

Evaluation of polycyclic aromatic hydrocarbons in water from hand dug wells at Ile-Oluji, Nigeria

Richard Odunayo Akinyeye, *Adefusisoye Adegalu Adebawore, Emmanuel Eytayo Awokunmi and Edward Olorunsola Olanipekun
Department of Chemistry, Ekiti State University, Ado-Ekiti, Nigeria

Abstract: Spilling and seepage of gasoline to soil could be a source of organic pollution to the underground waters in such vicinities. This work evaluated the levels of polycyclic aromatic hydrocarbons (PAHs) in groundwater drawn from hand-dug wells in filling stations, and a control sample from a well very remote from filling stations in Ile-Oluji, Ondo State, Nigeria. The concentrations of PAHs for the samples varied from ND – 11.3 ng/μL with grand mean of 31.9±2.81 ng/μL. About 95% of the PAHs detected consisted of low molecular weights (2–3 aromatic rings), which are less carcinogenic but also pose toxic effect to many aquatic organisms. The remaining 5% of the PAHs were 4 – 5 member rings. The 5-member ring (benzo (k) fluoranthrene and all the 6-member rings were un-detected in the study. The total mean concentrations of PAHs present in the control sample varied appreciably with respect to where the filling stations were sited (ND – 0.07 ng/μL) with total PAHs of 0.12 ng/μL. Three locations (A, C and D) which indicated high levels of benzo (a) pyrene, pose health hazards. Periodical water quality assessment of such wells is recommended.

Keywords: Gasoline filling stations, Ile-Oluji-Nigeria, polycyclic aromatic hydrocarbons, toxicity, well-water.

I. Introduction

The presence and concentration of microbial and chemical pollutants in drinking water are one of the oldest routes of municipal health issue with a multitude of health related concerns. These concerns include that of polycyclic aromatic hydrocarbons and ensuring compliance with international guidelines for drinking water quality [1]. Because of deleterious effects on human beings and the entire environment, chemical pollutants, especially xenobiotic compounds are of foremost importance for timely detection and control. The presence of organic pollutants, including endocrine disruptors, organo-phosphorus pesticides and pre-cursors, trihalomethanes (THMs) and trichloroethylene (TCE) in water resources have been widely investigated by a large number of studies [2, 3, 4, 5]. Polycyclic aromatic hydrocarbons (PAHs) represent a group of xenobiotic chemicals made up of two or more fused rings of carbon and hydrogen, containing at least two benzene rings [6]. They are a group of ubiquitous contaminants with high melting and boiling points, low vapour pressure and very low water solubility [7]. PAHs are stable hydrophobic organic chemicals that persist in the environment and are capable of bio accumulating in animal and human tissues where it is deposited. PAHs exist in various combinations that manifest various functions. They are made up of two or more fused benzene rings and some “pentacyclic moieties” in linear, angular, and/or cluster arrangements [8]. The major sources of PAHs include incomplete combustion of wood and fossil fuels, vehicle exhaust as well as direct inputs from spillage of petroleum products [9]. Their molecular weight is in the range of 166 to 328. The molecular weight of each molecule depends on its number and position of fused rings and other components. Other anthropogenic sources include cooking ovens, and cigarettes.

Naturally, water pollution by PAHs has caused considerable concern worldwide. Inland water usually acts as receptors for these pollutants. The pathways through which PAHs enter surface water include atmospheric fallouts from incomplete combustion, municipal effluents, and oil spillages which could be grouped into petrogenic and pyrogenic sources [10, 11]. Davis [12] has shown that petrogenic PAHs enter the estuary by means of spills and leaks of oil and refined oil products. The anthropogenic activities, which distribute PAH contaminants includes industrial production, transportation, municipal and domestic waste incineration or disposal. According to Hellou *et al.* [13], Delistraty [14], Schirmer *et al.* [15, 16] and Swartz *et al.*, [17], PAHs potentially contribute many of the modern day diseases, including cancer, damage to the reproductive system, disrupted endocrine and immune systems, and neurobehavioral effects. Alani *et al.* [18] has shown that PAHs can easily spread and be transported across the globe via groundwater and surface water bodies. There are more than 100 PAHs but the following 16 United States Environmental Protection Agency (USEPA) [19] priority PAHs are chosen for this study: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chy), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo [k]fluoranthene (BkF), dibenzo[a,h]anthracene (DahA), indeno[1,2,3-cd]pyrene (IcdP), and benzo[g,h,i]perylene (BghiP) these 16

