

ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS, POLYCHLORINATED BIPHENYL, IN USED ELECTRICAL TRANSFORMER OIL, CONDENSATE, THERMAL POWER EFFLUENT SOIL AND DUMP SITES

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ABSTRACT

Thermal power stations are the largest fossil-fuel-based power-generating station in the country. Hydro and thermal generation combines natural gas as a fossil fuel to generate electricity. Polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyl (PCBs), were determined in the used electrical transformer oil, condensate and power station effluent, including the soil obtained from the condensate and electrical transformer dump site. The results revealed that PAHs had 1.119, 6.483, 0.350, 4.695, 3.314 and 0.732 (mg/g/L), respectively. PCBs 0.052, 0.431, 1.576, 0.013 0.080 and 0.556(μg/L), respectively, in all the analysed samples. The power station effluent had the highest concentration of PCBs with few congeners not detected. The result suggests a risk for the community that uses river water which receives effluent from the thermal station for various domestic applications and the contamination of farm lands for various agricultural purposes.

Keywords: Polycyclic Aromatic Hydrocarbons; Polychlorinated Biphenyl; Water; Soil; Risk Assessment.

INTRODUCTION

Environmental pollution which encompasses water, soil and air is a serious problem in the world today. Different kinds of pollutants enter the environment affecting it greatly. The industrial sector is one of the major sources of pollution, but in addition to this, are thermal power stations, which also affect the environment adversely (Hullio *et al.*, 2012). In the last decades, highly toxic organic compounds have been synthesized and released into the environment from direct or indirect application over a long period. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), Pesticides, fuels, chlorophenols, and dyes are good examples. Some synthetic chemicals are resistant to biodegradation by native flora compared with the naturally occurring organic compounds that are readily degraded upon introduction into the environment. Similarly, hazardous wastes and chemicals have become the greatest problems of the modern world (Deiz, 2010). Studies have shown that industrial effluent is one of the main sources of surface water pollution in Nigeria (Ekiye and Zejko, 2010), industrial effluent when discharged directly into the river without prior treatment can increase water quality parameters. According to Dada (1997), less than 10 percent of industries in Nigeria treat their effluent before being discharged into the rivers. This has led to a high load of inorganic and organic pollutants like

Heavy metals, PCBs and PAHs PCBs are not single compounds, but mixtures of chlorinated hydrocarbon compounds comprised of a biphenyl backbone with substitutions of from one to ten chlorine atoms. Although there are 209 possible PCB isomers or unique patterns in which these chlorines can be substituted onto the biphenyl rings (Johnson *et al.*, 2000). PCBs do not occur naturally and were first synthesized in 1881. Industrial synthesis of PCBs was carried out by direct chlorination of biphenyl with chlorine gas. The commercial production of PCBs began in the United States in 1929. Since then, PCBs have been used industrially; as dielectrics in transformers and large capacitors, as heat exchange fluids, as paint additives, in carbonless copy paper, textiles and in plastics (Salihovic *et al.*, 2012). PAHs are hazardous organic chemicals consisting of two or more benzenoid groups. They are ubiquitous pollutants in our environment (Kanchanamayoon and Tatrahun 2008, Marce, and Borull, 2000) PAHs are by-products of combustion and are naturally occurring chemicals in the environment. Forest fires and volcanoes are major natural sources of PAHs. Anthropogenic sources include waste site incineration, burning of fossil fuels (including automobiles) industrial emissions, industrial waste incineration, and thermal power generation (Thamaraiselvan *et al* 2015). There are hundreds of PAH compounds in the environment, but only 16 of them are included in the priority pollutants list of the American Environmental Protection Agency US EPA (El Mekawy *et al.*, 2016). The 16 PAHs considered are naphthalene, acenaphthylene, acenaphthene., fluorene, anthracene, phenanthrene, fluoranthene, chrysene, benzo[a]anthracene, pyrene, benzo[k]fluoranthene, benzo[b] fluoranthene, benzo[a]pyrene, dibenzo[a,h] anthracene, dibenzo[b,c]fluoranthene indono (123c,d)pyrene and benzo[ghi]perylene due to their mutagenic and carcinogenic properties (ATSDR) 1995. Due to the adverse health effects of these pollutants, especially, Heavy metals PAHs and PCBs there is a desperate need to evaluate and determine their source in the environment as to enable proper monitoring and control of discharged or emission into the environment, especially water bodies (Kabzinski *et al.*, 2002). The unreasonable risks pose to human health, remedial actions must be taken by power stations to reduce risks to acceptable levels (Sameer *et al.*, 2013)

MATERIALS AND METHODS

Condensate was collected from the tank where it is stored before disposal from the power station, the power station effluent was collected at the point of disposal from the power station while the

used electrical transformer oil was collected from one of the transformers in the power station premises. All the samples were collected in a clean amber glass bottle rinsed with the content before collection.

