Pollution status and Fate Prediction of Dominant Polychlorinated Biphenyl (PCBs) Congeners in Major Dumpsites Around Warri Metropolis

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Abstract - *PCBs are synthetic compounds serving as additives for many industrial processes. Bioaccumulation and biomagnification properties of PCBs have resulted in significant adverse health effect and loss of aquatic life. For contaminants to cause environmental deterioration, they must exist within the different matrices of the environment. The aim of this study was to determine the concentration of PCBs in soil and predict its fate in the different matrix of the environment. Soil samples were taken from five (5) major dumpsites in Warri metropolis and PCBs were extracted following standard procedures. The results show that dumpsites do not differ significantly in the concentration of PCBs, with dumpsite history playing a significant role in determining the dominant congeners. In addition, PCBs levels in the sites posed no threat, as PCB concentrations at all locations were below the regulatory limits set by other countries. Despite the low concentrations, humans could still be exposed via inhalations, and these contaminants could still leach into the ground water table. The major recommendations were for waste categorisations to be carried out before waste incinerations at the dumpsites and regular monitoring should be carried out on this location because of the proximity to residential areas.*

1. Introduction

Polychlorinated biphenyls (PCBs) are synthetic stable compounds with many industrial applications, e.g. as additives in insulation materials, dye making, rubber and plastic production, added to components used in hydraulic machines [1]. Over 200 congeners exist, and they are based on the number of chlorines present [2]. Despite the industrial benefits for the applications of PCBs, their persistence and accumulative properties pose significant threat to the earth's biota [3]. PCBs are highly lipophilic; hence, they tend to bioaccumulate over an organism's lifespan. This property is important to both human and ecology toxicology, as bioaccumulation leads to biomagnification, the process by which persistent toxins increase in concentration through the food chain [4]. In most countries, there are restrictions on the use of PCBs in manufacturing processes, but studies show that 1.5 million tons were already in use and an estimate of more than 10% have already been introduced into the environment [5]. According to Reddy et al [1], leaks from transformers and waste incineration

are sources of PCBs in the environment. With regards to waste management in Nigeria, open incineration is the major way of addressing waste at disposal sites [6].

The different physical and chemical properties of the individual congeners determine their behavior during those various dynamic processes [7]. As a result, identifying the specific environmental characteristics of PCB in contaminated sediments is challenging. PCBs are classified as endocrine disrupters because of their ability to mimic hormones and activate, deactivate and even damage receptors that modulate and control cellular and body systems [8]. The specific receptor accepted varies based on congeners involved and these multiple mechanisms of action result in a wide range of possible human and environmental effects. Increased concentrations of PCBs in surface soils significantly correlates with the concentration in aquatic organisms [3]. In order to understand the fate of contaminants in the environment, the adsorption coefficients should always be considered. Reports by the IARC [2], notes that the congeners of PCBs have different partitioning coefficients. The exposure route for PCBs to humans is via inhalation, ingestion, and direct contact [9]. Based on our current search, there are limited studies carried out to determine the congeners of PCBs from dumpsites in Nigeria. The study looks to address this drawback, also determining the fate of these congeners and predicting their toxicity.

There main objectives of this paper were to:

1. Compare the concentrations across the different dumpsite and determine the dominant congener in relation to the type of refuse
2. To determine the dominant PCB congeners in Delta state
3. Predict the fate of PCBs in soils of the dumpsite
4. Determine if concentrations are above soil guideline values
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2. Materials and Methods
2. 1. Sample Collection
A total of fifteen (15) aproox.0.5 kg samples were collected from five (5) major dump sites around warri metropolis, South of Nigeria (Figure 1). Field survey of all sites records that similar materials were disposed for all locations. These included: plastics, ceramics, food waste and electronics. The waste was collected and transported to these dumpsites by the PSP; (Private Sector Partnership) collection trucks. Sample collections were done for soil samples [6]. Samples were stored in clean glass containers.
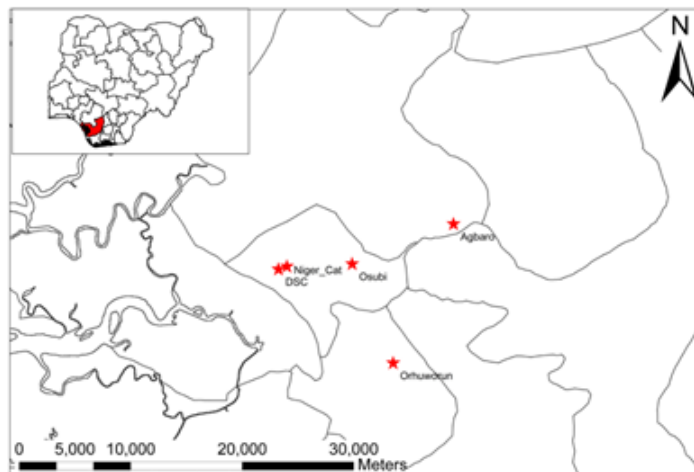

