Universiteit Antwerpen

This item is the archived peer-reviewed author-version of:

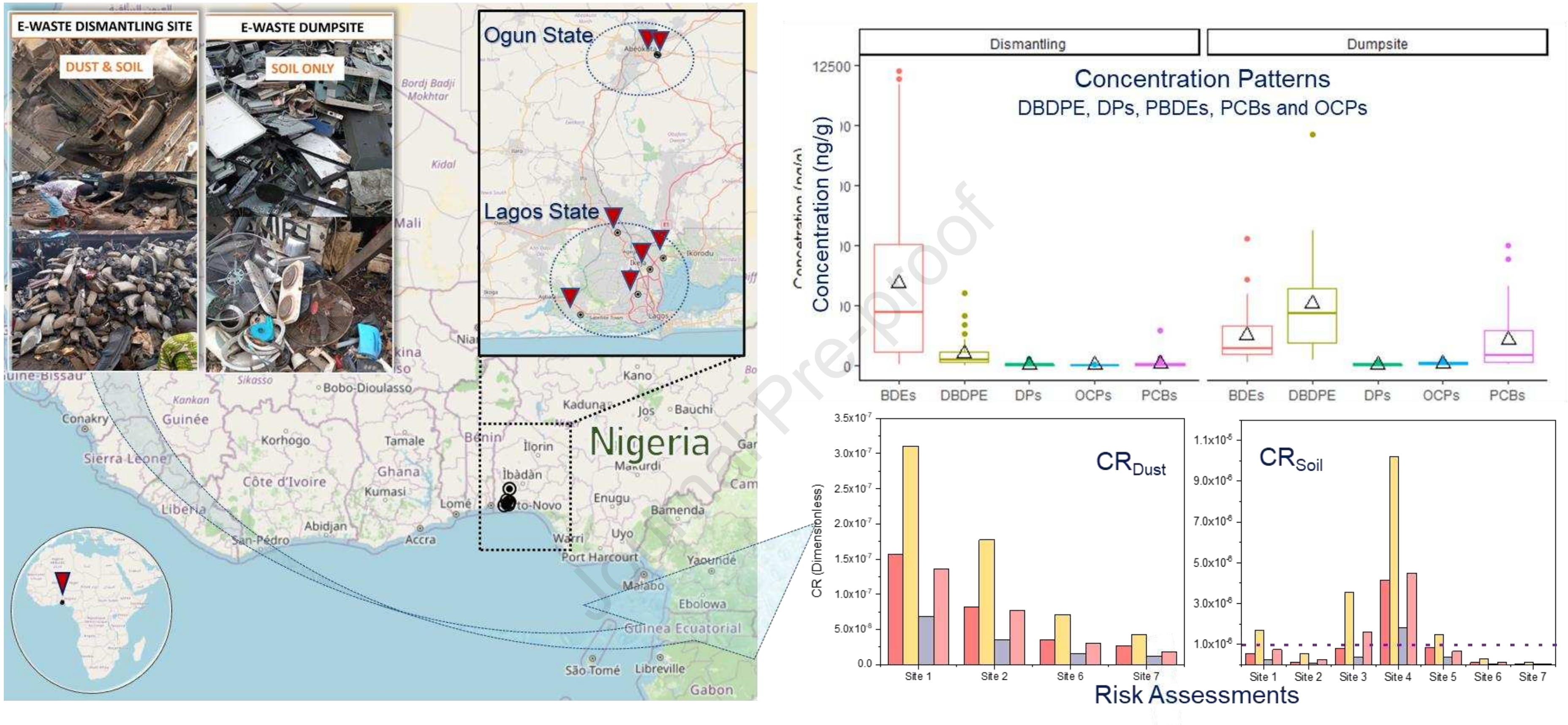
Assessment of legacy and alternative halogenated organic pollutants in outdoor dust and soil from e-waste sites in Nigeria : concentrations, patterns, and implications for human exposure

Reference:

Folarin Bilikis, Poma Giulia, Yin Shanshan, Altamirano Jorgelina, Oluseyi Temilola, Badru Gbolahan, Covaci Adrian.- Assessment of legacy and alternative halogenated organic pollutants in outdoor dust and soil from e-waste sites in Nigeria : concentrations, patterns, and implications for human exposure
Environmental pollution - ISSN 1873-6424 - 342(2024), 123032
Full text (Publisher's DOI): https://doi.org/10.1016/J.ENVPOL.2023.123032
To cite this reference: https://hdl.handle.net/10067/2028320151162165141

uantwerpen.be
Institutional repository IRUA

Graphical abstract



Journal Pre-proof

Journal Pre-proof

Assessment of legacy and alternative halogenated organic pollutants in outdoor dust and soil from e-waste sites in Nigeria: concentrations, patterns, and implications for human exposure