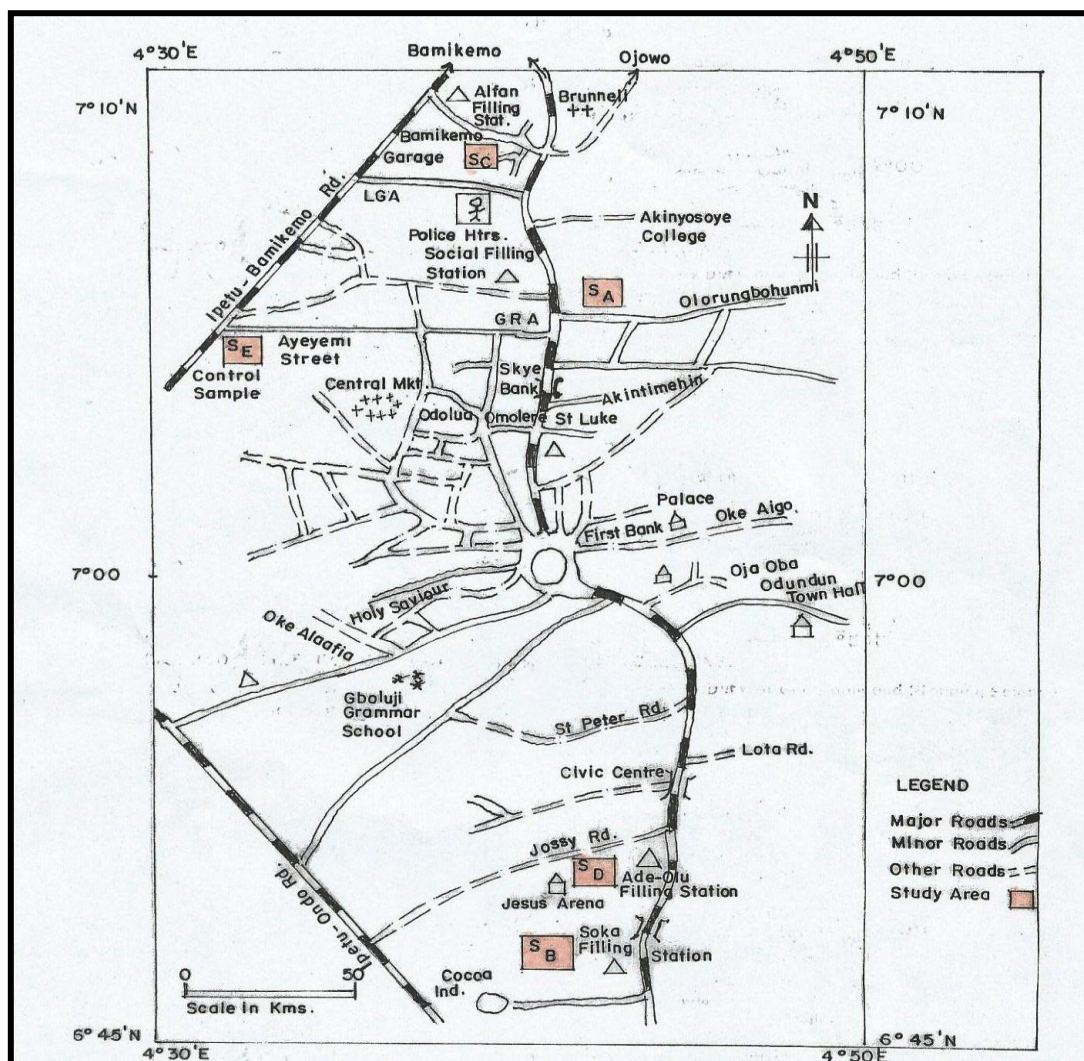


Figure 2: Map of Ile Oluji Township showing locations for Samples A, B, C, D and the Control Sample

2.2 Extraction and Clean Up

EPA method 3510C with slight modifications was employed [35]. Water samples were extracted using liquid-liquid extraction mode by thoroughly shaking 100 mL of water sample with 50 mL of dichloromethane (DCM). The solution was transferred into a separating funnel and samples were extracted by shaking the funnel for three mins with periodic venting to release excess pressure. The organic layer was separated from the water phase for a minimum of 10 min and the DCM extract was collected in a 250 mL Erlenmeyer flask. Another 60 mL portion of DCM was added to the sample bottle and the steps above repeated. The extracts were transferred into the Erlenmeyer flask. The extracts obtained were concentrated in a rotary evaporator to about 2 mL by evaporating the organic layer under a gentle stream of nitrogen. Activated silica gel was loaded into a glass-chromatographic column and 1 g of Na_2SO_4 was added to the column and conditioned with DCM. The concentrated extracts were dissolved in 5 mL n-hexane, loaded into the column, and then eluted with 50 mL n-hexane. The eluents were concentrated using a rotary evaporator and then reconstituted in 0.5 mL n-hexane for Gas-chromatography (GC) analysis [34].