Figure 1. Map showing the sampling location points.

2. 2. Sample Extraction Process
Samples were homogenised and then placed on a filter paper and air dried for 24hrs using an oven supplied by Pratham Engineering, India. 10 g of samples were weighed using a weighing balance (Mettler Toledo, Switzerland) and then introduced into a 500 ml Duran glass container with a seal [10]. Added to this was 10 g of sodium sulphate used as a drying agent. Then, 50 grams of the solvent mixture of Cyclohexane and Acetone (1:1 mix) used for extraction is then added. All Solvents were supplied by Fisher Scientific. The mixed samples were then placed in an ultrasonic bath (Edutek Instrumentation, India) for 20 minutes and then was transferred to a shaking machine where extraction lasted for two hours. After one hour of extraction, an aliquot of the extract was taken and added to 1 ml ISTD-Solution (2.5μl 1, 11-Dibromundecane in 250ml Cyclohexane) before being concentrated to 1ml [11].

2. 3. Clean up of glassware and reagent
Exhaustive cleanup of reagents and glassware were carried out to eliminate background signals that

are not derived from samples. Glassware were scrupulously cleaned. All glass wares were cleaned as soon as possible after use by thoroughly rinsing with the last solvent used followed by washing with hot water and detergent and thoroughly rinsed with tap and reagent water. The use of high purity reagent helped to minimize interference observed during the analysis of PCBs. Purification of solvents by distillation in all glass systems was also done.

2.4. GC Analytical Method

The sample extract dissolved in 1ml hexane extract was injected (1μl) split-splitless into a gas chromatographic system at 200℃ (GC6000, Vega Series 2, Carlo Erba Instruments) with an electron capture detector attached (ECD 80/800, Fisons Instruments), operating at a constant flow of 3.3ml/min and temperature of 320 ℃.. The sample was carried through the column by helium gas, using nitrogen as the make-up gas. The GC system was fitted with a fused silica capillary column compose of 5% phenyl-substituted dimethylpolysiloxane phase of dimension 0.25 mm i.d. × 60 m, 0.25 μm film thickness (CP-Sil 8 CB Low Bleed/MS, Varian (1) or HP-5, Hewlett Packard (2). The oven temperature program was held isothermally at 90 ℃ for 1 min, then programmed at 40 °C·min^{-1} to 210 °C, held for 0.5 min, again programmed at 5.6 °C·min^{-1} (1) or 2.6 °C (2) to 230 °C, held for 10 min, next increased by 5.6 °C·min^{-1} (1) or 2.6 ℃ (2) to 275 °C and held for 20 min. The identification and determination of PCB concentration peaks was based on retention time comparisons and the individual peak areas in the sample chromatogram with peak retention times and areas of standards respectively. The chromatographically separated PCBs were detected and measured using ECD-detectors. The calibration of the analyte and the Surrogates was done using a linear or quadratic curve over the peak areas in ng/ml. The calibration was done with 1, 11-Dibromundecane as an internal standard (ISTD).