Bilikis T. Folarin [1, 2, 3], Giulia Poma [1], Shanshan Yin [1, 4, *], Jorgelina C. Altamirano [1, 5, 6], Temilola Oluseyi [2], Gbolahan Badru [7], Adrian Covaci [1]

[1] Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
[2] Department of Chemistry, University of Lagos, Lagos State, Nigeria
[3] Chemistry Department, Chrisland University, Ogun State, 23409, Nigeria
[4] Key Laboratory of Pollution Exposure and Health Intervention of Zhejiang Province, Interdisciplinary Research Academy (IRA), Zhejiang Shuren University, Hangzhou 310015, China
[5] Instituto Argentino de Nivología, Glaciología y Ciencias Ambientales (IANIGLA), CONICET-UNCuyo-Government of Mendoza, P.O. Box. 331 (5500), Mendoza, Argentina
[6] Universidad Nacional de Cuyo, Facultad de Ciencias Exactas y Naturales (5500) Mendoza, Argentina.
[7] Department of Geographical and Environmental Education, Lagos State University of Education, Oto-Ijanikin, Lagos State, Nigeria.

* Corresponding author: Shanshan Yin (Shanshan.Yin@uantwerpen.be and Shanshanyin@zjsru.edu.cn)

Journal Pre-proof

Abstract

E-waste is often processed informally, particularly in developing countries, resulting in the release of harmful chemicals into the environment. This study investigated the co-occurrence of selected persistent organic pollutants (POPs), including legacy and alternative halogenated flame retardants (10 polybrominated diphenyl ethers (PBDEs), decabromodiphenyl ethane (DBDPE), *syn* and *anti*-dechlorane plus (DP)), 32 polychlorinated biphenyls (PCBs) and 12 organochlorine pesticides (OCPs), in 20 outdoor dust and 49 soil samples from 7 e-waste sites in Nigeria. This study provides the first report on alternative flame retardants (DBDPE and DP) in Nigeria. The total concentration range of the selected classes of compounds was in the order: $\sum_{10}$PBDEs (44 - 12300 ng/g) > DBDPE (4.9 - 3032 ng/g) > $\sum_{2}$DP (0.7 - 278 ng/g) > $\sum_{32}$PCBs (4.9 - 148 ng/g) > $\sum_{12}$OCPs (1.9 - 25 ng/g) for dust, and DBDPE (4.9 - 9647 ng/g) > $\sum_{10}$PBDEs (90.3 - 7548 ng/g) > $\sum_{32}$PCBs (6.1 - 5025 ng/g) > $\sum_{12}$OCPs (1.9 - 250 ng/g) > $\sum_{2}$DP (2.1 - 142 ng/g) for soil. PBDEs were the major contributors to POP pollution at e-waste dismantling sites, while PCBs were the most significant contributors at e-waste dumpsites. DBDPE was found to be significantly associated with pollution at both e-waste dismantling and dumpsites. Estimated daily intake (EDI) via dust and soil ingestion and dermal adsorption routes ranged from 1.3 to 2.8 ng/kg bw/day and 0.2 to 2.9 ng/kg bw/day, respectively. In the worst-case scenario, EDI ranged from 2.9 to 10 ng/kg bw/day and 0.8 to 5.8 ng/kg bw/day for dust and soil, respectively. The obtained intake levels posed no non-carcinogenic risk, but could increase the incidence of cancer at some of the studied e-waste sites, with values exceeding the USEPA cancer risk lower limit (1.0×10^{-6}). Overall, our results suggest that e-waste sites act as emission point sources of POPs.

Keywords: e-waste dismantling sites; e-waste dumpsites; flame retardants; organochlorine pesticides; polychlorinated biphenyls; Sub-Saharan Africa

Journal Pre-proof

1. Introduction

Persistent organic pollutants (POPs) are synthetic chemicals that have been heavily produced, up to millions of tonnes by mass, and extensively used at the time they were not recognized as harmful (Li et al., 2023). However, due to their environmental persistence and toxicity, their use was restricted or completely banned under the UNEP Stockholm Convention (UNEP, 2008). POPs are a diverse group of compounds that include organochlorine pesticides (OCPs) such as hexachlorobenzene (HCB) and dichlorodiphenyltrichloroethane (DDT), and chlorinated industrial chemicals such as polychlorinated biphenyls (PCBs) (Jayaraj et al., 2016). There is growing concern about the release of HCB into the environment as a by-product of the manufacture of other chemicals and the incineration of waste (Kumar et al., 2013). Antifouling paints contain DDT and could be released during the recycling of coated e-waste devices, especially in less developed countries with lax regulations on the use of DDT (Xin et al., 2011). Due to their excellent dielectric properties, PCBs were produced commercially and used primarily in electrical equipment (Mao et al., 2020). These chemicals are subsequently released into the environment throughout the product life cycle (Folarin et al., 2018).

