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CONCENTRATIONS AND TOXIC IMPLICATIONS OF DIOXIN-LIKE PCBs IN SOIL SAMPLES FROM ELECTRICAL POWER STATIONS IN LAGOS, NIGERIA

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Abstract

Dioxin-like polychlorinated biphenyls (dl-PCBs) are ubiquitous chemicals which mediate toxicity in a similar way as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). *In silico* modelling was used to predict the absorption, distribution, metabolism, excretion and toxicity (ADMET) properties of eight dioxin-like PCBs in soil samples of 12 power stations in Lagos, Nigeria. Concentrations of Σ dl-PCB₈ in soil samples ranged from 490 pg/g to 61,000 pg/g with mean concentrations of 17,000 pg/g. The corresponding toxic equivalent (TEQ) concentrations of Σ dl-PCB₈ ranged from 0.01 pg TEQ/g to 450 pg TEQ/g, with a mean value of 42 pg TEQ/g. Mean TEQ concentrations for Σ dl-PCB₈ in soil samples from all but one of the sites exceeded the Canadian guideline value of 4 pg TEQ/g and the US and German guideline values of 5 – 10 pg TEQ/g. However, the TEQ concentrations obtained were all below the US action level of 1000 pg TEQ/g. ADMET predictions revealed that all studied dl-PCBs are inhibitors of three major isoforms (1A2, 2C9, and 2C19) of cytochrome P450 enzyme. Acute oral toxicity (LD₅₀) predictions revealed all target dl-PCBs as class III compounds. Hepatotoxicity and carcinogenicity were positive, signifying that the studied compounds all have tendency to elicit these effects. Occupational daily TEQ exposure via soil ingestion was estimated for an average adult worker weighing 70 kg. The maximum exposure obtained was 0.14 pg TEQ kg⁻¹ bw day⁻¹, which is half of the EFSA tolerable daily intake (TDI) for dioxin-like compounds. This raises concern over the possible exceedance of the EFSA TDI for these workers if other dietary and non-dietary exposure pathways and dioxin-like compounds are considered.

Keywords: ADMET predictions, Toxic equivalent (TEQ), soil, power stations, dioxin-like polychlorinated biphenyls (dl-PCBs)

Introduction

Global concern exists over the hazardous effects to human health and the environment from persistent organic pollutants (POPs). POPs are largely synthetic organic chemicals of which many have been intentionally produced and used in a variety of applications (Dai *et al.*, 2020; UNEP, 2017). They persist in the environment for long periods and are capable of long-range transport leading to global pollution. Polychlorinated biphenyls (PCBs) are industrial chemicals listed as POPs under the Stockholm Convention. They were 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 everyday products; as flame retardants in electrical appliances, wires and cables, extenders in pesticides and insecticides, additives in pigments and dyes, paints, building sealants, and adhesives (Erickson and Kaley, 2011; Xing *et al.*, 2011). The soil act as sink for myriad of pollutants including dl-PCBs, which could be deposited directly from day to day operation of transformers in power stations and other related facilities.

Human dietary exposure to PCBs through ingestion of contaminated food or fluids and non-dietary exposure via ingestion, inhalation and dermal uptake of contaminants in polluted soils, dusts and air, can adversely affect many organs of the body, including visible skin effects like chloroacne and related dermal lesions. PCBs can also disrupt the endocrine system causing physiological and developmental damage, as well as mediating carcinogenic effects as a result of hormonal imbalance resulting in hormone sensitive cancers in humans and animals (Bakhlyl *et al.*, 2018; Egloff *et al.*, 2011; Pascale *et al.*, 2018; WHO, 2016).

The structure of PCBs consists of a biphenyl ring with varying numbers of chlorine atoms attached leading to 209 possible PCB congeners. Of these congeners, only 12 have one or no

ortho chlorine substitution, which enables them to rotate and form a planar structure similar to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). This class of PCBs are collectively called dioxin-like PCBs (dl-PCBs), as they mediate toxicity in a similar way to PCDDs and PCDFs (Trinh *et al.*, 2108; Tue *et al.*, 2016, WHO, 2010).

Toxic equivalency is an approach employed to assess the environmental health impact of complex mixtures of dioxins and dl-PCBs. In using the toxic equivalent approach, the toxicities of the 12 dl-PCBs are expressed as a fraction of that of the most toxic dioxin 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) to generate a value for each individual dl-PCB called the toxic equivalent factor (TEF). The TEF approach uses an underlying assumption that takes into account the structure and behaviour of each chemical to assign a single scaling factor. The approach employs comparative measures from individual toxicity assays, known as relative effect potency (REP). Different biological models are used to generate the REPs database used in determining TEFs of chemicals according to WHO established criteria. The TEF is typically selected from the 75th percentile of the REP logarithm scale in order to be protective of health (WHO, 2005).

Toxic equivalent concentrations of dioxin-like compounds in soil have not been exhaustively reported across the globe. Among the few that exist is the work by Domotorova *et al.*, (2012), the study reported levels of dl-PCBs in soil from five selected areas in Slovakia, four of which were industrial areas (with Σ dl-PCB₁₂ as high as 14,000 pg/g) and the fifth area was a remote area without industrial sources of contamination (with highest Σ dl-PCB₁₂ of 300 pg/g). In Domotorova's study, metallurgical activities, combustion of coal and hazardous waste incineration were reported as significant sources of dl-PCBs in soil samples from industrial areas. Another study by Nieuwoudt *et al.*, (2009) investigated the presence of dioxin-like chemicals in soils and sediments from residential areas and the 'Vaal triangle' area of South Africa, which was reported as the largest industrial area in South Africa and houses many

industries with potential for release of dioxin-like compounds. In this study, concentrations of Σ dl-PCDDs/Fs/dl-PCBs that ranged from 120 – 4900 pg/g in industrial areas, were about four times higher than those in some non-industrial areas; while a few non-industrial areas had concentrations below detection limits. A study in Ghana by Tue *et al.*, (2016) measured dioxin-like compounds in soil samples from Agbogbloshie market, a major hub of informal waste recycling in Ghana. The study revealed that uncontrolled burning activities resulted in elevated concentrations of dioxin-like compounds in investigated samples, with concentrations of Σ dl-PCB₁₂ as high as 80,000 pg/g and TEQ concentrations for PCDD/Fs and dl-PCBs in samples from open burning e-waste areas exceeding significantly the US action level of 1,000 pg TEQ/g. It could therefore be inferred from previous findings that the release of dioxin-like chemicals may largely be attributed to anthropogenic activities like: metallurgical processes, petrochemical plants, electricity generation, paper and pulp treatment, building material, hazardous waste incineration and indiscriminate burning to mention a few (Tue *et al.*, 2016).