Aqueous Sample Extraction

A litre each of the sample and reagent water was transferred to a 2-litre different separatory funnel. For all samples and blanks, 1 mL of the concentrated surrogate spiking solution was added directly to the separatory funnel. The pH was noted and adjusted to pH <2. 60 mL of DCM was added to the separatory funnels. The separatory funnel was sealed and shaken vigorously for at least three (3) minutes with periodic venting to release excess pressure. Then the organic layer was allowed to separate from the water phase for a minimum of 5 minutes. Then collect the solvent extract in an Erlenmeyer flask. The extraction was repeated two more times using an additional 60 ml portions of solvent. The three solvent extracts were then combined in a 250-mL Erlenmeyer flask. A rotary evaporator apparatus was placed on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapour. The vertical position of the apparatus and the water temperature were adjusted as required to complete the concentration in 10 minutes, then the extract was dried by passing it through a glass powder funnel containing anhydrous sodium sulfate or other suitable drying agent. The extract was concentrated to less than 10 mL, by raising the temperature of the water bath, if necessary, to maintain proper distillation. The Snyder column and evaporation flask were removed from the 10-mL concentrator tube. The concentrator tube containing the DCM extract was placed in an air blow-down apparatus. The extract volume was adjusted to 1 mL under a gentle stream of nitrogen or air. If the extract is highly coloured, forms a precipitate, or stops evaporating, the final volume should be higher.

Soil/Sediment/biota Sample Extraction

A solvent mixture of acetone and methylene chloride 50:50 was prepared. 10g aliquot of well-mixed sample was measured into a solvent-rinsed beaker, and then 50 mL of the solvent mix was added to the samples. Spike with 1 mL of the surrogate mix. The sample was placed in the sonicator and sonicated for about 10 – 15 minutes at about 70 °C. 10g of anhydrous sodium Sulphate was added to the sample until a clear extract developed. Then, the extract solvent was poured into a round bottom flask. The process was repeated once more with an additional 50ml of solvent mixed sonicate and the beaker was allowed to settle and decanted into the same round bottom flask. The solvent was concentrated to about 1 to 3mL. The sample was then ready for cleanup using a silica gel column. The columns were packed with 10g of 100-200-

mesh silica gel pre-conditioned (baked) at 105°C overnight. The silica was mixed with DCM to form a slurry. The analysis was carried out using a gas chromatography/ Flame Ionization Detector (GC/FID).

Extraction and Analysis of Polychlorinated Biphenyl (PCBs)

Approximately 10.0 grams of anhydrous sodium sulfate was added to a pre-cleaned mortar and 5 grams of fresh earthworm (was added to the mortar and homogenized to a complete mixture with a pestle. The mixture was carefully transferred to a pre-cleaned PTFE extraction tube which has a PTFE screw cap. 5 to 10 pre-cleaned glass beads were added. 25 mL of a mixture of hexane (1:1) was added to the 100 mL PTFE extraction tube; the extraction tube was tightly capped and allowed to stand for a minimum of 20 minutes. This allows complete permeation of solvent to the matrix. 20µg/l of the internal standard decafluorobiphenyl in iso-octane directly was added to the sediment and sodium sulphate mixture. The tube was shaken vigorously until the slurry is free-flowing. Any chunks were broken manually with the glass rod, working quickly but gently. The cap was replaced immediately after the breaking of the chunks. More sodium sulfate was added and manually mixed as necessary to produce a free-flowing, finely divided slurry. The samples were extracted by rotating end-over-end for at least 30 minutes. Care was taken to release pressure by opening and closing the flasks at intervals. The solids were allowed to settle for one to two minutes. The solvent layer was filtered through a small glass funnel containing a layer of anhydrous sodium sulfate over a plug of glass wool into a receiving conical flask. The sodium sulfate was thoroughly pre-wetted with hexane before sample filtration. The sodium sulfate was rinsed with 2 to 3mL of hexane as soon as the surface is exposed. The top of the sodium sulfate layer was not allowed to go dry. The earthworm sample was extracted twice more by adding approximately 15 mL of hexane mixture to the sample, capping the extraction tube tightly, and shaking vigorously by hand for 2 minutes. All the extracts are combined and poured into the round bottom flask of the rotary evaporator. The round bottom flask of the rotary evaporator is placed in a constant temperature hot water bath so that the concentrator flask is partially, but not completely, immersed. The temperature of the bath was adjusted and the position of the apparatus so that, the solvent was heated evenly. The sample volume was reduced to approximately 1.0 mL. The Micro Cold Solvent Extraction and Cleanup for earthworms was according to Steindwandter and Shutler (1978). The analysis was carried out using a gas chromatography/ Electron capture detector (GC/ECD).