In addition, large amounts of brominated and chlorinated flame retardants (FRs), such as decabromodiphenyl ethane (DBDPE), dechlorane plus (DP) and polybrominated diphenyl ethers (PBDEs), have been used as additives in interior features of motor vehicles (including seats and paddings), upholstered furniture, electrical and electronic products, to increase fire resistance. These flame retardants, especially PBDEs, have been extensively used and then banned as POPs. DP has recently been added to the list of POPs (UNEP, 2023), while DBDPE is being evaluated due to its POP-like properties (de Wit et al., 2010). DBDPE is used as an alternative brominated FR, introduced as a replacement for the banned decabromobiphenyl ether (Deca-BDE) (Ali et al., 2019; Nakari and Huhtala, 2010; Schuster et al., 2021). It has now been reported to bio-transform and elicit endocrine-disrupting toxicities (Wang et al., 2019). DP has been reported to be ubiquitous in the environment, biota, and humans (Sverko et al., 2011). *In vivo* studies have shown that severe exposure to DP can cause potential health risks, such as genetic damage and oxidative stress (Li et al., 2020), neurobehavioral deficits (Chen et al., 2019), inflammatory and hepatocellular toxicity (Wu et al., 2013).

Improper disposal and processing of electronic waste (e-waste) have become significant environmental and public health issues in less developed and developing countries, where obsolete electronics and automobiles are disassembled using informal approaches (Nnorom

Journal Pre-proof

and Odeyingbo, 2020; Perkins et al., 2014). When e-waste is inappropriately handled, toxic pollutants can be released into the environment, posing a risk to both ecological and human health (Awasthi et al., 2018; Rautela et al., 2021; Shamim et al., 2015).

As known, POPs used as polymer additives in consumer goods dumped in e-waste sites can be released into the environment and be transported in a gaseous phase or added to particles from the emission source, as well as re-emitted from environmental sinks, including soil. Thus, humans can be exposed to such pollutants especially in proximity of e-waste sites through both dietary routes, including consumption of contaminated food and drinks, and non-dietary exposure routes such as accidental ingestion, dermal absorption, and or inhalation of vapour phase emissions. (An et al., 2022; Chandra Yadav et al., 2019). Non-dietary exposure to POPs is likely to be more significant in an e-waste environment, where exposure to POPs in e-waste soil can cause both acute and systemic toxicities following short-term and prolonged human exposures respectively (Szabo and Loccisano, 2012). Soils serve as both a sink for organic pollutants through wet and dry deposition, and as a secondary source of pollution through the reemission of previously deposited pollutants (Wang et al., 2012). As such, the concentration levels of POPs in soils are considered an indicator of the proximity of pollution sources and air pollution. It is therefore essential to study soil contamination with POPs to understand their fate and distribution. The relatively high lipophilicity of POPs contributes to their strong affinity for soil organic matter and the cumulative effect of deposition of air-bound pollutants (Delle Site, 2001; Safder et al., 2018).

To the best of our knowledge, among the few data that exist on the contamination status of POPs in Nigerian e-waste sites (Eze et al., 2023; Ohajinwa et al., 2019; Sindiku et al., 2015), none investigated the presence of DBDPE and DP. Environmental management and protection of human health from exposure to these harmful chemicals may therefore be difficult without adequate monitoring.

This study aims to investigate the presence of selected POPs in soil and outdoor dust samples collected from seven e-waste dismantling and dumping sites in Nigeria, to explore their source apportionment and spatial patterns, and to assess human health risks from exposure to these compounds. Overall, the study investigated the impact of environmental pollution on human health, thus contributing to the achievement of the United Nations' Sustainable Development Goals.