2.3 GC analytical conditions

The Gas Chromatograph model GC, Agilent 7890A (Shimadzu, Japan) coupled to a flame ionization detector and DB-1 fused silica capillary column (30 m x 0.25 mm, 0.25 μm film thickness) was employed for the separation of the analytes via liquid/liquid chromatography separation. The GC temperature ramp and other gas chromatography conditions are presented in Table 1 and a 1.0 μL of the extract was injected in a split-less mode. The mean elution times of the PAHs were identified by repeating five injections and peaks were identified using the retention times of the standards. The concentrations of PAHs were determined by extrapolation of peak area using the calibration curves of the standards.

Table 1: Gas chromatography conditions [36]

Conditions	Values
Carrier flow gas	Helium
Make-up	Nitrogen
Flow rate	1.2 mL/min
Inlet temperature	270°C
Injection volume	1 µL
Column	HP5 (30m x 320µm x 0.25µm)
Inlet mode	Split-less
Initial temperature	60°C Hold 1min
Ramp rate 1	12°C increase to 210°C
Ramp rate 2	8°C increase to 320°C (final temp.), Hold 5mins
Total run time	32.25mins
Detector temperature	325°C

III. Results And Discussion

3.1 Mean concentrations of PAHs at various locations

A summary of analytical results of the PAHs in water samples from Ile-Oluji, Nigeria is presented in Table 2. The total mean concentrations of PAHs in the four different water samples A, B, C and D varied between 29.0 – 35.7 ng/µL, which are far greater than that in the control (0.12 ng/µL). They are widely distributed in all the sampling locations except in the control, suggesting that the origin of the PAHs is probably from non-point sources such as runoffs or industrial effluents resulting from factors such as land use, climate, hydrology, topography, native vegetation, and geology [37]. The maximum concentration limits for PAHs set by the European Community and United States Environmental Protection Agency is presented in Table 3. The 2 and 3 member rings PAHs comprising: naphthalene, phenanthrene, acenaphthylene, acenaphthene and fluorene constitute larger concentrations ranging between 1.59 – 11.3 ng/µL, and amounting to about 95% of the total PAHs in the four different water samples. This group of PAHs could be treated with water via exposure to sunlight, biodegradation using microorganisms [34]. Benzo (k) fluoranthene, benzo (b) anthracene, dibenzo (a, h) anthracene and indeno (1, 2, 3 – cd) pyrene were below detection limits in all the samples analyzed. In this study, there was no correlation between the catchment samples and control. Un-combustion PAHs sources (e.g. Oil seeps and petroleum spills) contain predominantly two- and three- ring compounds whereas combustion sources (e.g. Automobiles, domestic heating with coal, forest fires, etc.) result in predominantly four to six rings species [38]. The two and three ring compounds detected in all the samples were at higher concentrations. Eisler [39] in Alani *et al.* [18] states that many PAHs such as naphthalene and phenanthrene are severely toxic and deleterious at concentrations above 50,000 ng/µL (i.e. 50 µg/µL). A manifestation of its toxicity shows at concentrations of 100 – 5000 ng/µL. Studies have shown that the most likely sources of such low molecular weight PAHs are petrogenic, from spillages of petroleum products and human activities around the well water samples. The mean concentrations of 2-3 rings PAHs were relatively higher in all the investigated samples; acenaphthene (10.4 – 11.3 ng/µl) was the most predominant at location D. For instance, previous reports have shown that in a petroleum spillage containing about 25% aromatic hydrocarbon content, there is likely contamination (at percent levels) with more of 2 and 3 rings PAHs [34, 40]. In this study, the cumulative mean concentrations in samples A to D of the four and five rings PAHs being < 2.12 µg/µL were relatively lower than for the 2 and 3 rings PAHs which ranged from 27.2 – 33.5 µg/µL (Table 4). The 6- rings PAHs were not detected in all samples collected.

