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EXTENT OF INDUSTRIAL ACCUMULATION OF POLY-SUBSTITUTED ORGANIC BIPHENYL POLLUTANTS IN SOIL, PLANT AND WATER BODIES IN AGBARA INDUSTRIAL AREA IN OGUN STATE NIGERIA

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ABSTRACT

The level of poly-substituted organic biphenyl pollutants in the surrounding soils, plant and water bodies in Agbara Industrial area has been investigated and results show that the concentration of poly-substituted biphenyls were highest in the sewage and amounted to over 1.80 µg/L and closely followed by the sample from the lagoon having over 1.60 µg/L. The concentrations of the pollutants in the drainages fall within 1.20 µg/L to 1.30 µg/L. These values however show that the drainages form the route of the pollutants from neighboring industries while the lagoon and sewage form the receptacles and storage facility where they accumulate. The action limit for PCBs in sewage is 0.005 mg/L or 5.0µg/L. This shows that the sewage has PCBs level up to 36 % of the action limit. The PCBs obtained in the soils had the initial sample exceeding 5.6 x 10^{2} µg/Kg or 0.56 mg/Kg amounting to 5.615 % of the action limit of 10 mg/Kg while the least sample had values exceeding 4.67 mg/Kg amounting to 4.7 % of the action limit.

The plant samples analyzed accordingly had high values of 2.53 x 10^{-1} ng/Kg and lower values 1.161 x 10^{-1} ng/Kg amounting to 7.44 % and 4.74 % respectively of the action limit of 3.40 ng/Kg.

KEYWORDS: *Biphenyls, pollutant, sewage, lagoon, effluent, organic, accumulation*

INTRODUCTION

Poly-substituted organic pollutants (biphenyls) are group of compounds in which more than two or three hydrogen atoms are replaced especially with halogens on the biphenyl rings. There exist chloro-, bromo- and fluoro- derivatives. Ultimately the prevalent class of man-made chemicals within this family is the popular polychlorinated derivatives which consist of more than 209 isomeric structurally related compounds consisting of two benzene rings and one to ten chlorine atoms; Greenfacts, (2006); Shen, Ding, Wu., Pan, Zhou, Han, Li and Wen (2012). Each single form of PCB is referred to as a congener and is often identified by a number (e.g. PCB 153). Their chemical formula is represented as $C_{12}H_{10-\chi}$ Cl $_{\chi}$.; Ballschmiter and Zell, (1980). Polychlorinated biphenyls PCBs in pure form are odourless or mildly aromatic solids or oily liquids often found in mixtures with other organic chemicals and they range from light oily fluids to heavier, greasy or waxy substances; US Environmental Protection Agency EPA, (1996). Commercial production of PCBs started in 1929 even though their use has been banned or severely restricted in many countries since the 1970s and 1980s because of the possible risks to human health and the environment. As PCBs are resistant to acids and bases, as well as to heat, they have been used as insulating materials in electrical equipment like transformers, capacitors etc. and also in heat transfer fluids, hydraulic fluids and in lubricants. PCBs have also been used in a wide range of products such as plasticizers, surface coatings, inks, adhesives, flame retardants, paints and micro encapsulation of dyes for carbonless duplicating papers; ASTDR, (2005); Greenfacts, (2006). They are also used in a variety of industrial applications like impregnation of wood and paper. They are often intentionally released into the atmosphere to reduce dust emission from dirty roads or as extenders in some herbicides and pesticides. Since 1929, over 2 million tons of PCBs have been produced and used in a variety of industrial applications until concerns over the adverse effects on health and environment resulted in a ban of PCBs manufacture by some countries and agencies. However, about 10% of PCBs still remain in the environment today as a result of continued usage. Greenfacts, (2006); Njoku, Eziukwu and Madu, (2008). It has been found that incineration of municipal waste often lead to PCB pollution; Njoku et al. (2008). These produce dangerous by-products such as hydrogen chloride and dioxins (PCDDs and PCDFs). They can also evaporate from contaminated water bodies and poorly maintained waste dumpsites; Lawton, Ross, Feingold and Brown, (1985). The vaporized PCBs eventually return to soil and water bodies by settling as dust or rain and snow. They may also be transported by currents attached to bottom sediments or particles in water and evaporate in air; Alcock, McGrath and Jones, (1995).