Considering the lack of knowledge on the fate, behaviour and toxic implications of the presence of POPs in Africa, specifically in areas with potential input sources in Nigeria; this study will provide information on the occurrence and toxicity of dl-PCBs in the vicinity of Nigerian power stations. This present study provides the first data on concentrations of dioxin-like PCBs in Nigerian soils by: (i) determining the absolute and toxic equivalent concentrations of eight dl-PCBs (PCB #s- 105, 114, 118, 123, 156, 157, 167, and 169) in soil samples from electrical power station areas in Nigeria, and comparing them with those reported elsewhere and with guideline values; (ii) analysing statistically the impacts of power station activities (generation, transmission, and distribution) on the concentrations of dl-PCBs in soil; and (iii) determining the ADMET properties (adsorption, distribution, metabolism excretion and toxicity) of the studied dl-PCBs and discussing the potential toxic implications of human exposure to these chemicals via ingestion of contaminated soil.

2.0 Materials and Methods

2.1 Sample collection and Site information

Soil samples (n=48) of approximately 100 g per sample were collected during two sampling campaigns conducted in June and December, 2015 within the vicinity of 12 (A to L) power stations (PS) in Lagos, Nigeria (Figure 1). Samples were collected using a pre-cleaned hand trowel at a depth of 0-5 cm, sieved through 2mm mesh, wrapped in aluminium foil and stored at -20 °C prior to extraction and analysis. To prevent cross contamination, hand trowel was properly washed and rinsed with hexane before and after each sample collection.

We assigned each of the investigated power stations to one of three categories based on their primary purpose, *viz.*: generation station, transmission station, or distribution sub-station. In addition, samples were collected from a former generation station in Nigeria (I), that actively produced electricity before the ban of PCBs in transformer oils. Samples were collected from this site to assess if PCBs released when the power station was fully operational are still present as residual contaminants in the soil within the facility. Currently, a section of this power station is used as a transmission station, while the other section is used for repairs of damaged transformers. Samples were also collected from 5 transmission stations. All the investigated transmission stations are located in the Lagos region, under the transmission company of Nigeria (TCN). Two of the transmission stations are primary transmission stations (B and H) while the remaining three are secondary transmission stations/ transmission sub stations (E, J, and L). The primary stations help to step down the 330 kVA transmission grid of the generation station to 132 kVA while the secondary stations step 132 kVA to 33/11 kVA. Each transformer in the primary transmission stations has capacity in the range of 90 MVA to 150 MVA while the secondary transmission station has capacity in the range of 45 to 60 MVA for each transformer (Oseni, 2011; Edomah *et al.*, 2016). Additionally, samples were collected from 6

distribution stations. Five (A, C, D, F, G) of the stations are distribution injection power stations, with one (PS K), a distribution substation of the University of Lagos. Each transformer in the injection distribution station has a capacity of 15 MVA and is used to step down 33 kVA to 11 kVA. The distribution substation transformers are used to step down 11 kVA to 0.415 kVA (Emodi and Yusuf, 2015; Edomah *et al.*, 2016). From each power station, two soil samples were collected at a distance of ~3 metres from the functioning transformers (non-functioning transformers for PS I) and two additional samples were collected at each site ~100 metres away from the transformers. Overall, four samples were obtained from each of the studied 12 power stations to make a total of 48 soil samples (24 samples per month). Figure 1 presents a map showing locations of the study area. Detailed sample and site information are presented in Table S1 of the supplementary material.

2.2 Sample Preparation and Instrumental Analysis

Organic solvents used for sample preparation were HPLC grade, inorganic solvents and reagents were analytical grade. Sample preparation and analysis was conducted according to a previously published method (Folarin *et al.*, 2018). Briefly, one gram of freeze-dried soil samples was spiked with internal (surrogate) standard mixture (comprising 30 ng of each of the following native PCBs: 34, 62, 119, 131, and 173), followed by ultrasonic-assisted extraction using 1:1 v/v hexane: dichloromethane. The crude extract under went rigorous purification. Briefly, extracts were cleaned up sequentially using concentrated sulphuric acid (H₂SO₄), dimethyl sulphoxide (DMSO) back extraction and florisil chromatography. Detailed sample preparation methods are presented in the supplementary information. Instrumental analysis of target PCBs was carried out on GC-MS (Agilent Technologies 6850 GC system,

5975C VL MSD) fitted with a RestekRXi capillary column (30 m (length) × 180 μm (i.d) × 0.01 μm (film thickness). The GC inlet temperature was set to 280 °C, injection was performed in splitless mode. Helium was used as the carrier gas and the flow rate was set at 0.5 mL/min. The initial oven temperature was set at 140 °C and held for 2 mins, and then ramped at 5 °C/min to 215 °C held for 5 mins, thereafter ramped at 2 °C/min to 245 °C. The temperature of the ion source was 230 °C and an energy beam of 70 eV was employed. The temperatures of the quadrupole and transfer line were 150 °C and 280 °C respectively. For quantitative analysis, the two most abundant ions of each target analyte were monitored in selected ion monitoring (SIM) mode.

2.3 QA/QC

As a result of unavailability of standards in our laboratory at the time of this study for four of the dl-PCBs, only eight of the twelve dl-congeners were analysed in the present study. Calibration standards at concentrations of 20, 50, 200, 500, and 1000 pg/μL were prepared from individual single standards of the 8 target dl-PCBs (PCB #s 105, 114, 118, 123, 156, 157, 167, and 169). To each level of calibration, a constant concentration (200 pg/μL) of internal (surrogate) standards, was added, along with 250 pg/μL of PCB 129 as recovery determination (syringe) standard (RDS). The RDS was used to calculate the recovery of surrogate standards. 150 μL of the RDS solution at 250 pg/μL was used as the final reconstitution solvent for the sample extracts prior to instrumental determination of target congeners on GC-MS. The regression coefficients of the calibration curves for target PCBs were all above 0.99. The relative standard deviation (RSD) of the response factors for target PCBs in the calibration standards were all below 6%. To evaluate method accuracy and precision, CRM 481 (chlorobiphenyls in industrial soil), a soil reference material of the European Commission Institute for Reference Materials and Measurements, Belgium, (purchased from Sigma Aldrich, UK) was analysed. Results revealed good percentage recoveries of surrogate standards ($80.4 \pm$

5.0 % to 93.8 ± 8.6 %). Tables S2 and S3 of the supplementary material present the surrogate standard recoveries and PCB congeners in CRM 481 following 6 replicate determinations. The precision estimated as the RSD of the concentrations obtained for PCBs in the 6 replicate determinations of CRM was less than 12% for each congener.

