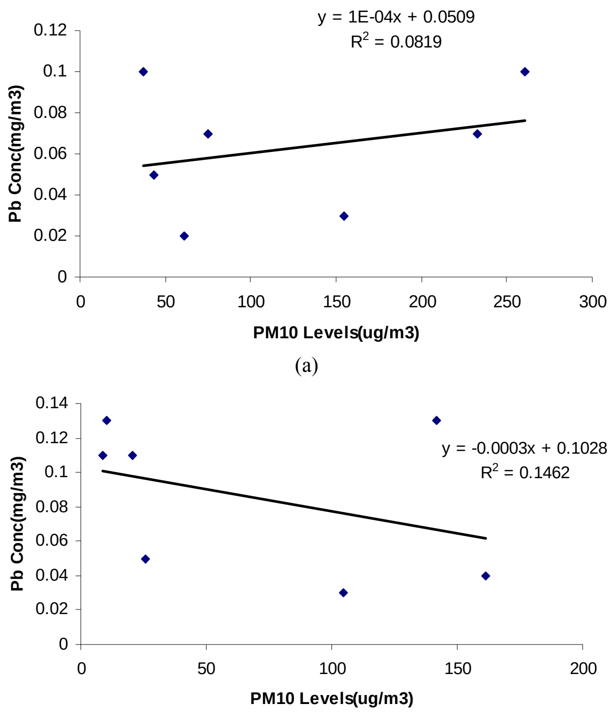
The relationship between the PM_{10} and trace metals was assessed based on the level of correlations. Given the place of Pb among the most toxic heavy metals in the EPA priority list only the result of the correlation test for PM_{10} and Pb is reported here (**Figures 4(a)** and **(b)**). In all the cases no significant correlations were observed.

4. Discussion

The concentrations of PM_{10} were assessed in relation to trace metals in two communities of Nigeria's premium oil producing area with different levels of industrial activities and urbanization. The results of the respirable fraction of particulate matter and the trace metals adsorbed on the surface of the particles are given in **Tables 2(a)** and **(b)** with **Figures 4(a)** and **(b)** showing the correlation between these two parameters.

At Eleme the spatial distribution of PM_{10} in the various sampling locations showed the following order: APE5 > APE3 > APE7 > APE1 > APE4 > APE6 > APE2.The first four sampling points represent locations at Ebubu where Shell Petroleum has its oil locations (APE5), refinery complex at Alesa (APE3), chemical fertilizer complex at Onne (APE7) and the petrochemical complex at Akpajo (APE1) recorded the highest concentrations.

The presence of these industrial facilities associated with increased human activities viz automobile emissions, burning of biomass, must have contributed to the higher PM_{10} concentrations in these locations than the others.



(b)

Figure 4. (a) Correlation between PM_{10} and Pb in ambient Air at Eleme; (b) Correlation between PM_{10} and Pb in ambient air at Ahoada East.

This observation is in concert with studies by Efe [37] where PM_{10} concentrations were higher in more urbanized settings with higher industrial and traffic conditions. In the same vein at Ahoada East, the order of PM_{10} was: APA2 > APA3 > APA4 > APA1 > APA5 > APA7 > APA6 with the most prominent urban communities of Ahoada (APA2) and Ula Ehuda (APA3) recording the highest concentrations.

The mean PM_{10} concentration observed at Eleme was expectedly higher (1.83 times) than that recorded at Ahoada East. This could be explained by the fact that there are more anthropogenic activities especially automobile and industrial emissions at Eleme which is considered to be more urbanized than Ahoada East. The presence of the refinery, petrochemical complex, chemical fertilizer company and other industries have certainly contributed to the burden of particulate emissions in the ambient air environment of these localities.

The mean levels of PM_{10} at Eleme though higher than the values from Ahoada East were comparable to that reported by Efe [37], close to that reported by Singh *et al.* [41], higher than that reported in most European countries [42,43] and some American countries [44]. Overall, these levels were lower than Nigerian Max permissible limits [45] but higher than USEPA limits.

