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Atmospheric Concentrations of Polychlorinated Biphenyls, Brominated Flame Retardants, and Novel Flame Retardants in Lagos, Nigeria Indicate Substantial Local Sources

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Abstract

Polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs) like polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), and novel flame retardants (NFRs) like decabromodiphenyl ethane (DBDPE) are ubiquitous environmental pollutants. Despite this, little is known about their concentrations in outdoor air in the African continent. To address this knowledge gap, concentrations of BFRs, NFRs, and PCBs were measured in outdoor air at 8 sites located within the metropolitan area of Lagos, Nigeria. Concentrations of $\sum_8$BDEs, $\sum$HBCDD, $\sum_7$NFRs and $\sum_8$PCBs were: 21 – 750 (median = 100) pg/m^3, < 12 – 180 (median = < 12) pg/m^3, 34 – 900 (median = 300) pg/m^3 and 85 – 460 (median = 300) pg/m^3, respectively. Decabromodiphenyl ether (BDE-209, range: <16 - 620 pg/m^3, median = 71 pg/m^3) and DBDPE (range: <37 - 890 pg/m^3, median = 280 pg/m^3) were the dominant BFRs detected, while the non-Arochlor PCB 11 (range: 49 – 220 pg/m^3, median = 100 pg/m^3) was the dominant PCB. To the authors' knowledge, these are the first data on the non-Arochlor PCB 11 in outdoor air in Africa. In general, concentrations of all target contaminants in this study were within the range reported elsewhere in Africa and worldwide. Likely due to the tropical climate of Lagos, no seasonal variation in concentrations was discernible for any of the target contaminants. While concentrations of PBDEs and some NFRs were correlated with population density, concentrations of PCBs appear more impacted by leaks from electrical transformers and for PCB 11 to proximity to activities like textile factories that produce and use dyes.

Key words: PCBs, BFRs, PBDEs, HBCDD, DBDPE, urban air, Africa

1. Introduction

Between 1929 and the mid-1980s, polychlorinated biphenyls (PCBs) were manufactured as various commercial mixtures around the world. Applications included as dielectric fluids in electric power transformers and capacitors, as well in lubricating fluids, adhesives, building sealants, plasticisers, fire proofing agents, paints, and ink products (Breivik et al., 2016, Wong and Warner, 2010; Zhang et al., 2011).

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have been two of the most widely used brominated flame retardants (BFRs) applied to consumer products such as soft furnishings and electrical and electronic equipment (EEE), to help meet fire safety regulations (BSEF, 2020; Fatunsin et al., 2020; Muenhor and Harrad, 2018). Commercial PBDE formulations include: pentaBDE (comprising primarily tetra-, penta-, and hexa-BDEs), octaBDE (comprising mainly hexa-, hepta- and octa-BDEs), and decaBDE (principally decabromodiphenyl ether (BDE-209)), with the latter the most widely used (Abb et al., 2011; Wemken et al., 2019). HBCDD was applied mainly as an additive to expanded and extruded polystyrene (EPS/XPS) building insulation foam. To a lesser degree it was also applied to high impact polystyrene (HIPS) used in enclosures for electronic equipment as well as a back-coating for fabrics like sofa covers and curtains (Desborough et al., 2016; Stubbings and Harrad, 2019). Technical HBCDD comprises predominantly γ-HBCDD (70%), along with lower proportions of α- and β-HBCDD (de Wit et al., 2010).

In light of evidence of their toxicity, persistence, and potential to undergo bioaccumulation and long-range atmospheric transport; PCBs, PBDEs, and HBCDD are listed as persistent organic pollutants (POPs) under the Stockholm Convention of the United Nations Environment Programme (UNEP) (UNEP, 2020). Listing of these chemicals as POPs led to ceasing of their manufacture and deliberate use at various points since 1979. With respect to PBDEs and HBCDD (referred to collectively as POP-BFRs), restrictions on their

manufacture and use without concomitant changes in fire safety regulations has led to increased use of so-called 'alternative', 'emerging', or 'novel' flame retardants (NFRs) in a similar range of applications (Covaci et al., 2011; Zuiderveen et al., 2020). Examples of NFRs include: decabromodiphenyl ethane (DBDPE), dechlorane plus (DP), hexabromobenzene (HBBz), pentabromobenzene (PBBz), pentabromoethylbenzene (PBEB), and pentabromotoluene (PBT). Both DBDPE and DP have found use as replacements for decaBDE in HIPS, back-coated furniture fabrics, electrical hard plastic connectors in televisions and computer monitors, and wire coatings (de Wit et al., 2010; Sverko et al., 2011). Meanwhile, HBBz, PBEB, and PBT are all additive flame retardants applied to paper, thermoset resins in circuit boards, textiles, adhesives, wire and cable coating, polyurethane foams, thermoplastic resins, polyester resins, and paint emulsions (de Wit et al., 2010).

Information regarding the toxicity of such NFRs remains limited. However, the USEPA's 2014 assessment of alternatives to decaBDE, rates DBDPE a similarly high hazard to decaBDE with respect to developmental toxicity (USEPA, 2014). This is concerning as the endpoint that drives the EPA's reference dose for decaBDE is neurodevelopmental toxicity (USEPA, 2008). Moreover, *in silico* assessment suggests HBBz, PBBz, PBEB, and PBT are potentially persistent, bioaccumulative, and toxic (PBT) compounds (Gramatica et al., 2016), with DP thought capable of long-range atmospheric transport (Wang et al., 2016).

While data on concentrations of PCBs, PBDEs, and HBCDD in outdoor air from East Asia, Europe, and North America are relatively abundant; such information is far scarcer elsewhere, particularly in Africa (Akinrinade et al., 2020). This dearth of information for Africa is an important oversight, given concerns about issues such as: poor management of waste electrical and electronic equipment (WEEE) containing FRs, and of obsolete electric transformers containing PCBs. Moreover, there exist increasing reports and concerns about the environmental presence of non-Aroclor PCBs like PCB 11 (3,3'-dichlorobiphenyl)

thought to be formed from diarylide dyes and/or degradation of more highly chlorinated PCB congeners (Anh et al., 2021; Basu et al., 2009). To our knowledge, no data yet exist on atmospheric concentrations of PCB 11 in Africa.

With respect to recent data for outdoor air in Africa, the GAPS (Global Atmospheric Passive Sampling) monitoring program has recently reported concentrations of selected PBDEs, HBCDD, and NFRs in Egypt and Nigeria (Saini et al., 2020), while the MONET (MONnitoring NETwork) programme has reported PCB concentrations in a semi-urban location in Sheda, Abuja, Nigeria, in addition to several locations in Africa (Klánová et al., 2009; White et al., 2021). While studies elsewhere have demonstrated both seasonal and within-conurbation spatial variability in concentrations of PCBs and BFRs in outdoor air (Currado and Harrad, 2000; Hoh and Hites, 2005; Carlson and Hites, 2005; Harner et al., 2006; Motelay-Massei et al., 2005; Harrad and Hunter, 2006), such data are limited for Africa (e.g. Katima et al, 2018), and it is plausible that the temperature-driven summer peaks in concentrations observed in more temperate locations, will not be replicated in tropical and sub-tropical African cities where seasonal temperature differences are not pronounced.