2.5. Quality Control

As a routine measure, spiking using surrogate recovery in each sample was used to get information on losses of analyte from the extraction step through to analysis. However, no single PCB can be a representative of all the PCBs being determined, and thus recovery correction was performed with caution. Blank correction was carried out for all samples using a robust method based on a blank known to be representative of a batch of samples. Bachema AG Laboratory Switzerland, where the analysis was carried out used an internally validated version of EPA 8082, with method LOQ (limit of quantification) of 0.005 mg/kg, with a method error margin of ±0.0004 mg/kg (12-24%). The values are means of two runs after extraction of samples using a GC-ECD. The following Potential errors could have arisen from biodegradation of PCB congeners, adsorption of analytes to the walls of glass vessels used during pretreatment and storage, influence of excess solvent evaporation and adsorption to extraction column. However, all these were kept to a minimum through following standard operating procedures.

2.6. Fate Prediction

Information about the partitioning coefficient values were obtained from literature searches on Google Scholar. Values obtained were for the octanol-water partitioning (K_{ow}), solubility (mg/L), organic carbon-water partitioning coefficient (K_{oc}), Vapour pressure (mmHg) and the Henry's Law constant (atm-m^3/mol). These values were fitted alongside the measured concentrations of PCBs on a Fugacity model to predict the distribution along the different environmental matrices at 0.5% organic matter content. This approach is similar to those adopted by Wang et al., [12] for contaminant fate prediction.

2.7. Statistical Analysis

Data computation, analysis and visualisation were done using Sigmaplot version 14.0. Firstly, Shapiro Wilk's normality tests were carried out for the data. Then a two-way ANOVA was done to study the location differences for both types of PCBs. Pearson correlations were carried out to determine the relationship between the PCB congeners. A one-sample t.test was employed to compare data with the standard regulatory limits. Statistical analysis was based on a 95% confidence level with level of significance summarised as p<0.05. The

data was summarized using a multiple bar chart showing mean and the standard deviation.

3. Results

The chemical properties of the PCBs are displayed in Table 1. PCB138 had higher Kow, Koc, vapour pressure, molecular mass and solubility than PCB101. However, Henry's law constant was lower than that for PCB101. When compared to the soil guideline values of America (5000 µg kg⁻¹), Canada (500 µg kg⁻¹), and New Zealand (220 µg kg⁻¹), the concentrations of PCBs (4.3 - 9.2 µg kg⁻¹) in the dumpsites are lower.

The fugacity model predicts that PCB138 would be dominant in the soil fraction (Soil -85%, water -15%, Air -0%). It also showed that a certain fraction would be transferred into groundwater. The PCB101 congener follows the same distribution, being dominant in the soil phase. However, its distribution was 80% in soil and 20% in water. The spread of both PCBs across the five dumpsites are displayed in Figure 2. In four of the locations, PCB101 was higher than PCB138. Osubi had the highest concentrations (9.2 µg Kg⁻¹) of PCB101 and the lowest was in DSC (5.06 µg Kg⁻¹). PCB138 was the highest at Agbarho, while DSC had the lowest concentrations. PCB101 has five chlorine atoms attached to it, while PCB138 has six. All other analysed PCBs were 28, 52, 118, 153 and 180. Apart from Agbarho, their concentrations in other sites were below the limit of detection. PCB52 had a concentration of 7.2 µg Kg⁻¹ in Agbarho. The most toxic PCBs, PCB126 and PCB169 based on TEF values (0.1 and 0.01 respectively) [13] were not quantified in this study. Contrary to studies done in India and Midway atoll, the dominant congeners were the higher chlorinated homologues. However, they are in line with the dominant global fraction, which are penta and hexa-chlorinated biphenyls. There was no significant correlation between the PCB101 and PCB138 across the dumpsites (Figure 3). A large proportion of the contaminants appear to be present in the 0.005 - 0.008 mg/kg range. The range of PCB101 in the soils was higher than that of PCB138. PCB101 had higher concentrations in general and had a greater variation