Procedural blanks (1 g anhydrous sodium sulphate spiked with surrogate standards like the samples) were also extracted and analysed alongside samples. A procedural blank was analysed for every batch of 6 samples. Target dl-PCBs in procedural blanks were below the limit of detection for all congeners. A method blank chromatogram is presented Figure S1 of the supplementary material. Control sample obtained from a botanical garden at approximately 1 km from one of our sampling site was analysed for target congeners. DL-PCB 118 was the only congener found in the control sample present at a concentration higher than the LOD. Concentrations of PCB 118 in almost all the PS samples were between 100 – 1000 times greater than the background levels in the control sample which was found to be 200 pg/g.

Sample limits of detection, obtained at a signal to noise ration of 3:1, for target dl-PCBs were calculated as: 44, 40 , 34, 37, 35, 37, 54, and 61 pg/g for PCBs 105, 114, 118, 123, 156, 157, 167, and 169, respectively. The corresponding limits of quantification calculated at a signal to noise ratio of 10:1 are presented as follows: 147, 133, 113, 123, 116, 123 pg/g, 180, and 203 pg/g respectively.

2.4 Toxicity assessment

2.4.1 Toxic Equivalent Concentrations of dl-PCBs

To assess the toxicity of dioxin-like PCBs in this study, toxic equivalent concentrations were estimated in accordance with the World Health Organization toxic equivalent (WHO-TEQ) approach, by multiplying the World Health Organization TEFs (WHO-TEFs) of individual

dioxin-like PCB by the PCB concentration according to Eq. 1 (WHO, 2005). The TEF values of studied dl-PCBs are provided in Table S1 (supplementary information).

$$TEQ \text{ Concentration} = TEF \text{ Value} \times \text{Concentration of dl-PCB} \quad \text{Eq. 1}$$

The daily TEQ intake (pg TEQ kg⁻¹ bw day⁻¹) was estimated for workers' incidental ingestion of contaminated soil according to Eq. 2

$$\text{Daily TEQ intake} = \frac{TEQ \text{ Concentration} \times \text{Ing.rate} \times \text{exposure fraction}}{BW} \quad \text{Eq. 2}$$

A soil ingestion rate of 100 mg/day was employed (Stanek *et al.*, 1997; Sun *et al.*, 2016). The exposure fraction for occupational scenario (0.238) was estimated based on an assumption of 8 hours a day at work for 5 days a week (i.e. 40 hours/week). 70 kg body weight was employed as the average weight for an adult.

2.4.2 Modelling the toxicity profile of studied dl-PCBs using ADMET predictions

The adsorption, distribution, metabolism, excretion and toxicity (ADMET) profiles of the studied PCBs were predicted using ADMET modelling. *In silico* ADMET predictions are models based on thousands of experimental data (*in vivo* and *in vitro*), capable of determining the behaviour of compounds by finding quantitative structure–property relationships (QSPR), which connect structural information to physical and chemical characteristics. *In silico* ADMET predictions for compounds of therapeutic benefits have been relatively published. Of concern to this present study is the application of *in silico* methods for prediction of toxicity of environmental chemicals (Rim, 2020). The Swiss ADME webserver was employed to screen multiple pharmacokinetic properties of studied dl-PCBs. Toxicity profiling was achieved using admetSAR (version 2) and pkCSM modelling web server. AdmetSAR2 is an integrated server capable of *in silico* predictions of ADME and toxicity (ADMET) properties of chemical compounds. pkCSM was used in combination with ADMETSAR2 and Swiss ADME for

ADMET predictions. Canonical smiles of individual dl-PCBs (Table S4) were retrieved from the PUB CHEM database and imported into the servers for modelling (Daina *et al.*, 2017; Pires *et al.*, 2015; Yang *et al.*, 2018).

2.5 Statistical Analysis

Shapiro-Wilk tests of normality were conducted in R for both absolute and TEQ concentration data. Results revealed that both the absolute and TEQ concentrations significantly deviated from a normal distribution. Considering this, a Kruskal-Wallis non-parametric test was performed in R to determine the statistical significance of the observed differences in target PCB concentrations in samples from the three categories of power stations. The R commands used for conducting the Kruskal-Wallis test are provided as supplementary information. Four conditions were met before performing the test *viz.*; (i) There were more than two independent categorical variables (power station types - generation, transmission, and distribution) (ii) The dependent variable was numerical (iii) The independent variables were made factors, and (iv) the data were not normally distributed (R Core Team, 2014).

3.0 Results and Discussion

3.1 Concentrations (pg/g) and TEQ Concentrations (pg TEQ/g) of dioxin-like PCBs in power station soils

The concentrations of individual dl-PCBs and Σ dl-PCB₈ in the 48 analysed soil samples are presented in Table S5. Bar chart comparison of the mean and median concentrations is presented in Figure 2. Concentrations of Σ dl-PCB₈ in soil samples ranged from 490 to 61,000 pg/g with median (mean) concentrations of 8,000 (17,000 pg/g) (Table S4). Considering samples from individual power stations, concentrations of Σ dl-PCB₈ indicated the most contaminated samples were from PS I (with mean concentration of 44,000 pg/g), while samples from a distribution station (PS A) was the least contaminated at mean level of 1,300 pg/g. In terms of individual congener concentrations, the dominant dl-PCBs in the studied soil were

PCB 118, PCB 105, and PCB 156, with median (mean) concentrations of 2,200 (5,300) pg/g, 1,700 (4,400) pg/g, and 1,800 (2,500) pg/g, respectively. Similar trend of PCB 118 > PCB 105 > PCB 156 was reported for mean values obtained by Liu and Liu (2009). The study investigated the presence of dl-PCBs in areas around an old, deserted e-waste site in Eastern China and reported highest mean concentrations from PCBs 118, 105 and 156, with values of 2760 pg/g, 1495 pg/g and 372 pg/g respectively. This trend was also reported in the study of Nieuwoudt *et al.* (2009), with mean values of 644 pg/g, 179 pg/g and 166 pg/g for PCBs 118, 105 and 156 respectively.