Table 2: A summary of analytical results of the PAHs in water samples from Ile Oluji, Nigeria

PAHs	Mol. Wt. (g/mol)	No. of rings	A (ng/μl)	B (ng/μl)	C (ng/μl)	D (ng/μl)	Control (ng/μl)	Mean	SD	CV
Nap	128	2	10.1	8.62	9.08	9.92	0.00	9.44	0.71	7.48
Acy	152	3	6.64	4.04	6.22	7.08	0.01	6.00	1.35	22.5
Ace	154	3	10.4	10.8	10.6	11.3	0.03	10.8	0.38	3.49
Fl	166	3	1.59	3.21	4.20	4.50	ND	3.38	1.31	38.9
Phe	178	3	0.42	0.38	0.50	0.56	ND	0.46	0.08	17.4
Ant	178	3	0.13	0.16	0.21	0.22	ND	0.18	0.04	23.2
Flu	202	4	0.30	0.69	0.25	0.81	0.07	0.51	0.28	55.2
Pyr	202	4	0.54	0.52	0.56	0.61	ND	0.56	0.04	7.03
BaA	228	4	0.38	0.20	0.19	0.22	ND	0.25	0.09	35.9
Chy	228	4	0.21	0.19	0.19	0.21	ND	0.20	0.01	5.32
BbF	252	5	0.14	0.14	0.15	0.16	ND	0.14	0.01	6.23
BkF	252	5	ND	ND	ND	ND	ND	ND	ND	ND
BaP	252	5	0.10	ND	0.10	0.11	ND	0.10	0.00	4.31
DahA	276	6	ND	ND	ND	ND	ND	ND	ND	ND
IcdP	276	6	ND	ND	ND	ND	ND	ND	ND	ND
BghiP	276	6	ND	ND	ND	ND	ND	ND	ND	ND
Σ PAH			31.0	29.0	32.2	35.7	0.12	31.9	2.81	8.81

ND: Not detectable

The European Community (EC) [41] and United States Environmental Protection Agency (USEPA) [19] Standards for some PAHs in drinking water are presented in Table 3.

Table 3: PAHs standards in drinking water [18]

PAHs	MCL in μg/μL (EC)	MCL in μg/μL (USEPA)
Naphthalene	-	-
Acenaphthylene	-	-
Acenaphthene	-	-
Fluorene	-	0.0002
Phenanthrene	-	0.0002
Anthracene	-	0.0002
Fluoranthene	0.00003	-
Pyrene	-	0.0002
Benzo (a)anthracene	-	0.0002
Chrysene	-	0.0002
Benzo (b)fluoranthene	0.00003	0.0002
Benzo (k)fluoranthene	0.00003	0.0002
Benzo (a) pyrene	0.00001	0.0002
Indeno(1,2,3-cd)pyrene	0.00003	0.0002
Dibenzo(a,h)anthracene	-	0.0002
Benzo (g,h,i) perylene	0.00003	-

MCL – Maximum contaminant level, EC – European Community, USEPA – United States Environmental Protection Agency

Tables 3 confirms that the PAH levels in underground water under this study were far above the MCLs set by United States Environmental Protection Agency (USEPA) [19] and the European Community (EC) [41] member states for maximum contaminant levels in drinking water. In most cases, the values obtained in this work were about 100 to 1000 times higher than the set standards.

Table 4: Classification of detected PAHs in the water samples from Ile Oluji, Nigeria

Samples	Total PAHs (ng/μl)	2 – 3 rings (LMW)		4 – 6 rings (HMW)	
		Conc. In (ng/μl)	%	Conc. In (ng/μl)	%
A	31.0	29.3	95	1.66	5
B	29.0	27.2	94	1.74	6
C	32.2	30.8	96	1.43	4
D	35.7	33.5	94	2.12	6
Control	0.12	0.05	41	0.07	59

The mean concentration of the higher molecular weight (HMW) aromatic hydrocarbon, benzo (a) pyrene (BaP) (0.01±0.00 ng/μl) resulting from samples A, C and D is much higher than the USEPA and EC maximum allowable limits (0.00001 ng/μL) except for sample B and control sample where it is not detectable. BaP is amongst the most toxic PAH compounds, causing deleterious effects on human health. Reports have shown that benzo (a) pyrene is the most widely investigated among the PAHs, as it poses a relatively stronger carcinogenic effect to laboratory animals and man [34, 42]. Figure 3 shows graphical representation of BaP at

each location. While the concentrations of BaP in the control sample and Sample B were below detection limit, signifying insignificant pollution, the concentrations of BaP in samples A, C and D ranged from 0.10 – 0.11 ng/μl (Table 2). This is very dangerous because of the possible bioaccumulation in humans over long period, which could lead to cancer.