across the sites (Figure 3). The ΣPCB ranged from 0.007 to 0.021 mg/kg.
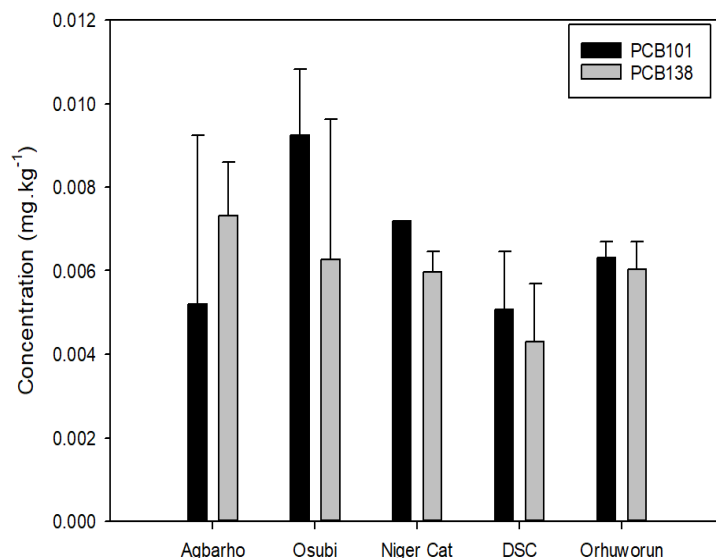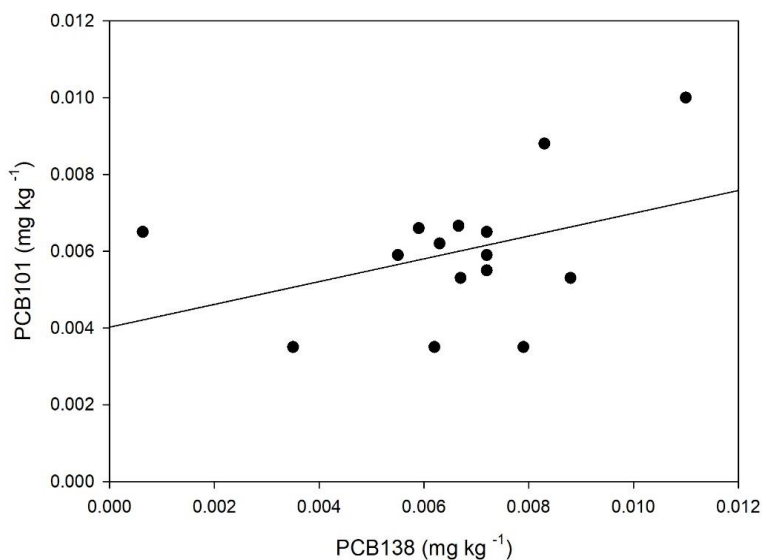

Figure 2. The concentrations of PCB101 and PCB138.

Figure 3. Correlation between the two PCB congener across the different dumpsites.

Table 1. Chemical Properties of the PCBs.

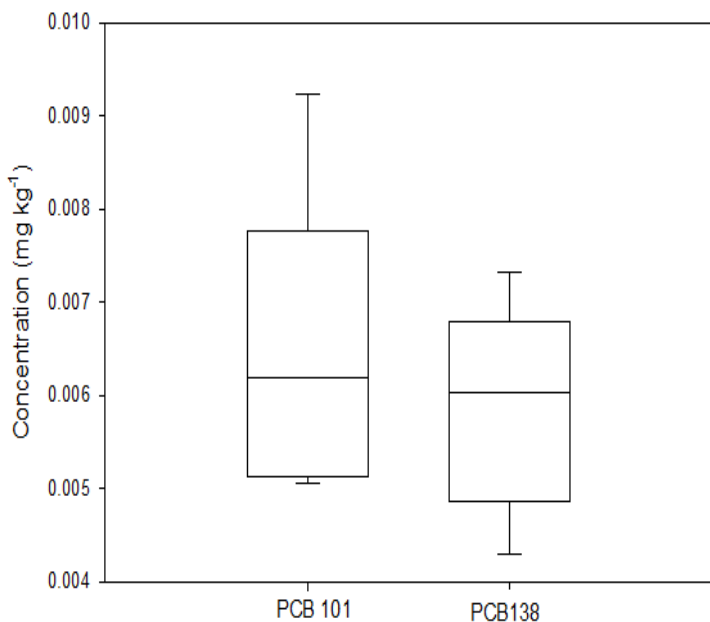| PCB	Log K_{ow}	Log K_{oc}	Vapour pressure (mmHg)	Molecular mass(g/mol)	Solubility (mg/L)	Henry Law constant (atm-m^3/mol)
101	6.38	2.23	2.52 e-05	326.4	0.0154	9 e-05
138	6.83	2.39	3.97	360.9	0.0159	2.1 e-05

Figure 4. Range of PCBs across the five sites.