Against this backdrop, the objectives of this study are to provide baseline data on the concentrations of BFRs, NFRs, and PCBs between May 2019 and May 2020 at 8 locations in the metropolitan area of the largest city in Nigeria (Lagos). Measurement of concentrations in these samples allowed us to place the pollution levels in Lagos within an international context. Moreover, by measuring concentrations in outdoor air during up to four 3-month periods at each location, we were able to examine seasonal and spatial variation in atmospheric concentrations of BFRs, NFRs, and PCBs within a major African urban centre.

3. Materials and methods

3.1 Sample locations

Lagos, Nigeria, is an urban centre with an approximate population of 24 million, housing numerous industrial activities. For the purposes of this study, we selected 8 locations across Lagos that reflected different levels of industrialisation, population density, and other anthropogenic activities. The sampling locations are: Agege (AGG), Apapa (APP), Ikeja (IKJ), Ikorodu (IKD), Lekki (LKK), Ketu (KTU), Oshodi (OSH), and Oko baba (OKB). The geographical location of these sites is shown in Figure 1, with relevant information related to population density and putative sources of each centre provided in Table 1. In brief, AGG, APP, IKJ, and OSH are mixed industrial – residential locations, while IKD, KTU, OKB, and LKK are more residential in character, with KTU and OKB additionally potentially impacted by an inactive waste dump/landfill and large-scale wood burning activities respectively.

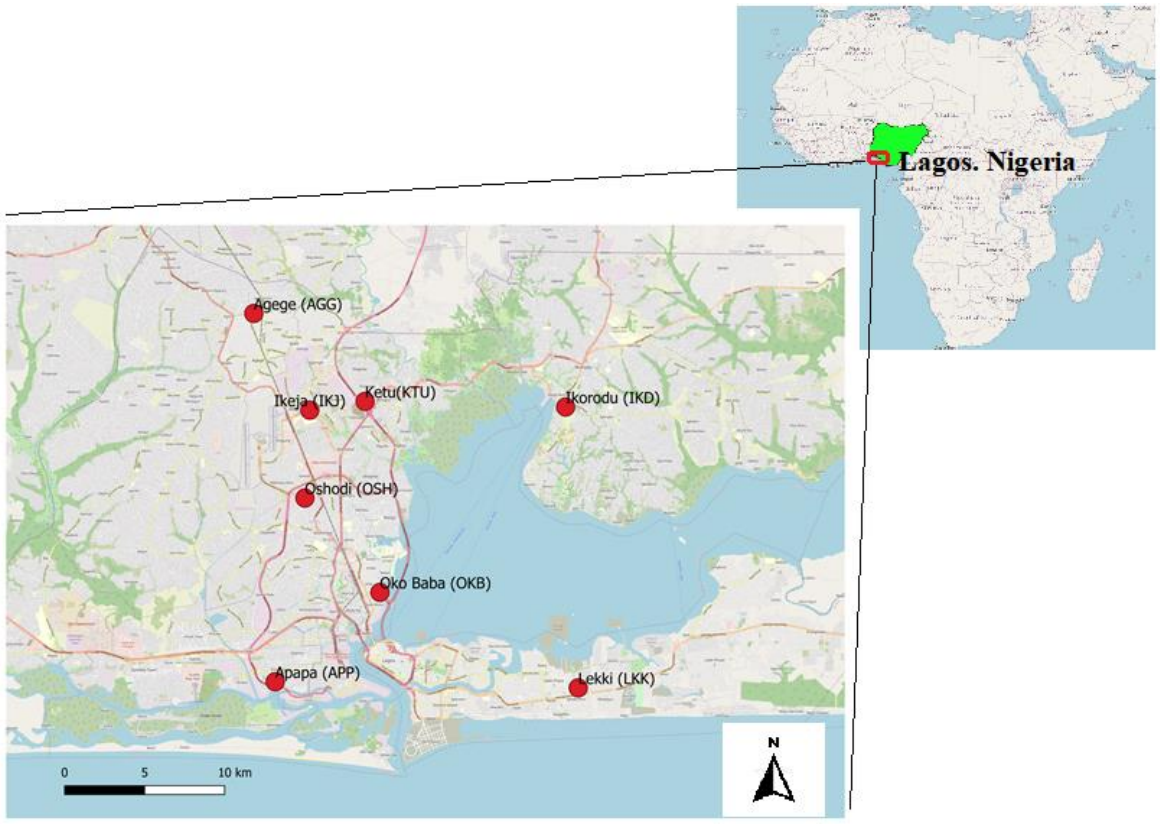


Figure 1: Sampling locations in Lagos, Nigeria

Table 1: Sample locations and attributes

	AGEGE (AGG)	APAPA (APP)	IKEJA (IKJ)	IKORODU (IKD)	KETU (KTU)	LEKKI (LKK)	OSHODI (OSH)	OKO BABA (OKB)	LAGOS (IN GENERAL)
Attributes	Mix residential and industrial areas	Mix residential and industrial areas	Mix residential and industrial area	Majorly a residential area	Majorly a residential area	Majorly a residential area	Mix residential and industrial area	Majorly a residential area	Large urban population
	Prominent abattoir	Proximate to port location	Home to Government offices	Sample location proximate to electric transformers and textile factory	High vehicular spots	Well-developed urban site	High vehicular spots	Sample location proximate to the University of Lagos	High vehicular spots
	Large local market	Large local market	State capital	-	Proximate to inactive dumpsite/landfill	-	Market Centre	Mass burning of wood wastes from local wood factories	High industrial complex
	-	-	Major industrial complex	-	-	-	Major industrial complexes	-	Wastes mostly managed by open land burning
Number of samples collected	2	3	4	4	2	3	4	1	23
Population[a]	1,415,547	715,792	888,903	944,158	1,280,646	136,394	1,554,604	862,524	24,051,762
Population density[a]	60,768.47	13,568.42	12,995.19	1,997.23	11,073.63	152.43	27,025.92	32,083.03	4,906.78

[a] Lagos Bureau of Statistics (2017)

3.2 Sampling procedures

Passive sampling of outdoor air utilised polyurethane foam (PUF) discs enclosed in stainless steel double dome housing (Klanova et al., 2009; Melymuk et al., 2011; Drage et al., 2016). Prior to deployment, PUF discs were pre-cleaned by soxhlet extraction for ~ 24 hours with HPLC grade hexane. Samplers were deployed for 90 days in each of the following periods: May-July 2019, August-October 2019, and November 2019-January 2020, and additionally for 100 days between February 2020-May 2020. At the end of each sampling event, samplers were harvested by careful removal of the PUF disc, which was wrapped in hexane-rinsed aluminium foil before sealing in a polythene zip lock bag and storing in a refrigerator at ~ 4 ˚C before transport to the University of Birmingham for chemical analysis.

3.2 Extraction and clean-up

High purity (HPLC grade) solvents and reagents were used for all analytical procedures and were purchased from Fisher Scientific (Loughborough, UK). Individual native BFR and NFR standards (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-209, DBDPE, *anti*–DP, *syn*-DP, PBT, PBBz, HBBz, α-HBCDD, β-HBCDD, and γ-HBCDD), internal (surrogate) standards (BDE-77, BDE-128, $^{13}C_{12}$-BDE-209, $^{13}C_{12}$-α-HBCDD, $^{13}C_{12}$-β-HBCDD, and $^{13}C_{12}$-γ-HBCDD) and recovery determination (syringe) standards ($^{13}C_{12}$-BDE-100 and d_{18}-γ–HBCDD) were purchased from Wellington Laboratories (Guelph, ON, Canada). Similarly, individual native PCBs (PCB-11, PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180), internal (surrogate) standards (PCB-14, PCB-34, PCB-62, PCB-119, PCB-131, PCB-147, and PCB-173), and recovery determination (syringe) standards (PCB-29 and 129) were purchased from Greyhound Chromatography (Birkenhead, Merseyside, UK). Silica gel and florisil of pesticide grade (60–100 mesh) were bought from Acros Organics (Geel, Belgium).