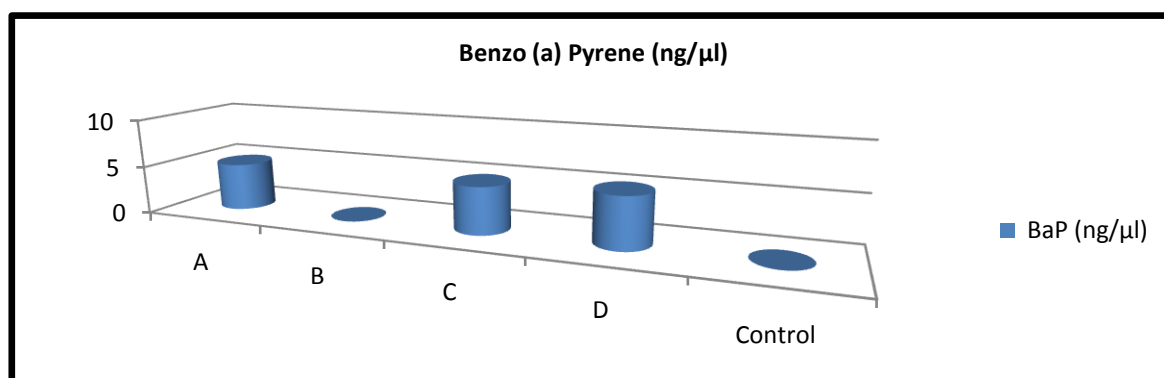


Figure 3: Benzo (a) pyrene distribution in water samples from Ile Oluji, Nigeria

Further studies [43, 44] have shown that benzo (a) pyrene (BaP) do accumulate to potentially hazardous levels in fish and invertebrates. The various forms of BaP intermediates such as diol and phenol epoxides were reported to concentrate mutagenesis and carcinogenesis of mammals [18].

PAHs concentrations previously reported in literature on different water samples were compared to the present data as shown in Table 5. The levels of PAHs in this study were higher than the values reported in studies around the world. This result is a re-affirmation of other studies in Nigeria that showed occurrence of PAHs in most potable water sources [34, 45, 46]. Therefore regular checks and control measures should be intensified to remediate the overwhelming effects for future generations to come.

The higher values of PAHs obtained in this study compared to previous publications (Table 5) could be due to the following factors apart from the proximity or remoteness to the gasoline filling stations.

Table 5: Comparison of mean concentrations of PAHs in Ile Oluji water samples with similar studies in other parts of the world

Study	Location	Mean concentrations of PAHs	Comment
Present study	Ile-Oluji hand dug wells close to filling stations, Ondo State, Nigeria (Samples A to D)	31.9±2.81 (ng/μL)	Highly contaminated due to proximity and anthropogenic influence.
		31900 (μg/L).	
Present study	Ile-Oluji hand dug well remote to filling stations, Ondo State, Nigeria (Control sample)	0.12 (ng/μL)	Values are lower by about 1000 times compared to those from wells very close to gasoline stations. However, the value is still higher by 10 - 100 times compared to other results below.
		120 (μg/L).	
Adedayo <i>et al.</i> [34]	Lagos lagoon, Nigeria	ND – 5.73(μg/L)	Present study was relatively much higher being about 1000 times higher than the control and 10 ⁶ times for the catchment samples.
		ND – 0.00573 (ng/μL)	
Adeboyejo <i>et al.</i> [45]	Previous studies – water samples of Lagos lagoon	ND – 3.73(μg/L)	Present study was relatively much higher being about 1500 times higher for the control and 10 ⁵ times for the catchment samples.
		ND – 0.00373 (ng/μL)	
Olajire <i>et al.</i> [46]	Water samples – Agbabu bitumen field, South-western, Nigeria	11.2 – 341.5(μg/L)	Present study was relatively much higher being about 10 orders for the control and 10 ³ orders for the catchment samples.
		0.0112 – 0.3415 (ng/μL)	
Kabziński <i>et al.</i> [47]	Łódź river, Poland YY	0 – 9.185(μg/L)	Present study was relatively much higher being about 100 orders for the control and 10 ⁵ orders for the catchment samples.
		0 – 0.009185(ng/μL)	
Karlsson <i>et al.</i> [48]	Water samples – Gully Pots, Northern Sweden	0.09 - 183(μg/L)	Present study was relatively much higher being about 10 orders for the control and 10 ³ orders for the catchment samples.
		0.0009 – 0.183 (ng/μL)	
European Community [41]		0.01 μg/L for BaP (a strongly carcinogenic PAHs)	Present study is > by over 100 orders, which far exceeded EU regulatory limit for BaP.

(a) Since the water in the well is virtually stagnant, any PAH introduced into the water body does not have much dilution effect compared to other samples taken from lagoons and rivers that had undergone series of dilution over time.

- (b) The types of rubber and plastic fetchers being used for drawing water could also be a source by which PAHs enter the well water.
- (c) Recently, personal observations on a sunny day revealed a thin film of greasy organic layer at the wells water surface. This layer might have resulted from seepage of petroleum products and could be responsible for the observed alarming results.