5. Discussion

Due to the chemical properties of PCB138, it has a higher potential for bioaccumulation in human 'fatty' tissue. In general, these higher chlorinated congeners tend to sorb to soil more strongly and have longer half-lives [13]. However, in a study of a highly contaminated site, it was the lower PCBs (28 and 52) that were elevated in human blood [14]. This highlights the need to ascertain the blood levels of residents around the dumpsites. Of greater concern should be the infants of which PCBs have been shown to negatively affect their gonadal hormones [15]. Inhalation of the gaseous products of refuse combustion would inadvertently lead to higher PCBs levels in blood. Field investigations reveals that there are several residential buildings, schools and commercial facilities within the area of the dumpsites. Similar to the USA, PCB138 is the congener most frequently detected [13]. Our study shows that the present levels are well below the regulatory limit and should pose no immediate risk to potential receptors. This is consistent with other values present in other locations except in some locations in China and reflects the effectiveness of the chemical ban [16], [17]. It is also an indication that the majority of the refuse burnt do not contain PCBs reflecting the pattern of product-use by residents in the area. It infers that there is a reduced quantity of electrical devices, flame-retardants and paint additives. Waste characterization would therefore be a necessary process to integrate into the waste disposal scheme.

The study showed through the fugacity model that the compounds would be dominant in the soil phase. However, a significant portion is transferred into the interstitial pore water and eventually into the groundwater. As most households derive their drinking water from wells and borehole systems, there is a high risk of exposure through ingestion of contaminated water. Irrigation of vegetation with this water can lead to uptake by plants, and eventually by humans. However, PCBs generally show poor leachability in soil due to strong adsorption with organic matter [18]. The higher the organic carbon content the stronger the retention. Also, lower chlorine-containing congeners are more mobile as shown by the models [19]. Mobility and the availability of PCBs to biota is greatly reduced because of their hydrophobic nature, reactions during ageing processes, and the kinetic processes involved. However, it could be greatly increased by the presence of DOC in water [20]. Therefore, characterization of soil properties in each dumpsite is necessary.

Osubi is a relatively new dumpsite and this is reflected by the comparably higher concentration of the more volatile PCB101. Accumulation of the less volatile PCB138 is present in the oldest dumpsite, Agbarho. PCB101 was the dominant pollutant in the majority of the dumpsites indicating that it was the major constituent of the refuse. Although DSC contained the lowest concentrations of PCBs, the lack of significant difference makes it impossible to draw any conclusion. Further explanation of the low PCB concentration in all sites is that the burning of refuse causes the large proportion of the PCBs to be concentrated in Areas beyond the dumpsite through long-range transport. This suggests the need to measure PCBs in areas beyond the dumpsites. The PCBs, through processes such as volatilization, partitioning, chemical and biological transformation have altered their form in the environment. In a similar study in the Niger Delta, transformer oils showed higher PCB concentration of several orders of magnitude [21]. PCB170 and PCB180 were the dominant congeners. PCB101 had a greater range than PCB138 due to its higher mobility in soil. A Second reason could be due to its volatility. Temperature is another factor that plays a key role in PCB partitioning, tropical regions would potentially have lower soil concentrations of PCBs. The lack of correlation of the two congeners (Figure 3), could be due to the different quantities and types of refuse at these dumpsites. Due to their low values, we cannot conclude that any Aroclor is being used. When compared with concentrations of ΣPCB across the world, the values in this site were higher than places in Ethiopia, Ghana, Portugal and some places in India and China [16]. However, values in studies on US soils were higher than the values obtained in this study. A rough conclusion is that countries that manufacture PCBs would have a higher PCB concentration than those that do not.