Statistical Analysis

Descriptive (mean and standard deviation) statistical analysis was used to present data in numerical and graphical forms.

RESULTS

Table 1: Polycyclic Aromatic Hydrocarbon level of all samples

PAHs	CS	PSE	UETO	CDS	ETS		
Naphthalene	0.112	ND	ND	0.013	0.013		
Acanaphthalene	0.347	0.021	ND	0.013	ND		
Acenaphthene	0.545	0.071	0.705	0.045	0.012		
Florene	0.239	0.102	ND	0.349	0.090		
Phenathrene	0.077	0.008	0.157	0.067	0.013		
Anthracene	0.118	0.018	0.196	0.011	0.110		
Fluoranthene	3.258	0.004	0.011	2.032	0.274		
Pyrene	0.018	0.008	0.002	0.015	0.018		
Benzo(a)anthracene	1.295	0.002	0.013	0.017	0.045		
crystene	0.467	0.002	0.013	0.067	0.028		
Benzo(b)fluoranthene	0.393	0.113	0.018	0.402	0.012		
Benzo(a)pyrene	0.162	ND	ND	0.071	0.072		
Benzo(k)fluoranthracene	0.632	ND	ND	0.132	0.013		
Indeno(123)perylene		0.832	ND	ND	0.032		
Dibenzo(a,h)anthracene	0.0184	ND	ND	ND	0.020		
Benzo(a,h,l)perylene		ND	ND	ND	ND		
Total(mg/kg/l)	6.483	0.350	1.119	3.314	0.732		
Mean values		0.432±0.133		0.035±0.009	0.140±0.045	0.221±0.125	0.052±0.017

Note: CS= condensate PSE= power station effluent UET = used electrical transform oil CDS = condensate site dumping soil ETS = electrical transformer site soil ND = Not detected

Table 2: Polychlorinated Biphenyl level of all the samples analyzed

PCB congeners	CS	PSE	UETO	CDS	ETS							
PCB 7	0.019	0.013	ND	0.009	0.004							
PCB 18	0.045	0.013	ND	0.005	0.014							
PCB 28	ND	0.011	ND	ND	0.030							
PCB 43	0.005	0.012	0.001	0.005	0.048							
PCB 52	0.081	0.126	0.001	0.001	0.022							
PCB60	0.144	0.002	0.039	0.044	0.060							
PCB 77	0.021	0.002	ND	0.001	0.046							
PCB 107	ND	ND	ND	ND	0.034							
PCB 105	0.007	ND	0.001	0.007	ND							
PCB 123	ND	0.001	0.001	ND	0.009							
PCB 126	ND	0.002	ND	ND	0.036							
PCB 128	0.001	ND	0.001	0.001	0.044							
PCB 137	0.003	0.002	0.002	0.003	0.062							
PCB 154	ND	ND	ND	ND	0.070							
PCB 170	0.001	0.003	0.001	0.001	0.028							
PCB 180	0.041	ND	0.001	0.001	0.024							
PCB 185	0.051	0.003	0.001	0.001	0.010							
PCB 195	0.021	0.068	0.001	0.001	0.011							
PCB200	0.001	0.004	0.001	0.001	0.004							
PCB 206	ND	ND	ND	ND	ND							
PCB 209	ND	1.314	0.003	ND	0.018	0.001						
Total PCBs	0.431		1.576	0.052		0.080	0.55					
Mean	0.031±	0.007	0.105±	0.062	0.004 ±	0.001	0.006 ±	0.002	0.029 ±	0.004	0.001 ±	0.000

CS= condensate PSE= power station effluent UET = used electrical transform oil CDS = condensate site dumping soil ETS = electrical transformer site soil BR = Banegbe river sample, BDL= below detectable level

DISCUSSION

Persistent organic pollutants (POP) are very toxic and are characterized by their high persistence in the environment, bioaccumulation and biomagnification ability along the food chain, and adverse effects on human health and the environment (Fernie *et al.*, 2003), these POPs include PAHs and PCBs. PCBs are a class of chlorinated organic compounds comprised of a biphenyl backbone with substitutions of one to ten chlorine atoms. PCBs are not produced in Nigeria but contamination arises mainly from the importation of electrical transformer oil containing PCBs from developed countries, between the 1970s and 1980s, these transformers were widely used in the energy-production sector, resulting in PCB oil leakage into soil and ground waters. Although the use of PCBs was generally stopped over 40 years ago, they still exist in old electrical equipment and environmental media to which humans can be exposed (Okpashi *et al.*, 2018). The presence of PCBs in the electrical transformer instillation site soil could be a result of accumulation over the years from the spilled oil of the electrical transformer since most of the Power Station in the country was built before the banned of PCBs as additives in electrical transformers.