Prior to extraction, each PUF disk was spiked with an internal (surrogate) standard mixture comprising 20 ng of each of PCB-14, 34, 62, 119, 147, and 173 and 50 ng of each of BDE–77, BDE–128, $^{13}C_{12}$-BDE-209; $^{13}C_{12}$-α– HBCDD, $^{13}C_{12}$-β–HBCDD, and $^{13}C_{12}$-γ-HBCDD. PUF samples were subjected to pressurised liquid extraction with HPLC grade hexane using an ASE-350 instrument (Dionex, CA, USA) under the following conditions: 90 ˚C for 5 mins, static time = 4 mins, minimum cycles = 3, rinse volume = 60%, and purge time = 90 s. (Abdallah et al., 2013). The extract was evaporated to ~ 2 mL on a TurboVap®, before purification on a 9 mm i.d. glass column packed with 1 g 44% H_2SO_4-impregnated silica topped with a 1 cm layer of anhydrous sodium sulfate. The column was pre-conditioned with 5 mL hexane before introduction of the crude extract and elution with 20 mL hexane. The consequent eluate was concentrated under a stream of nitrogen using a TurboVap® solvent evaporator to ~ 0.5 mL. The crude concentrate was then extracted with three 2 mL aliquots of dimethyl sulfoxide (DMSO). The combined DMSO extracts were diluted with milli-Q water (4 mL) containing 1 g of sodium chloride, and the target compounds back-extracted into hexane (using three 4 mL rinses) (Ayris et al., 1997; Folarin et al., 2018). The combined hexane back-extracts were concentrated to incipient dryness and reconstituted into 100 µL toluene containing 20 ng (PCBs–29 and -129) and 50 ng ($^{13}C_{12}$-BDE-100 and d_{18}-γ–HBCDD) as recovery determination (or syringe) standards (RDSs) (Ayris et al., 1997; Drage et al., 2016).

3.3 Instrumental Analysis

Target FRs were analysed on a TRACE™ 1310 Gas Chromatograph interfaced with an ISQ™ single quadrupole mass spectrometer (Thermo Fisher Scientific, Austin, TX, USA) operated in electron ionisation and selected ion monitoring (SIM) mode. One µL extract was introduced via splitless injection onto a Restek Rxi-5Sil MS column (15 m x 0.25 mm x 0.25

μm film thickness). Analysis of the target PCBs was carried out on a GC Agilent HP6850/5975 MS with 1 μL of extract introduced via splitless injection onto a Restek Rxi-5Sil MS column (30 m × 0.25 mm × 0.25 μm film thickness. Analyses of both PCBs and FRs were operated under 1.5 mL/mins flow of pure Helium as carrier gas. Details of the GC oven programmes, and the ions monitored for FR and PCB analyses are provided in Table S1 and Table S2 respectively.

Once PCB and FR analysis was complete, sample extracts were reconstituted in methanol and analysed for HBCDDs. This was conducted using a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan)/ Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an ESI ion source operated in negative ionisation mode. 10 μL extract was separated on a Varian Pursuit XRS3 C18 reversed phase analytical column (150 mm x 4.6 mm i.d., 3 μm particle size). Full details of the instrumental analysis conditions have been reported previously in Abdallah et al. (2016) and Drage et al. (2020).

3.4 Quality Assurance / Quality Control

All chemicals used were of high purity-grade, with all glassware baked at 425 ˚C overnight before use. To validate the methods used, ten aliquots of standard reference material SRM-2585 (NIST organics in house dust) were analysed. Concentrations recorded were within acceptable values (Table S3). Field blanks consisting of a PUF disc transported to and from a sampling site but not exposed to air and treated as a sample were analysed. A field blank was analysed for every 5 samples making a total of 5 blanks. Where the concentration of a target compound in a field blank was between 5 and 20% of that in a sample analysed in the same batch, the corresponding sample concentration was corrected by subtraction of the concentration detected in the blank. Where concentrations in the blank

exceeded 20% of those detected in samples from the corresponding batch, data for the compound(s) affected are discarded for that sample. However, in this study none of the blanks contained concentrations of any target compounds that exceeded 20%. Blank correction was made for BDEs 47 (4 samples), 99 (7 samples), 100 (7 samples), 153 (6 samples), 154 (4 samples); 209 (10 samples); *anti*-DP (13 samples), PBT (5 samples); PCBs 11 (20 samples), 28 (11 samples), 52 (11 samples), 101 (9 samples), 118 (7 samples), 153 (4 samples), 138 (3 samples); 180 (3 samples). For most target compounds, method detection limits (MDLs) were calculated from the instrument detection limit (IDL); while for those target compounds detected in blanks, MDLs were calculated based on the average + 3 x standard deviation of the concentration detected in the blank. (Tables S6a – S9a). Average internal standard (surrogate) recoveries were between 43% and 103% (Table S4 (a-c)).

3.5 Passive Sampling Rates

A passive sampling rate (PSR) of ~ 3.5 - 4 m^3/day has been applied for calculating concentrations in outdoor air of BFRs and PCBs in recent studies using fully-sheltered PUF disc PAS (Herkert et al., 2018, White et al., 2021). More specifically, calibration of the PAS design deployed in this study yielded PSR values of 3.92 m^3/day for BFRs except for BDE-209 and DBDPE for which the PSR was 2.23 m^3/day (Drage et al., 2016). These values were thus used here for BFRs. For PCBs, we used a value of 3.5 m^3/day, consistent with studies conducted in Accra, Ghana (Bohlin-Nizzetto et al., 2020) and Birmingham, UK (Jamshidi et al., 2007) (Table S5).

3.6 Statistical Analysis

Box plots were obtained using IBM SPSS Statistics v26. Pearson correlations and scatter plots were obtained using Microsoft Excel 2019. For statistical purposes, non-detect

values were replaced by a value equivalent to the fractional detection frequency x MDL. A p value of <0.05 was considered statistically significant.

4. Results and Discussion

4.1 BFRs and PCBs in Lagos Air

4.1.1 Concentrations of PBDEs and HBCDD in Lagos Air

Table 2 and Figure 2 summarise the concentrations of $\sum_8$BDEs and HBCDD measured at the eight locations in this study. Concentrations of $\sum_8$BDEs across all samples in this study fell in the range 21 – 750 pg/m^3 (median = 100 pg/m^3). The highest concentrations were reported at mixed residential – industrial locations and those with higher population densities (APP, OSH, AGG and IKJ), while the lowest concentrations were reported at sites with relatively low population densities (IKD and LKK) (Table S6b).

Possible sources of PBDEs to the atmosphere in Lagos include ventilation of indoor air from buildings containing BFR-treated consumer products, as well as volatilisation from polluted surfaces and e-waste as a result of activities like open waste treatment including burning. We explored the relationship between PBDE contamination and population density by plotting the former against the concentrations of individual PBDE congeners against population density. As we were only able to collect samples at all of our 8 locations during the 1st sampling period, we only plotted concentrations for this period. This analysis revealed significant positive correlations for BDEs- 28, 47, 99, and 183 ($p < 0.05$) (Figure S1a). Interestingly, significant positive correlations ($p < 0.05$) were also observed for BDEs- 100, 153, 154, and 209 when the samples from the two sites with the highest population densities (AGG and OKB) were excluded as outliers (Figure S1b). Overall, our data suggest that sources of PBDEs in the Lagos atmosphere are generally diffuse and related to population density.