The corresponding toxic equivalent concentrations of Σ dl-PCB₈ in soil samples ranged from 0.01 - 450 pg TEQ/g (Table 1). Comparing toxic equivalent concentrations of Σ dl-PCB₈ in soil samples from investigated power stations, a mean concentration, ranging from 0.13 pg TEQ/g for PSC - 150 pg TEQ/g for PSJ was obtained.

The toxic equivalent mean concentrations for Σ dl-PCB₈ in soil samples from all PSs (Table 1) exceeded the Canadian guideline value of 4 pg TEQ/g (CCME, 2007) and the US and German guideline values of 5 – 10 pg TEQ/g (Schulz, 1994; Tue *et al.*, 2016) (Figure 3) except for PS C with mean value below guideline limits. However the TEQ concentrations obtained were all below the US action level of 1000 pg TEQ/g (NSCEP, 2009). The highest TEQ concentrations obtained in this study was 450 pg TEQ/g, found in a soil sample from power station J. This value is almost half the US action level, which raises a concern given that the overall action level may be approached or even exceeded if the TEQ concentrations of the remaining 4 dioxin-like PCBs, and 17 PCDD/Fs were included in the present study. As hypothesized, soil samples obtained at ~3 metres from the transformer plants had significantly higher absolute and TEQ concentrations (P-value = 0.005) than soil samples farther away (~100 metres). Similar trends have been reported by researchers who compared concentrations of PCBs in environmental

samples around industrial areas and non-industrial areas or at a distance farther away from potential sources of emissions (Hu *et al.*, 2013; Tue *et al.*, 2016; Wang *et al.*, 2016).

3.2 Comparison of concentrations of dl-PCBs in soil samples based on power station activity

Figure 4 compares the mean concentrations of individual target PCBs and TEQ values in soil samples from the three categories of power stations. Soil samples from the generation station displayed the highest mean concentrations for each target dl-PCB except for PCB 169 that was highest in soil from the transmission station. This is not surprising as the highest PCB 169 concentration was found in soil sample from PS J, which is a PS that occupies a section of the old generation station (PS I). The overall mean Σ dl-PCB₈ concentrations were 5,400 pg/g (for generation station samples) > 2,200 pg/g (for transmission station samples) > 1,500 pg/g (distribution station samples).

Interestingly, the overall mean TEQ concentrations were: 8.60 pg TEQ/g (for transmission station samples) > 6.79 pg TEQ/g (for generation station samples) > 2.15 pg TEQ/g (distribution station samples), indicating that the transmission station had the highest overall mean TEQ concentration of the three power stations. This opposing trend is a result of the dominance of PCB 169 (which has a TEF that is 1,000 times higher than that of any of the other target PCBs in this study) in samples from the transmission stations. The high TEF value correspondingly translates to high TEQ concentrations observed for PCB 169 and highest mean TEQ concentrations observed for samples from the transmission stations where PCB 169 was dominant (Dai *et al.*, 2020; Trinh *et al.*, 2018; WHO, 2016). To investigate if the concentrations of dl-PCBs in samples from the three categories of power stations differ significantly, a Kruskal Wallis test was conducted. Results revealed that the null hypothesis (H_0) can be accepted, implying both the absolute and TEQ concentrations were statistically indistinguishable for all power station types (P-value = 0.1 and 0.2, respectively).

3.3 Comparison of soil dl-PCBs concentrations in the present study with related reports elsewhere

As mentioned above, a study by Domotorova *et al.* (2012) reported the concentrations of dioxin-like compounds in soils from 5 selected areas in Slovakia, four of which were industrial areas with the fifth area a remote area without any industrial source of contamination. Σ dl-PCB₁₂ in soil samples ranged from 330 – 11,000 pg/g; 220 – 14,000 pg/g; 240 – 2300 ; 140 to 8100 pg/g for industrial areas 1, 2, 3, and 4 respectively and 130 pg/g to 300 pg/g for the remote area. Soil samples collected at a distance of ~3 metres from the transformer plant in this study had Σ dl-PCB₈ in the range of 2,200 pg/g (PS A) to 58,000 pg/g (PS I) while those obtained at ~100 metres from the transformers contained from 490 pg/g Σ dl-PCB₈ (PS A) up to 29,000 pg/g (PS I). Correspondingly, a similar trend was observed for TEQ concentrations, with Σ dl-PCB₁₂ TEQ concentrations that ranged from 0.07 – 6.5 pg TEQ/g for industrial areas of Slovakia and 0.08 – 0.17 pg TEQ/g for non-industrial areas. Consistent with the findings of Domotorova *et al.* (2012), TEQ concentrations obtained close to power transformers in our study varied from 0.2 to 450 pg TEQ/g. On the other hand, soil samples collected farther away from transformers had TEQ concentrations of 0.01 – 74 pg TEQ/g. Similarly, Nieuwoudt *et al.* (2009) reported a concentration range of 0.12 – 16 pg TEQ/g for dioxin-like compounds (PCDDs/Fs/dl-PCBs) in soils obtained from industrial areas of central South Africa, while non-industrial areas had TEQ concentrations that were about four times lower. Overall, many of the TEQ concentrations obtained in our study (Table 1), especially in soils from the generation and transmission stations, were higher than those reported by Domotorova *et al.* (2012) and Nieuwoudt *et al.* (2009) for both industrial and non-industrial areas.

A study in Ghana by Tue *et al.* (2016) analysed dioxin-like chemicals in soil samples from e-waste sites and non e-waste (control) sites. Results revealed that the highest contamination levels were found in the open burning e-waste areas of Agbogbloshie followed by e-waste areas

with no burning activities, with the non e-waste area displaying the lowest level. The study concluded that burning activities contributed significantly to levels of dioxin-like compounds in e-waste sites. The median concentrations of dioxin-like PCBs obtained in our study, specifically for the generation station (43,600 pg/g) were slightly higher than those reported by Tue *et al.*, 2016 for dioxin-like PCBs in soil from open burning e-waste (42,000 pg/g). Our samples obtained from transmission station and some distribution station samples displayed concentrations (Table 1) in the range of those reported for an e-waste open burning site in Agbogbloshe (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) reported by Tue et al (2016).