The spatial variation in the concentration of Pb in the ambient air at Eleme is as follows: APE5 > APE2 > APAE3 = APE1 > APE6 > APE7 > APE4.Excluding APE2, the first four locations have very high industrial presence with its attendant human activities and this must have contributed to the high levels of Pb in the ambient air. Also the spatial variation at Ahoada East shows the following trend: APA7 = APA3 > APA5 = APA6 > APA1 > APA2 > APA4.

In contrast to the observations at Eleme, Ahoada (APA2) the most urbanized community and the administrative headquarters of the local government area recorded the lowest Pb level. The spatial variation for other trace metals was also noted. Pb mainly from anthropogenic sources was found to be higher at Ahoada East than Eleme and about a 1000 times higher than values reported by Lopez *et al.* [43], despite the higher industrial outlook of Eleme. These values were 60 folds (for Eleme) and 90 folds (for Ahoada East) higher than WHO limits. Fe had higher concentrations at Eleme than Ahoada East and these levels were higher than levels recorded by Sharma *et al.* [21], Singh *et al.* [41]. The Fe could have been from both natural and anthropogenic origin [46].

The concentration of Zn was higher at Eleme than Ahoada East and these levels are higher than the values reported by Singh *et al.* [41] as well as the WHO guideline [2]. Nowadays, Zn has been proposed as a reliable tracer of unleaded fuel and diesel oil-powered motor vehicle emissions. Cd mostly from occupational origin was highest with values almost 10 times at Eleme as compared to Ahoada East. Ni emitted from both stationary and mobile sources had same mean concentrations for Eleme and Ahoada East suggesting similar inputs from probably automobile emissions.

Several studies have shown some level of correlation and linear relationship between the PM_{10} concentrations and trace metals. For instance Singh *et al.* [41] showed a correlation of PM_{10} with Zn ($r = 0.39$, $p < 0.05$) and Ni ($r = 0.36$, $p < 0.05$). Also Barman *et al.* [45] showed a correlation of Ni ($r = 0.71$, $p < 0.01$), Cd ($r = 0.65 < 0.01$) with PM_{10} and similarly Sharma *et al.* [21] showed correlation of Fe ($r = 0.71$, $p > 0.05$) with PM_{10}.This suggests that trace metals adsorbed on particulate matter are linearly dependent on the PM_{10} levels. In the present study nearly all the metals were poorly correlated with PM_{10} even though only the correlation between Pb and PM_{10} is being reported. The result was however at variance with those hitherto reported. This suggests that most of the sources of PM_{10} were not rich in the trace metals determined.

It is considered that elevated concentrations of PM_{10} and particle-bound trace metals have direct relation to adverse human health as well as on the environment

[47-49] Other studies have also implicated high levels of PM_{10} with various forms of respiratory and cardiovascular disorders as well as increased hospital visitations [7]. In this study the levels of PM_{10} and the associated trace metals were higher in the ambient air at Eleme as compared with Ahoada East, implying that the populations in the former than the later would be more prone to adverse health outcomes.

5. Conclusions

The study revealed that respirable particulate matter was nearly two folds higher in the ambient air at Eleme compared to Ahoada East and the levels even though lower than FEPA guidelines were higher than USEPA and WHO limits.

Three out of the five trace metals namely Fe, Zn and Cd recorded higher concentrations at Eleme compared to Ahoada East with Pb only recording the highest concentration at Ahoada East.

The concentrations of all the trace metals were higher than those from previously reported studies as well as the EC and WHO guideline limits.

Although linear relationship was established between the PM_{10} levels and Pb the correlation was poor and not statistically significant for both Eleme and Ahoada East.

Industrialized communities with elevated levels of PM_{10} and associated toxic elements are more likely to be vulnerable to related health hazards posed by these substances in the ambient air. Therefore as a matter of policy routine air monitoring and strict adherence to regulatory limits by industries operating in the Niger Delta area should be enforced.

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