The arithmetic mean concentrations of individual PBDEs observed in this study (Table 2) are consistent with those reported recently for a single sample at one location in Lagos (Nigeria) (Saini et al., 2020) but - except for BDE-209 - exceed those reported in single samples in the same (GAPS) study for London, UK and Beijing, China (Saini et al., 2020), as well as those reported in an earlier study for Entebbe, Uganda (Arinaitwe et al., 2014). Compared to concentrations reported in 2016 for the West Midlands of the UK (Drage et al, 2016), those reported here for Lagos are in a similar range for BDEs 28, 47, 99, and 100, but at the lower end of the range of those detected in the West Midlands for BDEs 153, 154, 183, and 209.

HBCDD was only detected in a single sample collected at OKB (11 pg/m^3) as well as in all 3 samples at APP at concentrations ranging between 13 and 180 pg/m^3 (Table S7b). In all other samples, it was not detected. Such low concentrations of HBCDD are likely attributable to the fact that its principal application is in expanded and extruded polystyrene building insulation foam (Stubbings and Harrad, 2019), for which there is little need in tropical climates like Lagos. Interestingly, the APP sampling site is in a location close to port activities. Similar observations of elevated HBCDD concentrations at a location near a port in Chile have been reported (Rauert et al., 2018). A possible explanation may be a greater abundance of polystyrene foam containers at ports for transporting foodstuffs at cold temperatures, as such containers have been shown previously to contain HBCDD (Abdallah et al., 2018; Rani et al., 2014).

Although HBCDD was infrequently detected in our study, Table 2 shows that the range of concentrations observed where it was detected, exceed those reported for the Great Lakes in North America (Olunkunle et al., 2018), are consistent with those for Concepción, Chile (Rauert et al., 2018) and Gauteng, South Africa (Katima et al., 2018), but are at the low end of the reported range of concentrations for Birmingham (Drage et al., 2016) and China

(Hu et al., 2011).

4.1.2 Congener/diastereomer profiles of PBDEs and HBCDD in Lagos air

Similar to previous observations elsewhere (Table 2), BDE-209 is the dominant PBDE congener observed in this study with a median contribution to Σ_8PBDEs of 70%. By comparison, the median contributions of BDE-47 and BDE-99 are 14% and 7.9% respectively (Table S6d). The dominance of BDE-209 suggests that Deca-BDE has been the major PBDE formulation used in Nigeria. Meanwhile, as observed elsewhere (Harrad and Hunter, 2006), while BDE-99 is present at higher concentrations than BDE 47 in commercial Penta-BDE formulations, the higher vapour pressure of BDE-47 results in more facile volatilisation of this congener, leading to the congener pattern observed here. The % contribution of BDE-47 to $\sum_{penta}$BDEs (BDE-47, -99, -100) in this study (range 43% – 79%, median = 58%) (Table S6c) is consistent with the range (44% – 78%) reported at a variety of locations worldwide in the GAPs program (Saini et al., 2020). Other congeners targeted in this study – namely BDEs -28, -100, -153, -154, and -183 - are – while frequently detected (78-100%) (Table S6a) - minor contributors (1.1-1.7%) to Σ_8PBDEs (Table 6c).

While HBCDD was detected in only four samples from two locations, we observed far higher median contributions for α–HBCDD (81% ΣHBCDD) compared to γ–HBCDD (19 % ΣHBCDD) with β–HBCDD not detected in any sample (Table S7c). This is a reversal of the diastereomer pattern present in the technical mixture of HBCDD in which γ-HBCDD dominates, comprising > 70% ΣHBCDD (de Wit et al., 2010). A similar dominance of α-HBCDD has been reported in outdoor air from the UK West Midlands (Drage et al, 2016), which may be attributable to the higher volatility and lower octanol-air partition coefficient (K_{OA}) of α-HBCDD (log K_{OA} = 9.96) relative to β- (log K_{OA} = 10.47) and γ-HBCDD (log K_{OA} = 10.40) (Marvin et al., 2011), favouring partitioning to air of α-HBCDD, especially in hot climates.

Table 2: Comparison of concentrations of PBDEs and HBCDD in outdoor air in Lagos, Nigeria with those reported in other similar studies

Location	Location classification	Sampling period (Sample number)	Concentrations (pg/m^3) - Range (mean, median)									References
			BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	∑HBCDDs	
Lagos, Nigeria	Urban	2018 / 2019 (n=23)	<0.3 – 4.7 (1.9, 1.3) *96%	2.2 – 49 (20, 16) *100%	<1.7 – 53 (13, 11) *96%	<0.5 – 10 (2.7, 1.5) *78%	0.25 – 7.6 (1.9, 1.2) *100%	0.28 – 4.8 (1.7, 1.4) *100%	0.41 – 5.8 (1.9, 1.6) *100%	< 16 - 620 (120, 71) *96%	11 – 180 (11, 0.7) *17%	This Study
African region	Rural to urban	2001 – 2019	-	-	-	-	-	-	-	0.6 – 11	0.1 – 1.8	White et al., 2021
New York, USA	Urban	2018 (n=1**)	3.3	36	12	3.2	0.41	0.3	-	53	<dl	
London, UK	Urban	2018 (n=1**)	0.73	1.1	0.46	0.09	0.02	<dl	-	85	3.7	Saini et al., 2020
Beijing, China	Urban	2018 (n=1**)	2.3	1.7	0.71	0.1	0.35	0.15	-	48	53	
Lagos, Nigeria	Urban	2018 (n=1**)	5.1	32	18	3.8	1.7	1.4	-	64	4.7	
Gauteng, South Africa	Urban	2016 /2017 (n= 8)	<dl – 120 (31, 0.01)	<dl – 212 (145, 183)	12 – 410 (206, 201)	<dl – 94 (49, 50)	<dl – 97 (35, 22)	<dl – 103 (36, 20)	5.6 – 35 (20, 20)	83 – 154 (108, 99)	31 – 70 (50, 50)	Katima et al., 2018
Entebbe, Uganda	Urban	2008 – 2010 (n= 56)	<0.4 – 61 (2.9, 1.4)	<2.1 – 50 (9.8, 7.0)	<1.7 – 77 (4.4, 0.9)	<0.3 – 4 (0.6, 0.3)	<0.1 – 2.3 (0.4, 0.1)	<0.1 – 1.7 (0.3, 0.1)	<0.1 – 4.5 (0.8, 0.3)	<1.6 – 170 (8.3, 1.9)	<0.3 – 6.2 (0.6, 0.2)	Arinaitwe et. al., 2014
Great Lakes	Urban	2014 (n=92)	-	-	-	-	-	-	-	-	#1.7 - 5.2	Olukunle et al., 2018
Concepción, Chile	Urban	2014 (n=4)	-	-	-	-	-	-	-	-	110 - 180	Rauert et al., 2018
Birmingham, UK	Urban	2012 – 2013 (n= 8)	<0.2 - 26	< 0.3 – 31	< 0.5 -43	< 0.5 - 30	< 1.1 – 70	<0.9 – 57	< 1.5 – 57	< 2.2 – 1500	< 0.1 – 408	Drage et al., 2016