Bioaccumulations of PCBs in aquatic organisms depend on species, habitat and specific type of PCBs. As the concentration of PCBs in sediments is several times higher than in water, levels of PCBs are often high in bottom feeding species and they also generally bio-magnify along the food chain which leads to greater PCB concentration in organisms that are higher in the food chain. In the aquatic environment, concentrations will be greater in shell fish than in the planktons on which they feed and even greater in animals at the top of the food chain such as large predatory fish or mammals (Seals, Dolphins and Whales). On land, the bio-magnification occurs through the accumulation of PCBs from soil or plant leaves to worms or insects and finally to birds and mammals. The environmental pollution and impact assessment of PCBs to public health in Nairobi has been studied; Njoroge, (2007). Soil and water samples from Dandora and Korogocho rivers were analyzed to determine their contents and concentration of various elements including polychlorinated biphenyls and pesticides. The association of diet and body burden of dibenzo-p-dioxin and dibenzofurans and other dioxin-like PCBs has observed the exposure of pregnant women from central Taiwan to PCBs; Huang, Chao, Wang, Hung, Wang and Pan, 2007). The study was to examine the relationship between placental PCBs, PCDD/Fs and PCBs toxic equivalent TEQ levels and the consumption of various food types in pregnant women in central Taiwan. Placental PCDD/Fs and PCB congener TEQ levels were evaluated in 109 women and dietary information was obtained by questionnaire. Placental PCDD/Fs and PCB congener TEQ levels were relatively positive ($p < 0.005$) and were associated with freshwater fish and dairy products consumption after adjustment for age and body mass index (BMI).

Persistent organic pollutants, PCDD/Fs and PCB congener TEQ in health supplements in Spanish markets have been monitored as well; Marti, Ortiz, Gasser, Marti, Montaña and Diaz-Ferrero, (2010). A lot of the supplements used in recent times in foods contain oils (from fish, animals or vegetables) and due to the persistence and lipophilicity of PCDD/Fs and PCB congener TEQ, the tendency to bio-accumulate in fatty tissues which show low metabolic capability becomes critical. It was found that the consumption of nutritional supplements with oil

components can increase the intake of PCDD/Fs and PCB congener TEQ and other Persistent Organic Pollutants (POPs). Polychlorinated biphenyls (PCBs), dioxins and furans, PCDD/Fs and PCB congener TEQ as well as organo-chlorine pesticides in human blood of pregnant women in Germany have been studied; Wittsiepe, Schrey, Lemm, Eberwein and Wilheim, (2008). Levels of PCDD/Fs and PCB congener TEQ and persistent organic pollutants were in the range of 4.38 – 97.3 picogram (pg). It was seen that the parameters influencing the POP levels had to do with food and age. A cross-section of 55 transformer repair men was studied for sperm count with exposure to POPs; Emmett, Schmidth, Levin and Jefferys, (1988). The study found no association between exposure to PCBs and sperm counts. Studies and follow-ups have been conducted on 912 children born to women with background PCB body burdens; Rogan, Gladen, McKinney, Carreras, Hardy, Thullen, Tinglestad and Tully, (1987); Rogan and Gladen (1991); Gladen, Talor, Wu, Ragan and Hsu, (1990). Breast milk concentrations ranged from 0 to > 4.0mg/kg in milk fat at birth. Higher levels of PCBs in milk were associated with decreased muscle tone and hyper-reflexia for infants tested at day 3 or earlier. Dermal effects (irritation and sensitization), particularly chloracne and skin rashes has been associated with occupational exposure to Arachlors. Chloracne is a type of acne eruptions associated with some chlorinated organic chemicals. The survey on organochlorine pesticides, PCDD/Fs dioxin-like PCBs and HCBs in sediments from the Han River in Korea has been studied; Kyoung soo, Sang, Ki-Ho, Won Joon, Sang, Kyung, Jun and Jong-Guk, (2009). The principal source of HCB, DL-PCBs and PCDD/Fs was identified as deposition of waste s as well as commercial PCBs product like Kanechlor-500 and or Arochlor-1254. This work aims at the determination of persistent organic pollutants PCCD/Fs dioxin-like PCBs, Marker PCBs and PBDEs in Agbara industrial estate and environs. The evaluation of the health effects of congeners was based on the reviews of available relevant information while the areas chosen are believed to be heavily laden with industrial waste as well as being prone with frequent use of herbicides and pesticides.