Soils from an informal e-waste recycling site in Bangalore (India) also contained high concentrations of dl-PCBs, with mean concentrations of 13,000pg/g. These concentrations were much higher than those in soils of another Indian e-waste facility where recycling of e-waste did not involve thermal processes, with mean dl-PCB concentrations of 6,500 pg/g(Karri *et al.*, 2008). Both dl-PCB mean concentrations were more than three times greater than those we observed - mean 1,700 pg/g for Σ dl-PCB₈ – although our omission of 4 dl-PCBs will have contributed to these apparently lower concentrations. Another study in India by Charkraborty *et al.*, (2018) reported mean dl-PCBs concentrations of 1,800 pg/g in soils from open dumpsites. This value was comparable to our mean concentration.

3.4 ADMET(adsorption, distribution, metabolism, excretion, and toxicity) predictions and toxic implications of the studied dl-PCBs

ADMET predictions were used to model the toxicity of the studied dioxin-like compounds. As highlighted in section 3.1, results from this study revealed that the TEQ concentrations of PCBs in soil samples exceeded the guideline values promulgated by some national authorities, which implies that these levels are capable of eliciting some toxic effects in exposed humans. It is

therefore important to understand the fate of these chemicals in the body and their toxic properties. At least one parameter was used to measure each of the five ADMET properties. The results are presented in Table 2. Absorption properties were measured using the Caco-2 cell line permeability which is used in *in vitro* models to predict the absorption of ingested substances. Predicted values greater than 0.9 as observed here, indicate high Caco-2 permeability (Pirex *et al.*, 2015). The intestinal absorption was also predicted (results in %, Table 2); this predicts the percentage of the chemical that will be absorbed through the human intestine. Values obtained for studied dl-PCBs were all above 80 %, implying high intestinal absorption of these chemicals. The skin permeability coefficient (K_p) was also predicted as an absorption descriptor, with results revealing that our studied compounds were averagely permeated (Daina *et al.*, 2017). Moreover, the blood brain barrier (BBB) permeability was used as a descriptor to measure the distribution properties of target compounds. BBB permeability measures the ability of a compound to cross into the brain. For xenobiotics like dl-PCBs, BBB should be low (< -1) to indicate poor distribution and less harm. BBB values > 0.2 as obtained in this study imply that the compounds can readily cross the blood brain barrier and pose deleterious effects.

Metabolism was another ADMET property considered. The cytochrome P450 inhibitive potentials of studied dl-PCBs were determined. Cytochrome P450 is an important enzyme in the human body that mediates oxidation of xenobiotics. The cytochrome P450 inhibition profiles for dl-PCBs were assessed for three isoforms (1A2, 2C9, and 2C19) (Grimmet *et al.*, 2015; Nisha *et al.*, 2016). Results revealed that all studied compounds displayed P450 inhibitory activity. Organic cation transporter 2 (OCT-2), plays an important role in clearing the renal system and as such, it was used as an excretion descriptor. Results revealed that all studied dl-PCBs are OCT-2 substrate, implying that excretion of these compounds from the human body will be difficult.

LD₅₀ (the dose of a compound that is capable of causing death in 50 % of a group of test animals) was determined as a descriptor for acute oral toxicity. The *in silico* LD₅₀ model which was built on several thousand compounds tested in rats predicted that the rat LD₅₀ toxicity obtained for all of the studied dl-PCBs belonged to class III (Table 2), as predicted by admetSAR, implying the compounds are toxic if swallowed (Banerjee *et al.*, 2018; Yang *et al.*, 2018). The model outcomes for hepatotoxicity and carcinogenicity were positive for the tested dl-PCBs. Hepatotoxicity and carcinogenicity predictive models on admetSAR were built on *in vivo* experimental data using animals. The positive results for hepatotoxicity and carcinogenicity (Table 2) signify that the studied compounds all have a tendency to elicit these toxic effects.

3.5 Human exposure to dl-PCBs via soil ingestion

The daily TEQ intake (pg TEQ kg⁻¹ bw day⁻¹) was estimated for incidental ingestion of contaminated soil by workers in the vicinity of the studied power stations at the 50th, 75th, and 95th percentile exposure concentrations with the assumption of an average adult body weight of 70 kg and an occupational exposure fraction of 0.238 (i.e. 40 hours/week). The results are presented in Table 1. TEQ intake values at 95th percentile concentration ranged from 0.005 - 0.14 pg TEQ kg⁻¹ bw day⁻¹. The highest daily intake TEQ exposure estimate obtained in this study was half of the tolerable daily intake of 0.28 pg TEQ kg⁻¹ bw day⁻¹ for dl-PCBs and PCDD/Fs recommended by European Food Safety Authority (EFSA) (EFSA, 2018). However, it should be noted that the intake levels estimated here represent only exposure via contaminated soil ingestion. This exposure was estimated for the work environment employing an exposure fraction of 40 hours of the 168 hours per week, while other non-dietary and dietary intake contributions were not considered. It should be noted that dermal uptake and inhalation have been reported as significant non-dietary exposure pathways to PCBs which may add to

the potential risk in these contaminated sites (Charkraborty *et al.*, 2018; Sun *et al.*, 2016; Tue *et al.*, 2013; Wang *et al.*, 2016). In addition, only 8 of the 29 dl-TEQ compounds were employed for this estimation. This is a cause for concern because the EFSA tolerable intake may have been exceeded if other dioxin-like compounds and other pathways of exposures were included in the estimate. The intake values obtained for some of our power stations were higher than 0.009 pg TEQ kg⁻¹ bw day⁻¹, 0.023 pg TEQ kg⁻¹ bw day⁻¹ and 0.081 pg TEQ kg⁻¹ bw day⁻¹ reported by Charkraborty *et al.* (2018), Suzuki *et al.* (2016), and Hu *et al.* (2013) via ingestion of dioxin like compounds in soils from India, Vietnam and China e-waste recycling sites respectively. An intake value of 0.11 pg TEQ kg⁻¹ bw day⁻¹ via soil ingestion was reported in Ghana by Tue *et al.* (2019) for soil contaminated with PCDD/Fs. This value is close to the highest daily intake recorded in this study.

Conclusion

Concentrations of eight dl-PCBs were generally high in soil samples collected in the vicinity of 12 power stations in Lagos, Nigeria with levels exceeding US and German guideline values. *In silico* ADMET predictions revealed that dl-PCBs are capable of eliciting various toxic endpoints e.g. hepatotoxicity and carcinogenicity, in exposed humans. The TEQ Σdl-PCB₈ concentration and estimated daily intake via incidental ingestion of soil sample from one of the studied power stations was about half the U.S action level (1000 pg TEQ g⁻¹) and EFSA TDI (0.28 pg TEQ kg bw day⁻¹) respectively. This raises concern considering that TEQ concentrations for only eight dl-PCBs were evaluated, and only occupational exposure through incidental soil ingestion were considered in the present study. It could be inferred that the US action level and EFSA TDI could be exceeded for the workers in this power station if the remaining 4 dl-PCBs, and 17 PCDD/Fs, as well as other dietary and non-dietary exposure pathways are considered.