IV. Conclusion

Contamination of water due to PAHs is becoming a major public health challenge in Nigeria. This study has revealed that domestic water in some selected locations in Ile-Oluji is not relatively safe and fit for consumption as the level of PAHs was alarming. Furthermore, the levels of PAHs in the samples are quite higher than the acceptable ranges. The major source of the detected PAHs can easily be traced to anthropogenic activities in the neighbourhood of the gasoline filling stations leading to contaminated groundwater. Locations A, C and D contain reasonable concentrations of carcinogens like benzo (a) pyrene at levels that could pose a risk to the environment. The work established levels of the PAHs contaminants investigated water samples from hand dug wells in the locations. The presence of these potentially toxic substances provide a legitimate basis for initial concern and call for a more detailed periodical assessment of PAHs of the locations. There is need for regular monitoring of groundwater in Ile-Oluji, Nigeria to minimize possible contamination and the health risks. This measure will partly help towards the attainment of the European Union, United States Environmental Protection Agency and United Nations Millennium Development Goal objectives by ensuring the quality and safety of potable water to the populace.

References

- [1]. R. Fehr, O. Mekel, M. Lacombe, and U. Wolf, Towards health impact assessment of drinking-water privatization-the example of waterborne carcinogens in North Rhine-Westphalia Germany). B. World Health Organization 81(6), 2003, 408–414.
- [2]. D. Berryman, F. Houde, C. DeBlois, and M. O'Shea, Nonylphenolic compounds in drinking and surface waters downstream of treated textile and pulp and paper effluents: a survey and preliminary assessment of their potential effects on public health and aquatic life. *Chemosphere*, 56(3), 2004, 247-255.
- [3]. S. Dobaradaran, A. H. Mahvi, R. Nabizadeh, A. Mesdaghinia, K. Naddafi, M. Yunesian, N. Rastkari, and S. Nazmara, Hazardous organic compounds in groundwater near Tehran automobile industry. *Bull Environ. Contam. Toxicology*, 85(5), 2010, 530–533.
- [4]. H. Karyab, A. H. Mahvi, S. Nazmara, and A. Bahojb, Determination of water sources contamination to diazinon and Malathion and spatial pollution patterns in Qazvin, Iran. *Bull Environ. Contam. Toxicol.*, 90(1), 2012, 126-131.
- [5]. A. J. Jafari, R. P. Abasabad, and A. Salehzadeh, Endocrine disrupting contaminants in water resources and sewage in Hamadan City of Iran. *Iran J. Environ. Health Sci. Eng.*, 6(2), 2009, 89–96.
- [6]. K. Sexton, J. J. Sahmas, T. J. MacDonald, R. M. Z. Gowen, R. P. Miller, J. B. McCormick, and S. P. Fisher-Hosh, PAHs in Maternal Umbilical cord blood from pregnant Hispanic women living in Brownsville, Texas. *International Journal Environmental Research and Public Health*, 8(8), 2011, 3365–3379.
- [7]. D. Mackay, W. Y. Shiu, K. C. Ma, and S. C. Lee, Handbook of Environmental Physical-Chemical Properties and Environmental Fate for Organic Chemicals. 2nd edition: CRC Press, Taylor and Francis Group, Boca Raton, Florida, 2006.