MATERIALS AND METHODS

Soil samples were collected from 30 locations within the industrial estate. 10 samples were collected from effluents within the area. One from the lagoon, one from the sewage and eight from the drainage, 10 plant samples were collected randomly within the nearby environment of the residential estate were herbicides are in constant use while 10 soil samples were collected in the same residential estate where the plant samples were collected. Altogether, 30 samples were collected and analyzed for the congeners.

SAMPLE PREPARATION

A measured volume or weight of soil sample is extracted using the appropriate Matrix Specific Extraction Technique MSEP as in EPA method 1668A. Aqueous samples (samples containing < 1.0% solid) was extracted at neutral pH with methylene chloride using Continuous Liquid-Liquid Extraction (CLLE). Solid, semi-solid and multi-phase samples were extracted with a solution of 1: 1 hexane – acetone using automatic soxhlet extractor. Plant tissue samples were extracted using fluid extraction technique. The samples were mixed with anhydrous sodium sulphate, allowed to dry for 12 – 24 hours and extracted using methylene chloride in a soxhlet extractor. The extract was evaporated nearly to dryness and the lipid content analyzed. The same extraction technique for other solid matrices was appropriate for the tissue samples.

RESULTS

Analysis of PCBs and congeners in soil, water and plant tissues in the selected locations were carried out and the following results were obtained.

Water sample	1st PCBs mass conc. mg/L x 10^{-3}	2nd PCBs mass conc. mg/L x 10^{-3}	Average mass conc. mg/L x 10^{-3}	Average mass conc. µg/L
Agbara lagoon	1.604	1.614	1.609	1.609
Sewage	1.802	1.820	1.811	1.811
Drainage 1	1.202	1.226	1.214	1.214
Drainage 2	1.264	1.272	1.268	1.268
Drainage 3	1.312	1.320	1.316	1.316
Drainage 4	1.214	1.206	1.210	1.210
Drainage 5	1.256	1.258	1.257	1.257
Drainage 6	1.324	1.328	1.326	1.326
Drainage 7	1.304	1.312	1.308	1.308
Drainage 8	1.284	1.278	1.281	1.281

Table 1 Results of PCBs in water samples. Action Limit = 0.005 mg/L (FDA, 1992)

Water sample	1st PCBs mass conc. mg/Kg x 10^{-1} µg/Kg	2nd PCBs mass conc. mg/Kg x 10^{-1} µg/Kg	Average mass conc. mg/Kg x 10^{-1} µg/Kg	Average mass conc. x 10^{2} µg/Kg
Sample A	5.624	5.606	5.615	5.615
Sample B	4.804	4.802	4.803	4.803
Sample C	4.614	4.604	4.609	4.609
Sample D	5.320	5.300	5.310	5.310
Sample E	4.742	4.764	4.753	4.753
Sample F	5.514	5.520	5.517	5.517
Sample G	4.822	4.824	4.823	4.823
Sample H	5.424	5.460	5.442	5.442
Sample I	4.760	4.764	4.762	4.762
Sample J	5.234	5.242	5.238	5.238

Table 2 Results of PCBs in soil samples. Action Limit = 10.0 mg/kg (FDA, 1992)

Water sample	1st PCBs mass conc. mg/Kg x 10^{-7} mg/Kg	2nd PCBs mass conc. mg/Kg x 10^{-7} mg/Kg	Average mass conc. mg/Kg x 10^{-7} mg/Kg	Average mass conc. x 10^{-1} ng/Kg
Sample A	1.213	1.242	1.223	1.223
Sample B	2.022	2.101	2.062	2.062
Sample C	1.174	1.148	1.161	1.161
Sample D	1.268	1.283	1.276	1.276
Sample E	2.215	2.246	2.231	2.231
Sample F	2.412	2.642	2.527	2.527
Sample G	1.728	1.648	1.688	1.688
Sample H	1.614	1.646	1.630	1.630
Sample I	2.281	2.234	2.258	2.258
Sample J	1.648	1.872	1.760	1.760

Table 3 Results of PCBs in Plant samples. Action Limit = 3.40 ng/kg (FDA, 1992)