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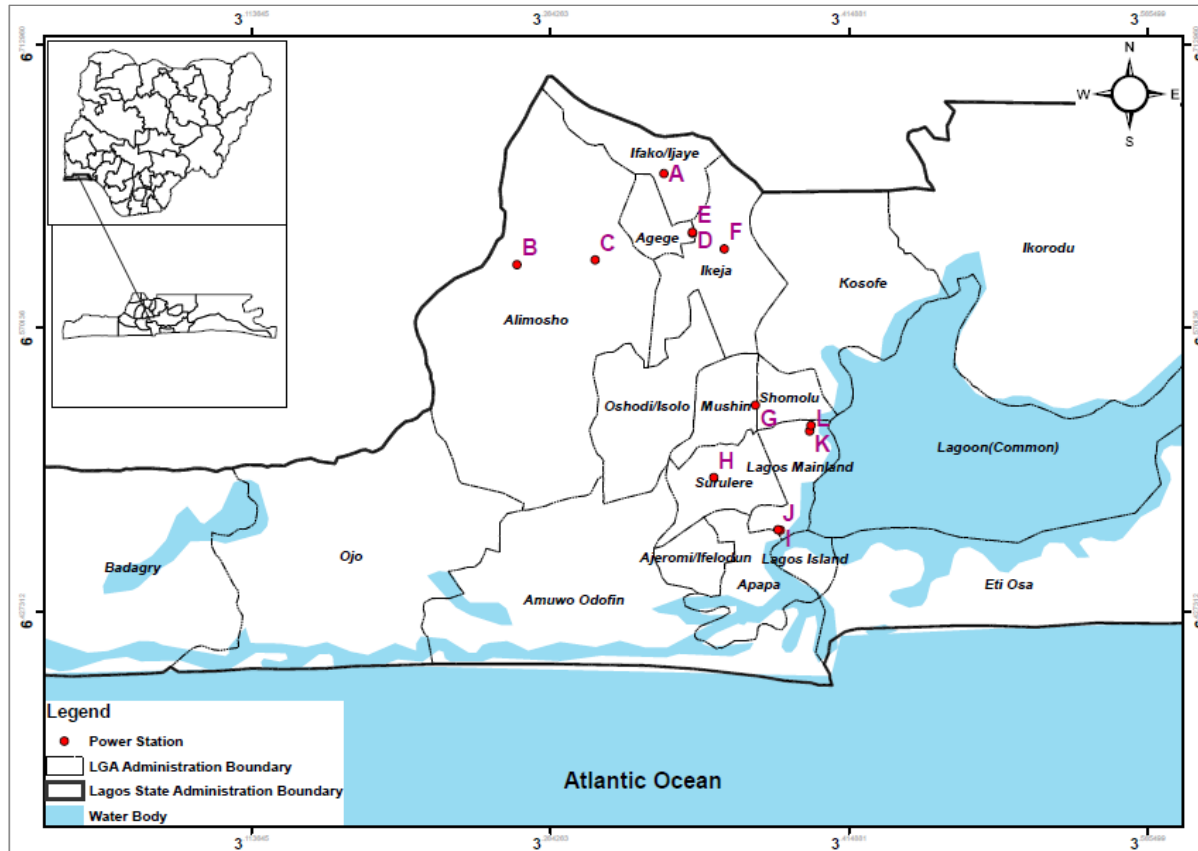


Figure 1: Map of sampling sites in Lagos, Nigeria

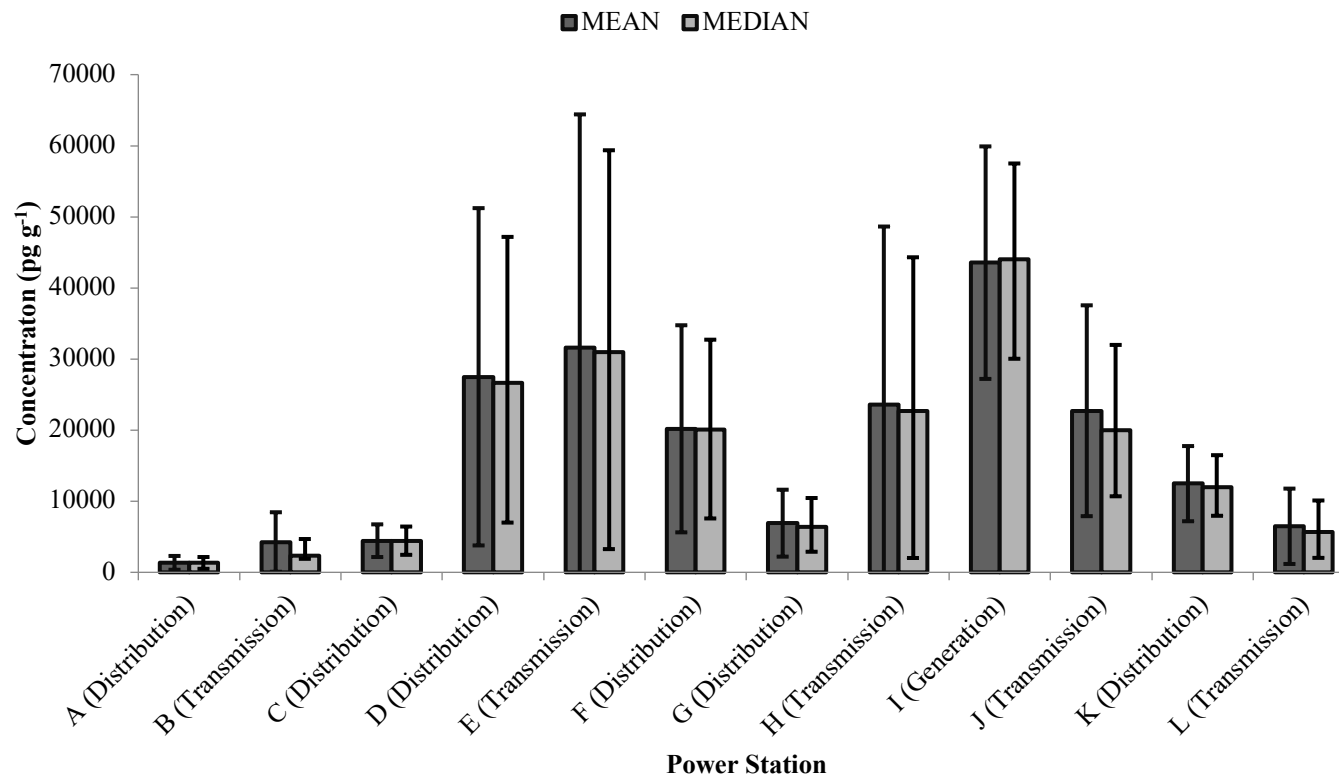


Figure 2: Mean and median concentrations (pg g⁻¹) of ΣDL-PCB₈ in power station soils with error bars showing standard deviation for mean concentrations and 25th and 75th percentile values for median concentrations.