China	Urban	2008 / 2009 (n= 28)	-	-	-	-	-	-	-	-	[#]20–1800	Hu et al., 2011
Harbin, China	Urban	2007/2008 (n = 57)	0.18 – 12 (2.5, 2)	0.32 – 7.3 (2.2, 1.5)	0.16 – 3.4 (1.1, 0.9)	<dl - 2.5 (0.44, 0.28)	<dl – 2.7 (0.70, 0.47)	<dl – 1.1 (0.23, 0.13)	<dl – 8.4 (1.8, 1.1)	<dl – 320 (57, 35)	-	Qi et al., 2014

 # Range of medians *** Detection frequency** **dl detection limit** **** denotes number of locations**

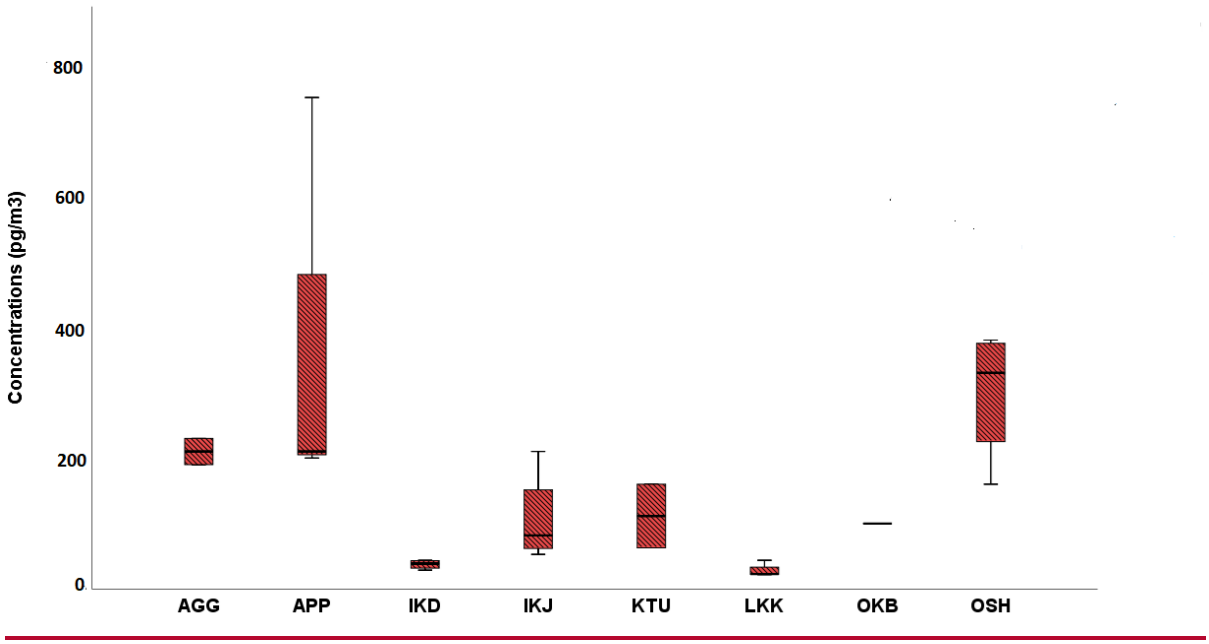


Figure 2: Concentrations of Σ_8BDEs in outdoor air samples at various locations in Lagos, Nigeria

* The boxes indicate the 25th to 75th percentiles, the whiskers indicate the max. and min. concentrations, while the black bar indicates the median concentrations.

4.1.3 Concentrations of NFRs in Lagos Air

Concentrations of NFRs observed in this study are summarised in Table 3 and Figure 3. All target NFRs were detected at each location in at least one sample, at average concentrations for all 23 samples of: DBDPE (330 pg/m^3), *anti*-DP (2.7 pg/m^3), *syn*-DP (2.1 pg/m^3), HBBz (1.4 pg/m^3), PBBz (0.88 pg/m^3), PBEB (0.56 pg/m^3), and PBT (2.3 pg/m^3). Interestingly, while $\sum_7$NFRs were observed at a higher mean concentration (330 pg/m^3) than $\sum_8$BDEs (120 pg/m^3), a similar trend in concentrations between locations was observed – i.e. APP > OSH > AGG > IKJ > KTU > OKB > IKD > LKK (Table S8b).

Plots of population density against NFR concentrations for each location in the first sampling period revealed significant positive correlations for PBBz and PBEB, but not for any other targeted NFRs (Fig S2). This suggests that emissions of most of our targeted NFRs

to the Lagos atmosphere are less diffuse and related to population density than are PBDEs. This may reflect lower use of NFRs than PBDEs currently in Lagos.

4.1.5 Relative abundance of NFRs in Lagos air

Table S8d expresses the relative abundance of our target NFRs as their % contribution to $\sum_7$NFRs. While only PBT was detected in all samples, DBDPE was overwhelmingly dominant with a median contribution of 97%. Median % contributions followed the order: DBDPE > *anti*-DP > PBT > *syn*-DP > HBBz > PBBz > PBEB. This dominance of DBDPE likely reflects its widespread use as a replacement for deca-BDE (de Wit et al., 2010). With respect to the relative abundance of the two DP isomers, the *anti*-isomer of the DP is known to be more abundant ($f_{anti\text{-DP}}$ = 0.59 – 0.80) in the technical mixture (Sverko et al., 2011). In this study, $f_{anti\text{-DP}}$ fell in the range 0.26 – 0.97 (mean = 0.68, median = 0.58) (Table S8c) consistent with values reported elsewhere, i.e.: 0.72 (Li et al., 2016), 0.69 (Vorkamp et al., 2015) and 0.67 (Schuster et al., 2021).

Table 3: Comparison of concentrations of target NFRs in outdoor air in Lagos, Nigeria, with those reported in other similar studies

Location	Location classification	Concentrations (pg/m^3) – Range (mean, median)								Reference
		Sampling period (Sample number)	PBBz	HBBz	PBT	PBEB	*syn* - DP	*anti* - DP	DBDPE	
Lagos, Nigeria	Urban	2019 / 2020 (n=23)	<0.28 – 2.4 (0.90, 0.56) *83%	<0.30 – 6.5 (1.4, 0.60) *87%	0.31 – 10 (2.3, 1.5) *100%	<0.28 – 3.2 (0.56, 0.15) *57%	<0.18 – 8.5 (2.1, 0.83) *57%	<1.8 – 8.1 (2.7, 2.2) *57%	<37 – 890 (330, 280) *87%	This Study
New York, USA	Urban	2018 (n=1**)	6.5	4.5	8.6	6.8	3.6	10.4		Saini et al., 2020
London, UK	Urban	2018 (n=1**)	2.2	1.0	3.4	3.6	0.81	0.44	-	
Beijing, China	Urban	2018 (n=1**)	7.9	0.95	8.7	0.32	0.50	0.88	-	
Lagos, Nigeria	Urban	2018 (n=1**)	4.6	9.0	7.5	0.86	16.7	11	-	
Entebbe, Uganda	Urban	2008 – 2010 (n= 56)	<0.05 – 2.3 (0.1, 0.11)	<0.09 – 1.5 (0.06, 0.05)	<0.06 – 22 (0.08, 0.03)	<0.06 – 1.8 (0.05, 0.03)	<0.05 – 4.4 (0.04, 0.03)	<0.05 – 1.4 (0.05, 0.03)	<5.9 – 220 (3.4, 3)	Arinaitwe et. al., 2014
Guangzhou, China	Urban	2014 (n= not provided)	-	19±8.8	-	6.2±10.3	4.9±4.5	5.0±4.1	316±285	Li et al., 2017
Harbin, China	Urban	2008 – 2013 (n=227)	-	-	-	-	<dl–52 (1.9, 0.46)	<dl–190 (5.8, 0.99)	-	Li et al., 2016
Chicago, USA	Urban	2005 – 2013 (n = not provided)	-	** 0.54 ± 0.08	-	0.44 ± 0.04	0.96 ± 0.15	1.8 ± 0.4	1.5 ± 0.5	Liu et al., 2016
Station Nord, Greenland	Arctic	2012 (n=13)	-	-	-	-	<1 - 9.0 (2.3)	<1 – 33 (5.2)	-	Vorkamp et al., 2015
Harbin, China	Urban	2007/2008 (n = 57)	<dl – 1.9 (0.46, 0.36)	<dl – 170 (4.8, 1.3)	0.15 -37 (6.1, 4.0)	0.02 – 1.4 (0.34, 0.23)	-	-	<dl – 370 (1.1, 0.69)	Qi et al., 2014

