Toxic Equivalent Concentrations of Dioxin-Like PCBs in Soil Samples From The Vicinity of Electrical Power Stations in Lagos, Nigeria

Folarin B.T.[1,2], Abdallah M.A.[2], Oluseyi T.[1], Harrad S.[2], Olayinka, K.[1]

[1]Department of Chemistry, University of Lagos, Lagos, Nigeria, 101212, rabiubilkiss11@gmail.com

[2]School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, United Kingdom, B15 2TT

Introduction

There is a global concern on the hazardous effects to human health and the environment from a group of chemicals known as "Persistent Organic Pollutants" or simply "POPs". POPs are largely synthetic organic chemicals that have been intentionally produced and used for variety of applications (UNEP, 2017).They persist in the environment for long periods and are characterized with long-range transport leading to global pollution. Twelve persistent organic pollutants (POPs) were first identified in the United Nation Environmental Programme in 1995, these POPs were then listed at the Stockholm convention in 2001. Polychlorinated biphenyls (PCBs) are industrial chemicals listed as persistent organic pollutants (POPs), amongst other compounds, at the Stockholm convention in 2001. PCBs have been used as heat transfer and dielectric fluids in transformers and capacitors because of their excellent insulating properties, as hydraulic fluids and diffusion pump oils for engines. PCBs have also been used as components in many of our everyday products; as flame retardants in electrical gadgets, wires and cables, extenders in pesticides and insecticides, additives in pigments and dyes, paints, building sealants and adhesives (Xing *et al.,* 2011). PCBs can damage many organs of the body, some more visible skin effects are the chloroacne and related dermal lesions; PCBs could also distupt the endocrine system causing physiological and developmental damages; carcinogenic effect as a results of hormonal imbalance resulting in hormone sensitive cancers in man and animals is also possible (Egloff *et al.,* 2011; Parkin, 2011).

The structure of PCBs consists of a biphenyl ring with varying numbers of chlorine atom(s) attached to the phenyl rings. There are 209 possible arrangements of the chlorine atoms around the biphenyl ring, hence the 209 PCB congeners. Of these congeners, only 12 have one or no ortho chlorine substitution, which makes them have the ability to rotate and form planar structure similar to poly chlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). This class of PCBs are collectively called "dioxin-like PCBs". They mediate toxicity in a similar way as PCDDs and PCDFs. Toxic equivalent concentrations of dioxin-like compounds in soil has been reported in some other African and non African countries (Nieuwoudt *et al.,* 2009; Domotorova *et al.,* 2012; Tue *et al.,* 2016) but the is dearth of information in Nigeria..This study aims at providing the much needed information in Nigeria by evaluating the toxic equivalent concentrations of eight dioxin-like PCBs (PCB #s- 105, 114, 118, 123, 156, 157, 167 and 169) in soil samples from measured concentrations.

Materials and Methods

48 soil samples were collected within the vicinity of 12 (A to L) power stations in Lagos, Nigeria. The investigated power stations could be categorized into three based on their power activities, *viz* generation station, transmission stration and distribution sub stations. Samples were collected using pre-cleaned hand trowel, sieved through a 2mm sieve, kept in Aluminium foil and stored at 4 ºC prior analysis. Organic solvents used for sample preparation were HPLC grade, Inorganic solvents and reagents were analytical grade. Samples were extracted ultrasonically using 1:1 v/v hexane: dichloromethane (DCM). Extracts were cleaned up with a sequential use of two or three of acid, florisil and dimethyl sulphoxide (DMSO) clean-up methods. Analysis was achieved using gas chromatography fitted with a mass selective detector (GC-MS).

The toxic equivalent approach of measuring toxicity was employed. The toxicity of dioxin-like compound are usually compared to the most toxic dioxin 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and they have been assigned toxicity equivalency factors (TEFs) (WHO, 2005; Van den Berg *et al.*, 2006). The corresponding

toxicity concentrations or toxic equivalent concentrations (TEQs) of each dioxin-like PCBs are determined by multiplying the WHO TEF values of each dioxin-like congener by the absolute concentrations obtained.