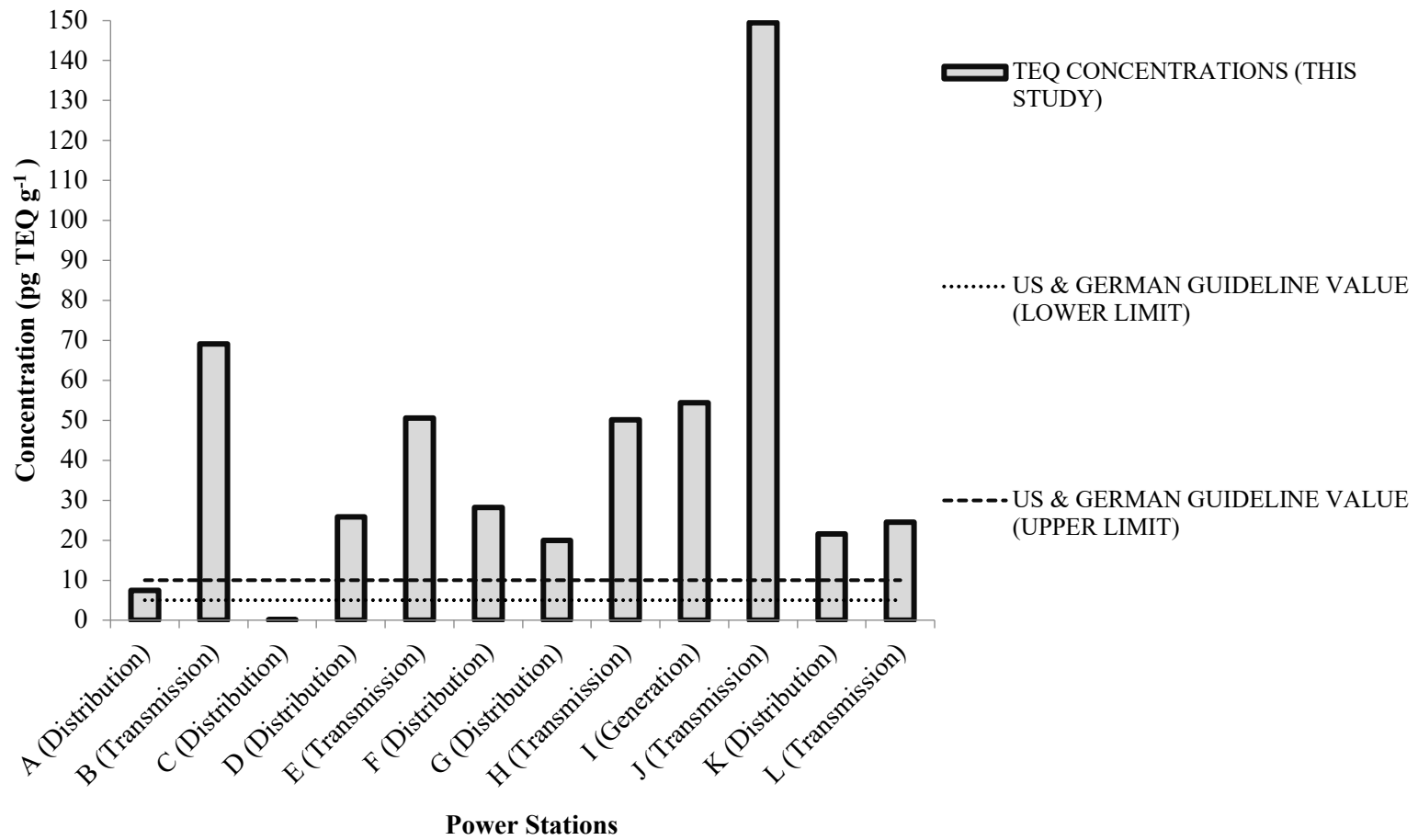


Figure 3: Comparison of mean TEQ concentrations (pg TEQ g⁻¹) obtained with health based guideline values from various jurisdiction