*** Detection frequency** **** Geometric mean ±standard deviation** **dl – detection limit** **** denotes number of locations**

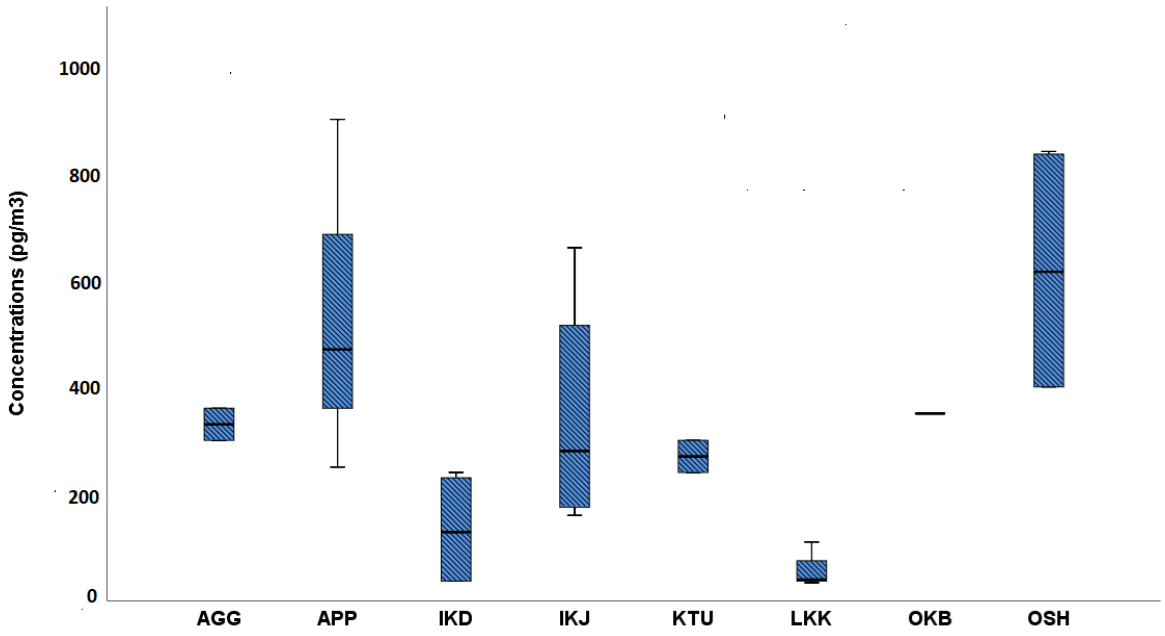


Figure 3: Concentrations of Σ_7NFRs in outdoor air samples at various locations in Lagos, Nigeria

* The boxes indicate the 25th to 75th percentiles, the whiskers indicate the max. and min. concentrations, while the black bar indicates the median concentrations.

4.1.6 Comparison of concentrations of NFRs in Lagos air with reports from other locations worldwide

The dominance of DBDPE amongst our target NFRs in this study is consistent with most other studies reporting concentrations of NFRs in outdoor air around the world (Table 3). The mean concentration of DBDPE observed in this study exceeds those reported for Chicago, USA (Liu et al., 2016), Entebbe, Uganda (Arinaitwe et al., 2014), and Harbin, China but is lower than that reported for Guangzhou (China) (Li et al., 2017). In general, concentrations of target NFRs in this study exceed those reported for Entebbe (Uganda) (Arinaitwe et al., 2014), are lower than those detected in Guangzhou (China) (Li et al., 2017), while are broadly of similar magnitude to those reported in a single sample in Lagos (Saini et al, 2020) and in other cities in Asia, Europe, and North America.

4.1.7 Concentrations of PCBs in Lagos air

Tables 4a and 4b and Figure 4 summarise the concentrations of PCBs detected in this study. Those of $\sum_7$PCBs (comprising only congeners from Aroclor sources) range between 23 – 280 pg/m^3 (median = 160 pg/m^3) while those of PCB 11 (considered to arise from non-Arochlor sources - Guo et al., 2014) range between 49 – 220 pg/m^3 (median = 100 pg/m^3). Similar to the situation for BFRs, higher concentrations of both PCB 11 and Σ_7PCBs were observed in more densely populated and urbanised settings, with the important exception of IKD where the sample location was proximate to transformer locations and a textile factory. As the production of dyes has been highlighted previously as a source of PCB 11 (Vorkamp et al., 2016); the likely use of dyes at the local textile factory is a plausible source of the elevated concentrations of this non-Aroclor congener at IKD. The lowest concentrations of both PCB 11 and Σ_7PCBs were observed at the least densely populated location (LKK) (Table S9b).

Plotting the population density of our sampling locations against the concentrations of individual PCB congeners detected at each location for the first sampling period indicated no significant correlation for any of our target PCBs (Figure S3). This suggests that unlike PBDEs and some NFRs, concentrations of PCBs in Lagos are less influenced by diffuse sources related to population density and more impacted by point source activities such as transformer leaks from electricity sub-stations and for PCB 11, activities such as the production of dyes and activities using such dyes like textile factories. Similar weak correlations between atmospheric concentrations of PCBs and population density have been previously reported (Du et al., 2009).

4.1.8 Congener profiles of PCBs in Lagos air

The dominant congener detected out of our 8 target PCBs was PCB 11, making a median contribution to ∑8PCBs of 47% (Table S9c), followed by PCB 28 (13%) and 138 (13%), with the least abundant PCB 118 (2.8%). That PCB 28 is the most abundant Aroclor congener is consistent with other reports on Africa (Bodgal et al., 2013; White et al., 2021) and is likely due to its higher vapour pressure which facilitates volatilisation compared to higher molecular weight congeners, especially in hotter climates.