Results and Discussion

Absolute concentrations of dioxin-like PCBs in power station soil

The Σdl-PCB_8 in soil samples ranged from 490 pg/g to 61, 000 pg/g with median (mean) concentrations of 8,000 pg/g (17, 000 pg/g). Considering samples from individual power stations, the median and mean concentrations of Σdl-PCB_8 ranged from 1300 pg/g for power station A to 44,000 pg/g for power station I. The top 3 dominant dioxin-likePCBs in the soil samples were PCB 118, PCB 156, and PCB 105, with median (mean) concentrations of 2,200 pg/g (5,300 pg/g), 1800 pg/g (2500 pg/g), and 1700 pg/g (4400 pg/g) respectively.

Table 1: Absolute concentrations (pg/g) ΣDL-PCB_8 in power station soils

PS	MEAN	MEDIAN	MIN	MAX
A (Distribution)	1334	1314	494	2214
B (Transmission)	4265	2322	1901	10514
C (Distribution)	4451	4451	2461	6440
D (Distribution)	27503	26671	6996	49676
E (Transmission)	31634	30994	3266	61283
F (Distribution)	20187	20110	7576	32954
G (Distribution)	6914	6434	2895	11893
H (Transmission)	23631	22696	2016	47116
I (Generation)	43555	43985	28199	58051
J (Transmission)	22727	19954	10297	40701
K (Distribution)	12473	11958	7953	18023
L (Transmission)	6476	5663	2033	12543

Toxic equivalent concentrations of PCBs in Power station soil

The corresponding toxic equivalent concentrations of ΣdlPCB_8 in soil samples ranged from 0.01 pg TEQ g^{-1} to 450 pg TEQ g^{-1} , with a mean of 42 pg TEQ g^{-1} while the corresponding toxic equivalent median (mean) concentrations of ΣdlPCB_8 in soil samples for each power station ranged from 0.13 pg TEQ g^{-1} for power station A (0.13 pg TEQ g^{-1} for power station C) to 67.3 pg TEQ g^{-1} for power station I (149.6 pg TEQ g^{-1} for power station J).

Table 2: TEQ concentrations (pg TEQ g^{-1}) ΣDL-PCB_8 in power station soils

PS	MEAN	MEDIAN	MIN	MAX
A (Distribution)	7.38	6.78	0.01	15.95
B (Transmission)	69.13	10.86	0.06	254.76
C (Distribution)	0.13	0.13	0.07	0.19
D (Distribution)	25.78	0.80	0.21	101.29
E (Transmission)	50.55	31.35	0.10	139.40
F (Distribution)	28.25	25.93	0.23	60.93
G (Distribution)	19.99	5.59	0.09	68.69
H (Transmission)	50.16	22.11	0.06	156.36
I (Generation)	54.35	67.25	0.85	82.06
J (Transmission)	149.56	66.38	14.69	450.77
K (Distribution)	21.50	6.05	0.24	73.67
L (Transmission)	24.54	0.17	0.06	97.78

Comparison of concentrations obtained in this study with previous studies

The study in Ghana (Africa) by Tue and co-workers who analysed dioxin-like chemicals in soil samples from e-waste sites and non e-waste sites (control) revealed that the highest contamination levels were found in the open burning e-waste area areas of Agbogbloshie followed by e-waste areas with no burning activities and the non e-waste area had the lowest level. The study concluded that burning activities contributed significantly to levels of dioxin-like compounds in e-waste sites. The absolute median concentrations of dioxin-like PCBs obtained in our study, specifically for the generation station (43, 555 pg/g) was slightly higher than what was reported by Tue *et al.,* 2016 for dioxin-like PCBs in soil from open burning e-waste (42,000 pg/g). Our transmission station samples and some distribution station samples had concentration (table 1) in range with that of e-waste open burning site of Agbogbloshie (3,400 – 82,000 pg/g) while other samples were in range of the e-waste site with no burning activities (1400 – 7500 pg/g) as reported by Tue and co-workers. Considering that Tue *et al.,* 2016 reported TEQ concentration for the 17 PCDDs/Fs/dl-PCBs, the TEQ values obtained for dl-PCB_8 in many of the power stations in this study were still in range with e-waste sites with no burning activities (11 – 92 pg TEQ g^{-1}) reported by Tue *et al.,* 2016.