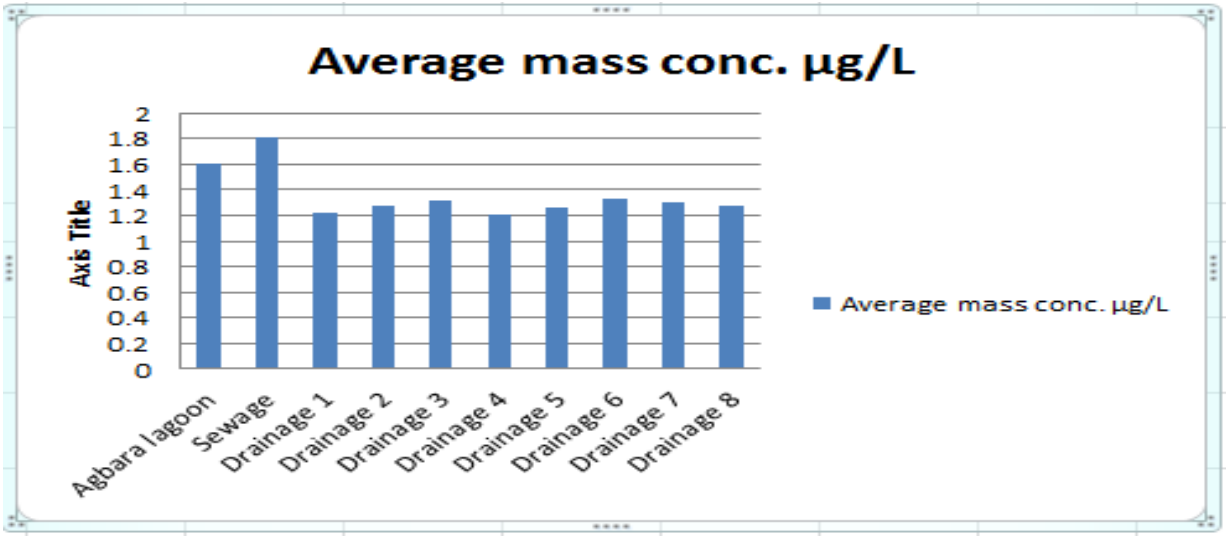

Fig 1 Histogram showing the results of PCBs in water samples. Action Limit = 0.005mg/L (FDA, 1992)

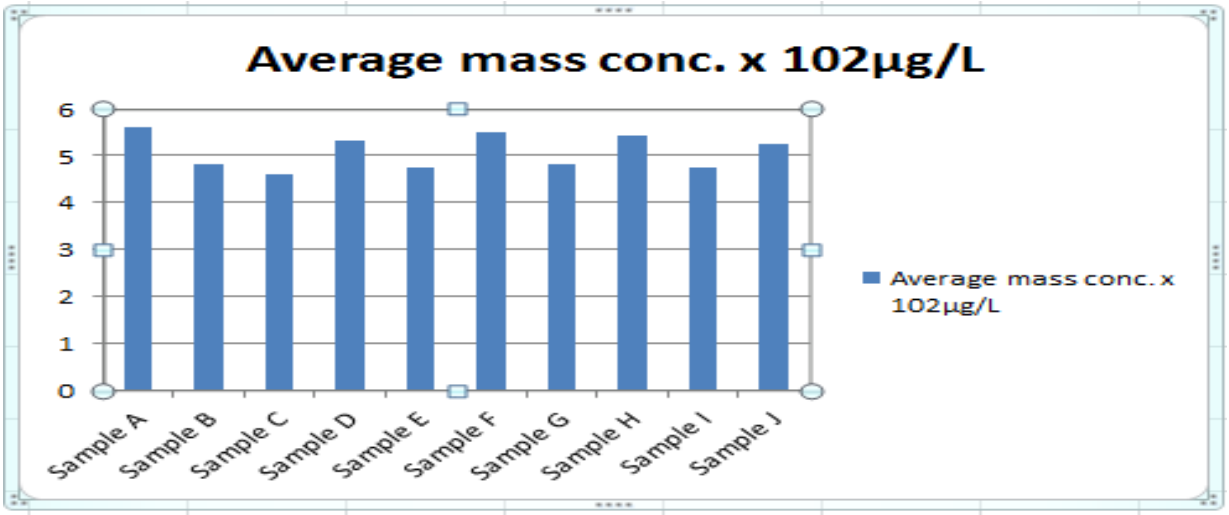

Fig. 2 Histogram of the results of PCBs in soil samples. Action Limit = 10.0 mg/kg (FDA, 1992)