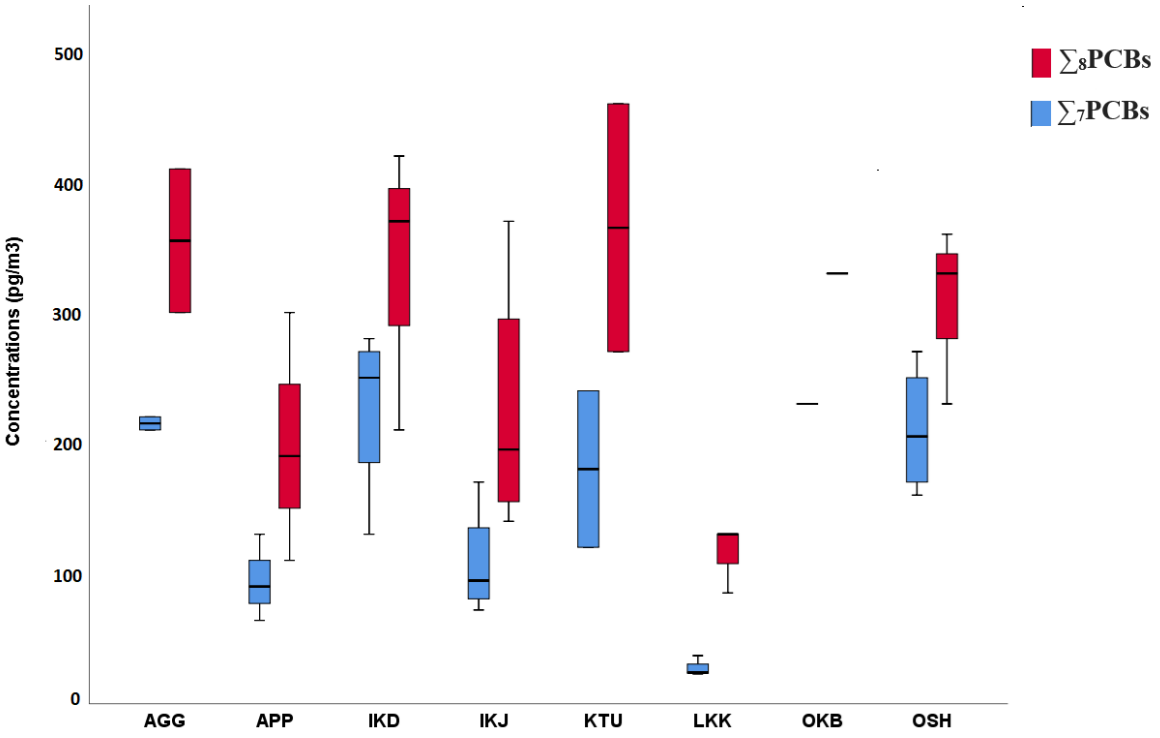


Figure 4: Concentrations of PCBs in outdoor air samples at various locations in Lagos, Nigeria – Σ_8PCBs = Σ_7PCBs + PCB-11

* The boxes indicate the 25th to 75th percentiles, the whiskers indicate the max. and min. concentrations, while the black bar indicates the median concentrations.

Table 4a: Comparison of concentrations of Aroclor-derived PCBs in outdoor air in Lagos, Nigeria with those reported in other similar studies

Location	Location classification	Sampling period (Sample number)	Concentrations (pg/m^3) – Range (mean, median)								References
			PCB-28	**PCB-52**	**PCB-101**	**PCB-118**	**PCB-138**	**PCB-153**	**PCB-180**	**Σ$_7$PCBs**	
Lagos, Nigeria	Urban	2018 / 2019 (n= 23)	7.6 – 95 (42, 34) *100%	2.9 – 52 (21, 17) *100%	2.4 – 44 (17, 15) *100%	0.5 – 26 (10, 9) *97%	3.8 – 80 (38, 35) *100%	1.8 – 43 (21, 19) *100%	0.60 – 12 (6.7, 6.9) *100%	23 – 280 (160, 160)	This study
Entebbe, Uganda	Urban	2008 – 2010 (n= 53)	-	-	-	-	-	-	-	4.4 – 48	Arinaitwe et al., 2018
Gambia	Not specified	2008 (n= 4)	-	0.8 – 18	-	-	0.9 - 6.2	-	0.4 - 2.3	30 – 130	
Ghana	Not specified	2008 (n= 5)	-	0.8 - 2.1	-	-	<dl - 2.3	-	<dl -1.1	3.1 – 12	Gioia et al., 2011
Ivory Coast	Not specified	2008 (n= 5)	-	7.0 – 20	-	-	4.9 – 20	-	1.7 - 6.5	6 – 110	
Bamako/Kati, Mali	Urban	2001 / 2008 (n= 49)	-	-	0.1 - 18	-	0.01 – 13	0.01 – 13	-	-	Garrison et al., 2014
Sheda, Nigeria	Semi-urban	2008 (n = 6)	-	-	-	-	-	-	-	**14 – 130 (15, 38)	Klánová et al., 2009
Dakar, Senegal	Urban	2008 (n = 6)	-	-	-	-	-	-	-	550 – 1300 (950, 1100)	
Africa region	Not specified	-	-	-	-	-	-	-	-	8 – 2100 (180, 84)	Bogdal et al., 2013
Canadian Great Lakes Basin	Remote to suburban	2012 (n ≅ 1300)	1.4 - 9.3 *** (4.1)	1.0 - 5.8 (2.8)	0.43 - 3.6 (1.5)	0.11 - 0.88 (0.40)	0.07 - 1.3 (0.53)	0.09 - 1.1 (0.42)	0.03 - 0.29 (0.12)	18 – 110 (55)	Shunthirasingham et al., 2016
Birmingham, UK	Urban	2003/2004 (n= 11)	-	0.4 – 33 ***(7.0)	<dl – 44 (5.5)	-	0.2 – 28 (2.9)	0.2 - 33 (3.4)	0.1 – 15 (2.0)	-	Jamshidi et al., 2007
India	Rural to urban	2006 (n= 18)	31 – 175	0.1 – 137 (27)	-	-	0.3 – 9.0 (2)	0.5 – 3.0 (2)	-	-	Zhang et al., 2008

***(66)

*** Detection frequency** **** using 98 m^3 as air volume** ***** Arithmetic mean** **dl – detection limit**

Table 4b: Comparison of Atmospheric Concentrations of PCB 11 in Lagos, Nigeria with those reported elsewhere

Location	Location classification	Sampling period (Sample number)	Mean	Median	Range	References
Lagos, Nigeria	Urban	2018 / 2019 (n= 23)	120	100	49 – 220	This study
China	Remote to urban	2016 – 2017 (n=62)	35	-	<dl – 249	Zhao et al., 2020
Northern Vietnam	Urban	2013 – 2015 (n=not specified)	-	140	68 - 300	Anh et al., 2020
Antarctica	Remote	2011 - 2014 (n = not provided)	21	-	4.8–62	Wang et al., 2017
Chicago, USA	Urban	2006/2007 (n = 184)	24	-	<dl - 140	Hu et al., 2008
Philadelphia/Camden, USA	Urban	2005 (n = 32)	-	-	* 2 – 22	Du et al., 2009
Cleveland, USA	Urban	2004 – 2007 (n = 106)	-	-	<dl - 307	Basu et al., 2009

*** using 315 m^3 as air volume dl – detection limit**

4.1.9 Comparison of concentrations of PCBs in Lagos with those reported elsewhere

Concentrations of $\sum_7$PCBs observed in this study are in the middle of the range reported in various previous studies conducted in Africa and other global studies (Table 4a). Similarly, concentrations of PCB 11 reported in this study are – while to our knowledge, the first reported for Africa - within the range reported from various studies around the world (Table 4b).