- [8]. R. O. Akinyeye, Nanostructured polypyrrole impedimetric sensors for anthropogenic organic pollutants. Ph.D. Thesis, University of the Western Cape, Bellville, South Africa. 2007, 67-72.
- [9]. L. Zoccolillo, D. Babi, and M. Felli, Evaluation of polycyclic aromatic hydrocarbons in gasoline by HPLC and GC-MS. *Chromatographia*, 52, 373-376.
- [10]. K. D. Bartle, C. Creaser, and R. Purchase, Food contaminants, sources and surveillance, The Royal Society of Chemistry, Cambridge, 1991, 41.
- [11]. C. Anyakora A. Ogebeche P. Palmer, H. Coker, G. Ukpo, and C. Ogah, GC-MS analysis of polynuclear aromatic hydrocarbons in sediment samples from the Niger Delta Region, *Chemosphere*, 60(7), 2005, 990-997.
- [12]. J. Davis, PAHs in Estuary. Regional Monitoring News, San Francisco Estuary Institute, 2(2), 2003, 1-20.
- [13]. J. Hellou, S. Steller, V. Zitko, J. Leonard, T. King, T. G. Milligan, and P. Yeats, Distribution of PACs in surficial sediments and bioavailability to mussels, *Mytilus edulis* of Halifax Harbour, *Marine Environmental Research*, 53, 2002, 357–379.
- [14]. D. Delistraty, Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. *Toxicol. Environ. Chem.*, 64, 1997, 81–108.
- [15]. K. Schirmer, A. G. L. Chan, B. M. Greenberg, D. G. Dixon, and N. C. Bols, Ability of PAHs to be Cytotoxic to a cell line from the rainbow trout gill, *Toxicology*, 127, 1998a, 143–155.
- [16]. K. Schirmer, A. G. L. Chan, B. M. Greenberg, D. G. Dixon, and N. C. Bols, Ability of 16 priority PAHs to be directly cytotoxic to a cell line from the rainbow trout gill. *Toxicology*, 127, 1998b, 129–141.
- [17]. R. C. Swartz, D. W. Chultz, R. J. Ozretich, J. O. Lamberson, F. A. Cole, T. H. Dewitt, M. S. Redmond, and S. P. Ferraro, PAH: A model to predict the toxicity of polynuclear aromatic hydrocarbon mixtures in field collected sediments. *Environ. Toxicol. Chem.*, 11, 1995, 1567–1581.
- [18]. R. Alani, K. Olayinka, and B. Alo, Studies on persistent organic pollutants (POPs) in the Lagos lagoon: Occurrence and levels of polycyclic aromatic hydrocarbons (PAHs) in surface waters of the lagoon, *Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS)*, 4(6), 2013, 811-818.
- [19]. USEPA, Polycyclic Organic Matter. Washington, DC: Environmental Protection Agency, 2002. <http://www.epa.gov/ttn/atw/hlthef/polycycl.html>, accessed 4th September, 2015.
- [20]. I. Martorell, G. Perelló, R. Martí-Cid, V. Castell, J. M. Llobet, and J. L. Domingo, Polycyclic aromatic hydrocarbons (PAH) in foods and estimated PAH intake by the population of Catalonia, Spain: temporal trend. *Environ Int. J.*, 36(5), 2010, 424–432.
- [21]. F. Halek, G. H. Nabi, H. Ganjidoust, M. Keyanpour, and M. Mirmohammadi, Particulate polycyclic aromatic hydrocarbons in urban air of Tehran, *Iran J. Environ. Health Sci. Eng.*, 3(3), 2006, 247–254.
- [22]. B. Maliszewska-Kordybach, B. Smreczak, and A. Klimkowicz-Pawlas, Concentrations, sources and spatial distribution of individual polycyclic aromatic hydrocarbons (PAHs) in agricultural soils in the Eastern part of the EU: Poland as a case study. *Sci.*