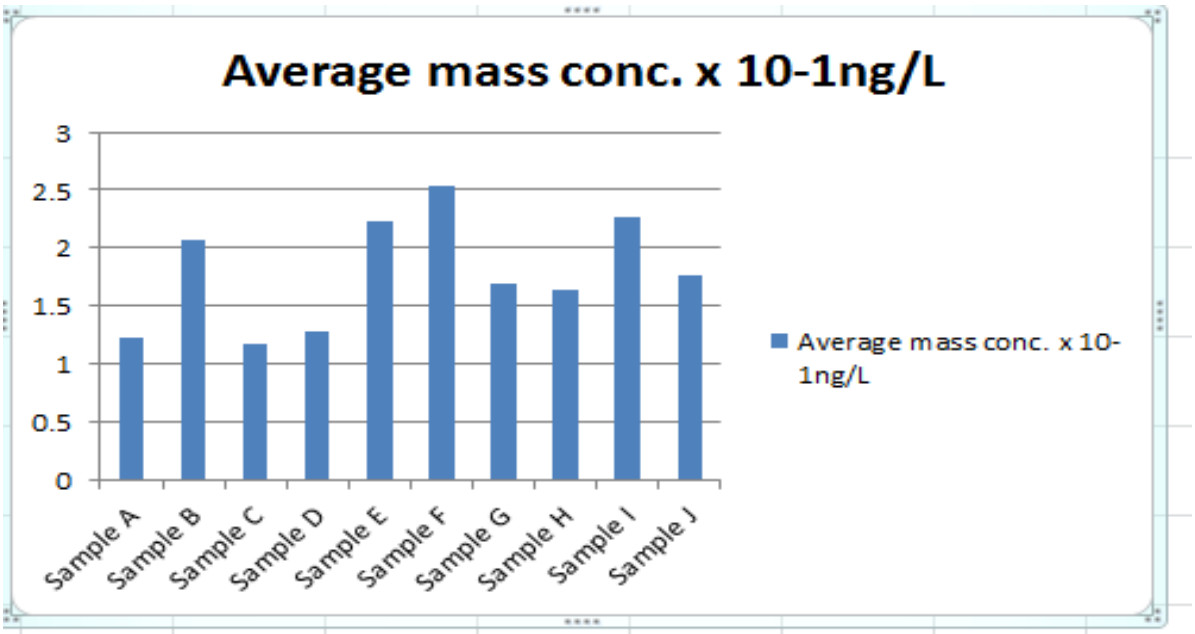

Fig. 3 Results of PCBs in Plant samples. Action Limit = 3.40 ng/kg (FDA, 1992)

DISCUSSION

The extent of poly-substituted organic biphenyl pollutants in the surrounding soils, plant and water bodies in Agbara Industrial area has been investigated as a function of the concentration of the amount of PCBs detected in the samples and results show that the concentration of poly-substituted biphenyls were highest in the sewage and amounted to over 1.80 µg/L and closely followed by the sample from the lagoon having over 1.60 µg/L as shown in the histogram in Figure 1. The concentrations of the pollutants in the drainages fall within 1.20 µg/L to 1.30 µg/L. These values however show that the drainages form the route of the pollutants from neighboring industries while the lagoon and sewage form the receptacles and storage facility where they accumulate. The action limit for PCBs in sewage is 0.005 mg/L or 5.0 µg/L. This shows that the sewage has PCBs level up to 36 % of the action limit. The PCBs obtained in the soils had the initial sample exceeding 5.6 x 10^2 µg/Kg or 0.56 mg/Kg amounting to 5.615 % of the action limit of 10 mg/Kg while the least sample had values exceeding 4.67 mg/Kg amounting to 4.7 % of the action limit as shown in the histogram in Figure 2. The plant samples analyzed accordingly had high values of 2.53 x 10^{-1} ng/Kg and lower values 1.161 x 10^{-1} ng/Kg amounting to 7.44 % and 4.74 % of the action limit of 3.40 ng/Kg respectively. The entire results show

that the PCBs are gradually accumulating in the lagoons and sewage. Though the results are still far from the action limit, there is a strong indication that the threat to the human life as a result of chromium toxicity may be imminent. This is essentially because some of the industries residing within the area are not more than a decade old and with the extent so far, given the little attention to the environmental pollution in some parts of the African continent the values may be critical in the near future. The need for remediation may also require the use of some of these clay minerals especially for the sewage and lagoons and for the planting of citrus within the environs to increase soil acidity.

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