Since PCBs are not naturally occurring, their presence in the condensate of natural gas must be from a point source. Their presence could be from the use of PCBs to compress the pipeline for transmission of the gas to their various destinations (El-Mekawy *et al.*, 2016). The compressor station is part of the pipeline system and serves the main purpose of recompressing the gas stream to keep it moving through the transmission system to its destination. Another way of PCBs contamination in the condensate could be from the PCBs-base lubricating oil used in the turbine unit of a thermal gas plant and sealant used for the maintenance of gas pipelines that were formulated with PCBs because of their resistance to ignition at higher temperatures (Giesy and Kannan, 1998). The presence of PCBs in the condensate dump site soil sample as shown in Table 2, could be a result of accumulation from the condensate over the years. Since PCBs are not easily degraded by native micro-organisms.

Also from our present result, the used electrical transformer oil had the lowest total PCB concentration of 0.052kg/mg, with the soil sample from the electrical transformer having 0.556. PCBs have been used over the years as dielectric in electrical transformers, but their use as been banned since the 1970s. Our present study has shown that the electrical transformer used in Transcorp Power Limited Ughelli uses oil, not PCBs as their dielectric in their electric transformer. The presence of a low concentration of PCBs in the used electrical transformer oil may be from other electrical equipment in the transformer that leaked into the oil or as a result of old transformers used in the past since the power station started before the 1970s before the banned of PCBs, that also could have been the source of PCBs in the soil from electrical transformer site and also as a result of an accumulation over the time from the spilt oil from the electrical transformer. The same happens in the condensate and condensate contaminated soil samples (Hussein *et al.*, 2016).

The power station effluent had a total concentration of 0.35 0mg/l with most of the high molecular PAHs absent, this can be attributed to their lower water solubility and great tendency to absorb onto the solid phase. Generally speaking, the composition of PAHs is

characterized by a greater number of aromatic rings with higher carcinogenicity (Caiyun *et al.*, 2015). The PAH composition pattern serves as a vital tool to track contaminant source and fate within a multimedia environment. In general, it has been reported that the petroleum-derived anthropogenic PAH residues contain relatively higher concentrations of two and three-ring PAH compounds (Ololade and Lajide 2010)

From our present study, condensate (a waste product) from the power station had the highest concentration of total PAHs with all the sixteen PAHs analysed present except benzo (g h i) perylene. The high-value PAHs may be a result of high lipophilicity and high partition coefficient of PAHs to organic compounds since the condensate is an organic compound. A wide range of PAHs can be formed during the combustion of organic material by a series of complex chemical reactions. (Okpashi *et al.*, 2020) The chemical composition of burning products varies depending on the source of materials and burning condition (Nwaichia *et al.*, 2016) A gas thermal power station that uses a gas turbine for the production of electricity like most of the power stations in the country. The concentration of PAHs in the condensate may be a result of combustion and condensation of gas used to turn the turbine and also the source of the natural gas used

Ratios of fluoranthene (Fla) to pyrene (Pyr) and phenanthrene (Ph) to anthracene (An) are often used to verify the sources of the PAHs detected in the samples. The ratio of fluoranthene to pyrene greater than one (Fla/Pyr>1) is attributed to a pyrolytic source while Fla/Pyr <1 is attributed to a petroleum hydrocarbon source (Collins *et al.*, 1998). Similarly, the ratio of phenanthrene to anthracene less than ten (Ph/An<10) indicates a combustion source and Ph/An >10 is attributed to a petrogenic source (Ezemonye *et al.*, 2008). From our result, it may be concluded that the source of the PAHs in the condensate and electrical transformer oil is attributed to the petroleum hydrocarbon source of the gas and oil, also from combustion processes. As indicated by the ratio of fluoranthene to pyrene which is < 1 and phenanthrene to anthracene < 10.

When PAHs enter the soil they pose an environmental risk to soil organisms, agricultural food grown in that soil and humans that eat the food grown in PAHs polluted soil. Our result showed PAH concentration was higher in condensate dump site soil when compared to electrical transformer site soil. A wide range of PAHs are produced from the combustion of organic materials by complex chemical reactions, the chemical composition of the burning material varies depending on the origin of the source of material and the burning condition (Sameer *et al.*, 2013).

Conclusion

In conclusion, we can say also the presence of PCBs in the thermal power plant is a result of other sources of PCB equipment used in the station or from the old electrical transformer used before the ban. And not from the oil used in the electrical transformer

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