- Total Environ*, 407(12), 2009, 3746–3753.
- [23]. G. Perra, K. Pozo, C. Guerranti, D. Lazzeri, V. Volpi, S. Corsolini, and S. Focardi, Levels and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) in superficial sediment from 15 Italian marine protected areas (MPA). *Mar Pollut Bull*, 62(4), 2011, 874–877.
- [24]. D. Lorenzi, J. A. Entwistle, M. Cave, and J. R. Dean, Determination of polycyclic aromatic hydrocarbons in urban street dust: implications for human health, *Chemosphere*, 83(7), 2011, 970–977.
- [25]. M. A. Olivella, Polycyclic aromatic hydrocarbons in rainwater and surface waters of Lake Maggiore, a subalpine lake in Northern Italy. *Chemosphere*, 63(1), 2006, 116–131.
- [26]. A. Mahvi, and G. Mardani, Determination of phenanthrene in urban runoff of Tehran, capital of Iran. *Iran J. Environ. Health Sci. Eng.*, 2, 2005, 5–11.
- [27]. J. Prycek, M. Ciganek, and Z. Srinek, Clean up of extracts for nitrated derivatives of polycyclic aromatic hydrocarbons analysis prior their gas chromatography determination” *Journal Brazilian Chemical Society*, 18, 2007, 1125–1131.
- [28]. E. O. Fagbote, and E. O. Olanipekun, Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in soils of Agbabu, Nigeria: first Annual International Interdisciplinary Conference, *AiIC*, 24–26 April, Azores, Portugal, 2013.
- [29]. J. Simon, and J. Sobieraj, Contributions of common sources of polycyclic aromatic hydrocarbons to soil contamination, *Remed. J.* 16, 2006, 25–35.
- [30]. C. Anyakora, H. Coker, K. Ogebeche, G. Ukpo, and C. Ogah, Hydrocarbon accumulation in fish as an index for level of hydrocarbon pollution, *Journal of Pharmaceutical Science and Pharmacy Practice*, 8(1-2), 2006, 40–44.
- [31]. M. Gómez-Guillén, J. Gómez-Estaca, B. Giménez, and P. Montero, Alternative fish species for cold-smoking process. *Int. J. Food Sci. Tech.*, 44, 2009, 1525-1535.
- [32]. O. Ajiboye, A. Yakubu, and T. Adams, A review of polycyclic aromatic hydrocarbons and heavy metals contamination of fish from fish farms, *J. Appl. Sci. Environ. Manag.*, 15(1), 2001, 235–238.
- [33]. J. Gómez-Estaca, M. Gómez-Guillén, P. Montero, P. Sopelana, and M. Guillén, Oxidative stability, volatile components and polycyclic aromatic hydrocarbons of cold-smoked sardine (*Sardina pilchardus*) and dolphin fish (*Coryphaena hippurus*), *Int. J. Food Sci. Tech.*, 44, 2011, 1517-24.
- [34]. A. Adedayo, D. Adeyemi, J. P. Uyimandu, C. S. Samuel, and C. Anyakora, Evaluation of the levels of polycyclic aromatic hydrocarbons in surface and bottom waters of Lagos lagoon, Nigeria. *AJPSP* 3(1), 2012, 58–74.
- [35]. EPA 3510C, Micro-methods for the extraction of water and waste water, American Environmental Protection Agency, USA. 2001.
- [36]. Interim Guinea Current Commission (IGCC), Shipboard Training Manual for Shipboard Coastal and Marine Oceanographic Surveys and Associated Laboratory Work, 2011. UNIDO/UNDP/UNEP/GEF/ NOAA/NEPAD/NIOMR
- [37]. J. K. Olayemi, Food security in Nigeria. Research Report No. 2, Development Policy Centre Ibadan, Nigeria, 1998, 1-85.
- [38]. P. C. Van-Metre, B. J. Manler, and E. T. Furlong, Urban Sprawl Leaves its PAH Signature. *Environ. Sci. Technol.*, 34, 2000, 4064-4070.
- [39]. R. Eisler, Polycyclic aromatic hydrocarbon hazards to Fish, Wildlife, and Invertebrates: A synoptic Review. US. Fish and Wildlife Service Biological Report, 85(1-11), 1987, 81.
- [40]. H. Mi, W. Lee, J. Chen, C. Yang, and S. Wu, Effect of fuel aromatic content on PAHs emission from a heavy-duty diesel engine, *Chemosphere*, 41, 2000, 1783–1790.
- [41]. European Communities, (EC), The quality of water intended for human consumption, *Official Journal of the European Communities. Council Directive 98/83/EC*, 1998. http://www.fsai.ie/uploadedFiles/Legislation/Food_Legislation_Links/Water/EU_Directive_98_83_EC.pdf
- [42]. K. Anderson, F. Kadlubar, and M. Kulldorff, Dietary intake of heterocyclic amines and benzo(a) pyrene: Associated with pancreatic cancer, *Canc. Epidemiol. Biomarkers Prev.*, 14, 2005, 2261–2265.
- [43]. P. Y. Lu, R. L. Metcalf, N. Plummer, and D. Mandrel, The environmental fate of three carcinogens, benzo(a)pyrene, benzidine, and vinyl chloride evaluated in laboratory model ecosystems. *Arch. Environ. Contam. Toxicol.*, 6, 1977, 129-142.
- [44]. U. Varanasi, D. J. Gmur, and W. L. Rechert, Effect of environmental temperature on naphthalene metabolism by juvenile starry flounder (*platichthys sllalatus*). *Arch. Environ. Chem. Contam. Toxicol.* 10, 1981, 203-214.
- [45]. O. Adebeyejo, E. Clarke, and M. Olarinmoye, Organochlorine pesticide residues in water, sediments, fin and shellfish samples from Lagos lagoon complex, Nigeria. *Researcher* 3(3), 2011, 38-45.
- [46]. A. Olajire, A. Alade, A. Adeniyi, and O. Olabemiwo, Distribution of polycyclic aromatic hydrocarbons in surface soils and water from the vicinity of Agbabu bitumen field of South-western Nigeria. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 42(8), 2007, 1043-1049.
- [47]. K. Kabziński, J. Cyran, and R. Juszcak, Determination of Polycyclic aromatic hydrocarbons in Water (Including Drinking Water) of Łódź, *Pol. J. Environ. Stud.* 11(6), 2002, 695-706.
- [48]. K. Karlsson, and N. Maria, Polycyclic aromatic hydrocarbons (PAH) in Water and Sediment from Gully Pots. *Water air soil pollut.*, 18(8), 2008, 271–282.