5. Conclusion

The level of PCBs in the soil of five dumpsites in Delta state, Nigeria were evaluated. The results show that the level of PCBs in the soil were medium levels compared to soils in other countries. The correlation of

the two dominant PCBs were weak, reflecting the difference in refuse type. Since the values are well below soil guideline values, there is no need for remediation and potential receptors are safe. Based on these results, recommendation for further studies are as follows:

1. A complete soil analysis for documentation of physicochemical properties

2. Analysis of nearby soil and surface water for PCB content to confirm the long-range transport hypothesis

3. Study on the PCB concentrations of human blood of residents of these areas and ascertain correlation with PCBs

4. Waste characterization should be introduced in waste management

References
[1] A. V. B. Reddy, M. Moniruzzaman and T. M. Aminabhavi, "Polychlorinated biphenyls (PCBs) in the environment: Recent updates on sampling, pretreatment, cleanup technologies and their analysis," *Chemical Engineering Journal (Lausanne, Switzerland : 1996),* vol. 358, pp. 1186-1207, 2019. Available: https://search.datacite.org/works/10.1016/j.cej.2018.09.205. DOI: 10.1016/j.cej.2018.09.205.

[2] *International Agency for Research on Cancer Polychlorinated biphenyls and polybrominated biphenyls* . Available: https://monographs.iarc.fr/list-of-classifications-volumes/.

[3] A. H. Buckman *et al*, "Biotransformation of polychlorinated biphenyls (PCBs) and bioformation of hydroxylated PCBs in fish," *Aquatic Toxicology,* vol. 78, *(2),* pp. 176-185, 2006. Available: http://dx.doi.org/10.1016/j.aquatox.2006.02.033. DOI: 10.1016/j.aquatox.2006.02.033.

[4] R. S. Williams *et al*, "Juvenile harbor porpoises in the UK are exposed to a more neurotoxic mixture of polychlorinated biphenyls than adults," *Science of the Total Environment,* vol. 708, pp. 134835, 2020. Available: http://dx.doi.org/10.1016/j.scitotenv.2019.134835 . DOI: 10.1016/j.scitotenv.2019.134835.

[5] L. Wolska *et al*, "Sources and Fate of PAHs and PCBs in the Marine Environment," *Critical Reviews in Environmental Science and Technology,* vol. 42, *(11),*

pp. 1172-1189, 2012. Available: https://search.datacite.org/works/10.1080/10643389.2011.556546. DOI: 10.1080/10643389.2011.556546.

[6] O. Edjere and C. E. Stephen, "Preliminary Screening of Polybrominated Diphenyl Ethers (PBDEs); Decabromodiphenyl Ether (BDE-209) and Tetrabromobisphenol-A (TBBPA) Flame Retardants in Municipal Dumpsite in Delta State, Nigeria," *International Journal of Environment and Climate Change,* pp. 1-10, 2020. . DOI: 10.9734/ijecc/2020/v10i730208.

[7] C. Liu *et al*, "Polychlorinated biphenyls in the soil–crop–atmosphere system in e-waste dismantling areas in Taizhou: Concentrations, congener profiles, uptake, and translocation," *Environmental Pollution,* vol. 257, pp. 113622, 2020. Available: http://dx.doi.org/10.1016/j.envpol.2019.113622. DOI: 10.1016/j.envpol.2019.113622.

[8] B. Lauby-Secretan *et al*, "Body Fatness and Cancer — Viewpoint of the IARC Working Group," *The New England Journal of Medicine,* vol. 375, *(8),* pp. 794-798,2016. Available:https://search.datacite.org/works/10.1056/nejmsr1606602. DOI: 10.1056/nejmsr1606602.

[9] A. Naqvi *et al*, "Screening of human health risk to infants associated with the polychlorinated biphenyl (PCB) levels in human milk from Punjab Province, Pakistan," *Environmental Science and Pollution Research International,* vol. 27, *(7),* pp. 6837-6850, 2020.Available: https://www.ncbi.nlm.nih.gov/pubmed/31879876. DOI: 10.1007/s11356-019-07126-2.

[10] D. L. Stalling *et al*, "Patterns of PCDD, PCDF, and PCB contamination in Great Lakes fish and birds and their characterization by principal components analysis," *Chemosphere,* vol. 14, *(6),* pp. 627-643, 1985. Available: http://dx.doi.org/10.1016/0045-6535(85)90171-7. DOI: 10.1016/0045-6535(85)90171-7.