Another study by Domotorova *et al.,* 2012 reported the toxic equivalent concentrations of dioxin-like compounds in 5 selected areas in Slovakia (Europe). The results show that the total PCDDs/Fs/dl-PCB-TEQ

concentrations varied from 0.34 to 18.05 pg g^{-1}. Nieuwoudt also reported toxic equivalent concentration range of 0.34 – 20 pg TEQ g^{-1} for dioxin-like compounds (PCDDs/Fs/dl-PCBs) in soils from central South Africa (Africa). Some of our distribution stations with low TEQ concentrations, had levels in range of what was reported by Domotorova *et al.,* 2012 and Nieuwoudt *et al.,* 2009.

Comparison of TEQ concentrations with guideline values

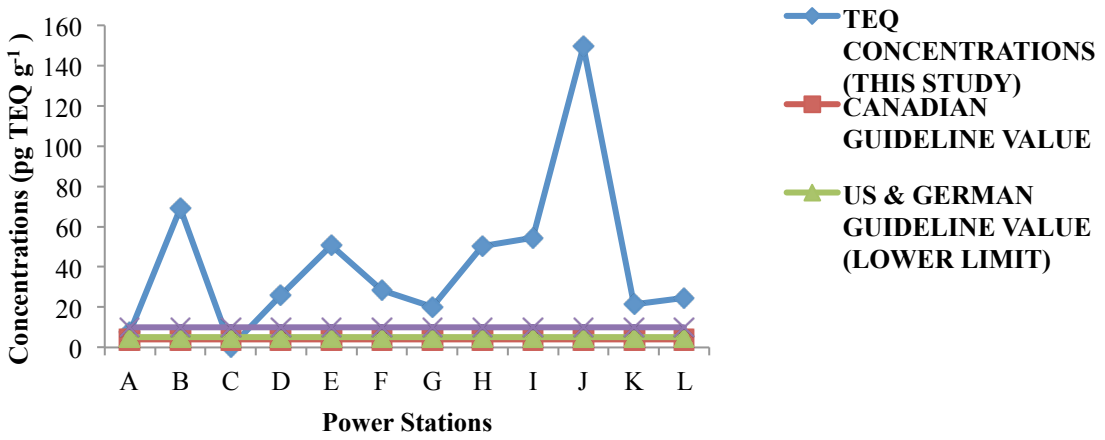

Figure 1: Comparison of mean TEQ concentrations (pg TEQ g^{-1}) obtained with limits

The toxic equivalent mean concentrations for $\Sigma dlPCB_8$ in soil samples of all but one (power station C) of the 12 power stations exceeded the Canadian guideline value of 4 ng TEQ kg^{-1} and the US & German guide line values of 5 – 10 ng TEQ kg^{-1}, however the TEQ concentrations obtained were all below the US action level of 1000 ng TEQ kg^{-1}. The highest TEQ concentrations obtained in this study was from 450 pg TEQ g^{-1} for power station J. This value is almost half of the action level set by the US, this therefore raises great concern.

Conclusion

Worthy of note is the fact that this guideline and action level values for soil are the sum of TEQ concentrations of PCDDs, PCDFs and dioxin-like PCBs. In this study TEQ concentrations for only eight of the 12 dioxin-like PCBs were evaluated. It therefore implies that there is great possibility that some of the power stations will have TEQ concentrations exceeding the US action level (1000 ng TEQ kg^{-1}) if the remaining 4 dioxin-like PCBs, PCDDs, and PCDFs are summed with the present TEQ concentrations for $\Sigma dlPCB_8$ in soil samples.

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