4.1.10 Seasonal variation in concentrations of BFRs and PCBs in Lagos air

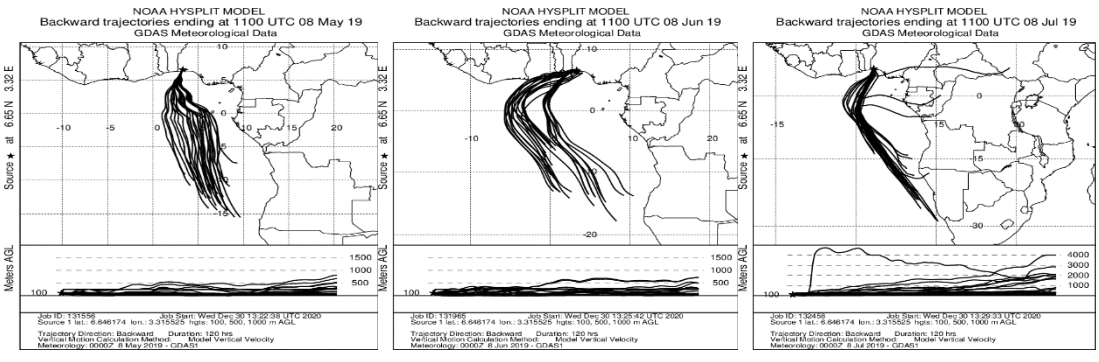
The Lagos climate is a typical tropical climate, divided mainly into the wet (rainy) season between April and September and dry season between October and May. There is little difference in temperature year-round, with the Nigerian Meteorological Agency (NIMET) reporting temperatures to average 27.3 ˚C in the wet period and 28.6 ˚C in the dry

period. It is therefore not surprising our study does not detect a seasonal peak in concentrations of PCBs in outdoor air similar to that reported in summer for North America (Carlson and Hites, 2005) and Northern Europe (Currado and Harrad, 2000) that have been attributed to higher summer temperatures facilitating volatilisation from surfaces.

4.2 Potential Sources of BFRs and PCBs to Lagos Air

Use of National Oceanic and Atmospheric Administration (NOAA) Hypslit back trajectory models (Figure 5) indicated that the air masses arriving at our sampling locations are predominantly sourced from the Atlantic Ocean within the sampling period. Coupled with the consistently low concentrations reported at the least urbanised and densely populated LKK location, this indicates that the elevated concentrations observed at the urban locations in our study, do not arise from long-range atmospheric transport but instead originate within the Lagos environment.

The presence of PBDEs and some NFRs in the Lagos atmosphere are therefore likely related to diffuse sources linked with urbanisation such as ventilation of contaminated indoor air, whereas the sources of PCBs appear more related to point activities such as historical or current leakages from electric power transformers, and industrial activities related to pigment production and use such as textile manufacture.



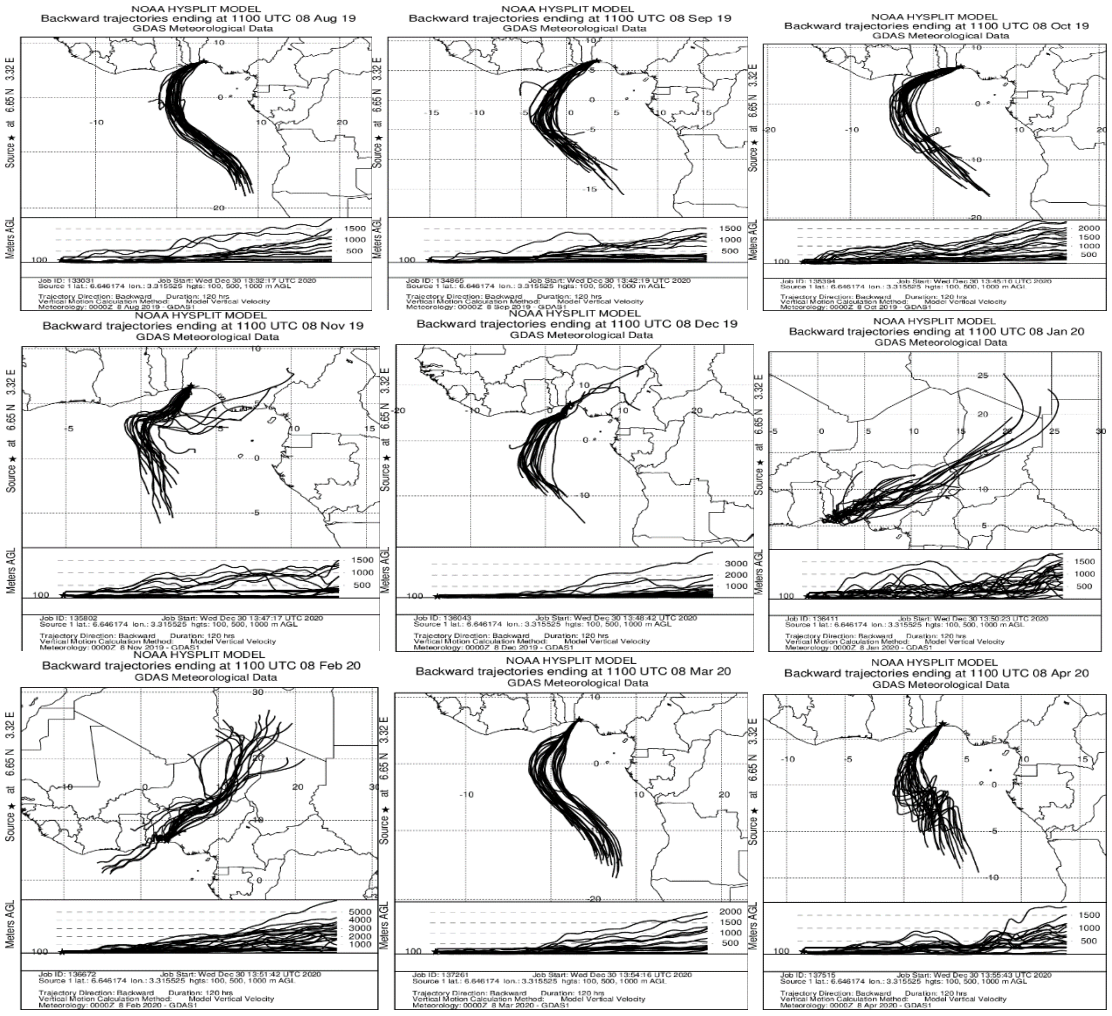


Figure 5: HYPSLIT back dispersion models (https://www.ready.noaa.gov/hypub-bin/trajasrc.pl) run at 120 hours at 100m, 500m and 1000m above ground arrival height.

5.0 Conclusions

This study examines concentrations, profiles, and potential sources of BFRs and PCBs in the atmosphere of Lagos, Nigeria. Our data reveal concentrations of our target pollutants to be comparable or higher than those reported elsewhere in the world and provide a valuable baseline against which the efficacy of actions to reduce environmental contamination with these chemicals can be evaluated. The concentrations of PCBs reported here exceed substantially those reported previously for semi-urban locations in Sheda and Abuja, Nigeria. Importantly, the non-Arochlor PCB congener 11 was reported in outdoor air for the first time in Africa.

Back trajectory analysis reveals that the observed target contaminants likely originate within Lagos itself, rather than via long-range atmospheric transport. Concentrations of PBDEs and some NFRs correlated with population density while for PCBs point sources appear to play a more important role. Combined, this suggests urbanisation and industrialisation exert important influences on BFR and PCB contamination in Lagos. The absence of any substantial seasonal variation in temperature in Lagos likely explains why no seasonal variation is observed in concentrations of any of our target contaminants.

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