[11] O. Osibanjo and A. Adeyeye, "Organochlorine pesticide residues in cereals in Nigerian markets," *Bulletin of Environmental Contamination and Toxicology,* vol. 54, *(3),* pp. 460, 1995. Available: https://www.ncbi.nlm.nih.gov/pubmed/7538363. DOI: 10.1007/BF00195121.

[12] Y. Wang *et al*, "Fugacity modelling of the fate of micropollutants in aqueous systems — Uncertainty and sensitivity issues," *The Science of the Total Environment,* vol. 699, pp. 134249, 2020. Available: https://search.datacite.org/works/10.1016/j.scitotenv.2019.134249.DOI: 10.1016/j.scitotenv.2019.134249.

[13] O. Faroon and P. Ruiz, "Polychlorinated biphenyls," *Toxicology and Industrial Health,* vol. 32, *(11),* pp. 1825-1847, 2016. Available: https://journals.sagepub.com/doi/full/10.1177/0748233715587849. DOI: 10.1177/0748233715587849.

[14] M. Schwenk *et al*, "Human biomonitoring of polychlorinated biphenyls and polychlorinated dibenzodioxins and dibenzofuranes in teachers working in a PCB-contaminated school," *Chemosphere,* vol. 47, *(2),* pp. 229-233, 2002. Available: http://dx.doi.org/10.1016/S0045-6535(01)00307-1. DOI: 10.1016/S0045-6535(01)00307-1.

[15] Y. Cao *et al*, "Environmental exposure to dioxins and polychlorinated biphenyls reduce levels of gonadal hormones in newborns: Results from the Duisburg cohort study," *International Journal of Hygiene and Environmental Health,* vol. 211, *(1-2),* pp. 30-39, 2008. Available: https://search.datacite.org/works/10.1016/j.ijheh.2007.04.005. DOI: 10.1016/j.ijheh.2007.04.005.

[16] B. Kumar *et al*, "Polychlorinated biphenyls in residential soils and their health risk and hazard in an industrial city in India," *Journal of Public Health Research,* vol. 3, *(2),* pp. 252, 2014. Available: https://search.datacite.org/works/10.4081/jphr.2014.252. DOI: 10.4081/jphr.2014.252.

[17] J. Ge *et al*, "Distribution, Sources and Risk Assessment of Polychlorinated Biphenyls in Soils from the Midway Atoll, North Pacific Ocean," *PloS One,* vol. 8, *(8),* pp. e71521, 2013. Available: https://www.ncbi.nlm.nih.gov/pubmed/23951182. DOI: 10.1371/journal.pone.0071521.

[18] H. J. Strek and J. B. Weber, "Behaviour of polychlorinated biphenyls (PCBs) in soils and plants," *Environmental Pollution. Series A, Ecological and Biological,* vol. 28, *(4),* pp. 291-312, 1982. Available: http://dx.doi.org/10.1016/0143-1471(82)90146-5. DOI: 10.1016/0143-1471(82)90146-5.

[19] R. Haque, D. W. Schmedding and V. H. Freed, "Aqueous solubility, adsorption, and vapor behavior of polychlorinated biphenyl Aroclor 1254," *Environmental Science & Technology,* vol. 8, *(2),* pp. 139-142, 1974. Available:

http://dx.doi.org/10.1021/es60087a009. DOI: 10.1021/es60087a009.

[20] C. M. Vitale *et al*, "How good are the predictions of mobility of aged polychlorinated biphenyls (PCBs) in soil? Insights from a soil column experiment," *The Science of the Total Environment,* vol. 645, pp. 865-875, 2018. Available: https://search.datacite.org/works/10.1016/j.scitotenv.2018.07.216. DOI: 10.1016/j.scitotenv.2018.07.216.

[21] E. Aganbi, C. M. A. Iwegbue and B. S. Martincigh, "Concentrations and risks of polychlorinated biphenyls (PCBs) in transformer oils and the environment of a power plant in the Niger Delta, Nigeria," *Toxicology Reports,* vol. 6, pp. 933-939, 2019. Available: http://dx.doi.org/10.1016/j.toxrep.2019.08.008. DOI: 10.1016/j.toxrep.2019.08.008.