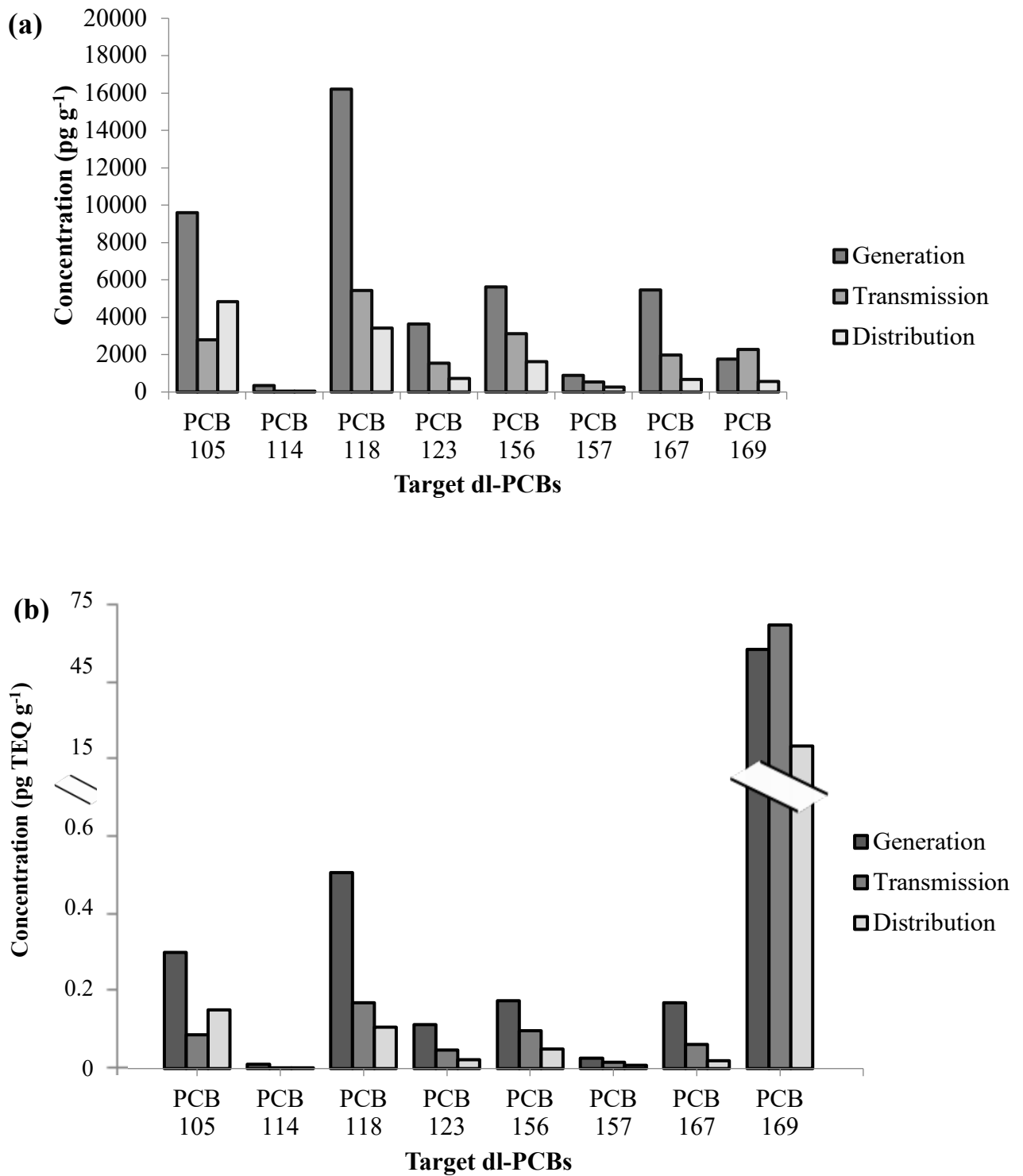


Figure 4: (a) Comparison of mean concentrations (pg g⁻¹) of individual dl-PCBs in samples from the three categories of power stations (b) Comparison of mean TEQ concentrations (pg TEQ g⁻¹) of individual dl-PCBs in samples from the three categories of power stations

Table 1: Mean, median, minimum and maximum TEQ concentrations (pg TEQ g⁻¹) of Σ DL-PCB₈ in power station soils and estimated daily intake values (pg TEQ kg⁻¹ BW day⁻¹)

Power station	December		June		TEQ Concentrations (pg TEQ g ⁻¹)				pg TEQ kg ⁻¹ BW day ⁻¹		
	S-01 ^a	S-02 ^b	S-03 ^a	S-04 ^b	Mean	Median	Min	Max	50 th percentile	75 th percentile	95 th percentile
A (Distribution)	13.55	0.01	15.95	0.01	7.38	6.78	0.01	15.95	0.0023	0.0048	0.0053
B (Transmission)	21.66	0.06	254.76	0.06	69.13	10.86	0.06	254.76	0.0037	0.027	0.075
C (Distribution)	0.19	0.07	0.19	0.07	0.13	0.13	0.07	0.19	0.000045	0.000066	0.000066
D (Distribution)	101.29	0.21	1.39	0.21	25.78	0.80	0.21	101.29	0.00027	0.0090	0.029
E (Transmission)	62.60	0.10	139.40	0.10	50.55	31.35	0.10	139.40	0.011	0.028	0.043
F (Distribution)	51.63	0.23	60.93	0.23	28.25	25.93	0.23	60.93	0.0088	0.018	0.020
G (Distribution)	11.09	0.09	68.69	0.09	19.99	5.59	0.09	68.69	0.0019	0.0087	0.020
H (Transmission)	156.36	0.06	44.16	0.06	50.16	22.11	0.06	156.36	0.0075	0.025	0.047
I (Generation)	60.16	74.35	82.06	0.85	54.35	67.25	0.85	82.06	0.023	0.026	0.028
J (Transmission)	102.17	30.59	450.77	14.69	149.56	66.38	14.69	450.77	0.023	0.064	0.14
K (Distribution)	73.67	0.24	11.87	0.24	21.50	6.05	0.24	73.67	0.0021	0.0093	0.022
L (Transmission)	0.28	0.06	97.78	0.06	24.54	0.17	0.06	97.78	0.000058	0.0084	0.028

a- Soil samples collected at a distance of ~ 3 metres from the transformers; b- Soil samples collected at a distance of ~ 100 metres away from the transformers.

Table 2: ADMET properties of dioxin-like compounds

Parameters		Compounds							
		PCB 105	PCB 114	PCB 118	PCB 123	PCB 156	PCB 157	PCB 167	PCB 169
A	Caco-2 ^{a,c}	1.664	1.664	1.57	1.674	1.674	1.674	1.628	1.628
	Intestinal absorption ^{a,c}	87	87	88	86	86	86	86	86
	log K _p ^{b,c}	-3.47	-3.29	-3.24	-3.36	-3.11	-3.11	-3.18	-3.24
D	Log BB ^c	0.305	0.305	0.337	0.263	0.263	0.263	0.279	0.279
M	CYP1A2 ^a	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	Inhibitor
	CYP2C19 ^a	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	Inhibitor
	CYP2C9 ^{a,b}	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	inhibitor	Inhibitor
E	OCT-2 ^c	substrate	substrate	substrate	substrate	substrate	substrate	substrate	Substrate
T	LD ₅₀ (mol/Kg) ^a	2.37065	2.73511	2.5035	3.08865	2.96386	2.10844	3.17892	3.36683
	LD ₅₀ Class ^a	III	III	III	III	III	III	III	III
	Hepatotoxicity ^a	+	+	+	+	+	+	+	+
	Carcinogenicity ^a	+	+	+	+	+	+	+	+

A- Absorption descriptors; D- Distribution descriptors; M-Metabolism descriptors; E= Excretion descriptors; T-Toxicity descriptors a- predicted using ADMETSAR2 webserver (Yang *et al.*, 2018); b- predicted using Swiss ADME webserver (Daina *et al.*, 2017); c-predicted using pkCSM Model (Pirex *et al.*, 2015).