2.1 Materials and Methods

Journal Pre-proof

2.2 Sample collection and site information

A total of 20 outdoor surface dust samples and 49 soil samples were collected from 7 Nigerian e-waste sites between December 2021 and January 2022 (Fig. S1). Samples were obtained from two States in Nigeria, *viz.*, Lagos and Ogun State. Lagos is considered the industrial centre of Nigeria; therefore it is hypothesised to produce more e-waste than other states in Nigeria. On the other hand, Ogun is a corridor state to Lagos and may suffer from the overburden of Lagos. Composite samples were obtained using a selective-random sampling approach. Here, we selected 7 e-waste sites based on activity at the sites with a focus on e-waste areas that have not been previously researched and reported. The first 5 sites were in Lagos State and the remaining 2 in Ogun State (Fig. S1). In terms of major e-waste activity conducted at the sampling locations, four of the seven sampling locations could be regarded as e-waste dismantling sites, and the remaining three locations as e-waste dumpsites. All e-waste sites where dust was collected were e-waste dismantling sites (sites 1, 2, 6, and 7). Soil samples were collected from all the seven sites investigated in this study, three of which were dumpsites (sites 3, 4, and 5). Sample details are presented in Table S1 and Table S2. Sampling was performed according to Folarin et al. (2018). Briefly, each surface dust sample was collected using a pre-cleaned paintbrush, while soil samples were collected in the upper layer at approx. 0 – 5 cm using a hand trowel. The soil samples were air-dried overnight and passed through a 2 mm sieve. The dust and soil samples were individually wrapped in aluminium foil, stored in aluminium zip-lock bags, and transported to the laboratory at the University of Antwerp. There, the soil samples were further sieved using a 500 µm mesh sieve to obtain a soil particle size suitable for exposure assessment, while outdoor dust samples, already characterised by finer particles, were further sieved using a 180 µm mesh sieve. Additionally, one soil sample per e-waste site was further sieved at 180 µm to test the effect of soil particle size fractionation on measured POP concentrations. The final samples were stored in closed recipients at room temperature and stored in the dark before sample preparation.

2.3 Sample preparation

The sample preparation was performed according to Van den Eede et al. (2012) and Ali et al. (2012) with minor modifications. About 100 mg of dust or 500 mg of soil sample was accurately weighed in a 15 mL polypropylene vial. For soil samples, approximately 1000 mg of activated copper powder was added to the tube. Each sample was then spiked with 50 µL of the mixture of internal standard (IS) (containing CB 143 at 1000 pg/µL, ^{13}C-HCB at 100 pg/µL,

Journal Pre-proof

^{13}C-*a*-DP, ^{13}C-*s*-DP and BDE 103 at 200 pg/µL, ^{13}C-BDE 209 at 500 pg/µL) and added with 2.5 mL of *n*-hexane/acetone mixture (3:1, v/v) and 0.2 mL toluene. The sample was vortexed for 1 min, sonicated for 5 min, and centrifuged for 3 min at 3000 rpm. The supernatant was transferred to a clean 15 mL glass vial. The extraction was repeated once more with fresh solvent. The combined extracts were then evaporated under a gentle nitrogen flow to near dryness and resolubilized in 1 mL of *n*-hexane and toluene (1:1, v/v). Extracts were then clean-up using ENVI Florisil® SPE cartridges (500 mg, 3 mL, pre-conditioned with 6 mL of ethyl acetate and 6 mL n-hexane) and eluted with 12 mL n-hexane/dichloromethane (1:1, v/v). This eluate was then evaporated under a gentle nitrogen stream to about 0.5 mL before further clean-up on 1 g of acidified silica (44%, w/w) preconditioned with 6 mL of n-hexane. The sample was then eluted with 10 mL of n-hexane/dichloromethane (1:1, v/v) and subsequently evaporated to near dryness under a gentle nitrogen stream. The final eluate was reconstituted in 100 µL of isooctane with 5 ng of CB 207 (50 pg/µL) as recovery standard (RS) and transferred to an injection vial for further analysis.

2.4 Instrumental analysis

The instrumental analysis for the POPs was performed on an Agilent 6890 – 5973N in electron capture negative chemical ionization (ECNI) mode using similar analysis and quantification methods as described by Van den Eede et al. (2012). Briefly, A DB-5 column (30 m × 0.25 mm × 0.10 µm) was used for the gas chromatography and the MS was deployed in single ion monitoring (SIM) mode. For BDE 209, a separate analysis using a DB-5 column (15 m × 0.25 mm × 0.10 µm) was used for the gas chromatography on an Agilent 7000C triple quad in ECNI mode. The injector was set in solvent vent injection mode with a temperature program at 92°C, held for 0.04 min, and ramped at 700°C/min to 295°C. The GC oven program was 90°C, hold for 1.50 min, ramp at 10°C/min to 300°C, hold for 3 min, ramp at 40°C/min to 310°C, hold for 5 min. Helium was used as a carrier gas with a flow rate of 1.0 ml/min. The ion source, quadrupole, and interface temperatures were set at 250, 150, and 300°C, respectively. The quantifier and qualifier for the targeted compounds and the internal/recovery standards employed were as reported by Ali et al. (2012).

2.5 QA and QC

The analyte identification was based on relative retention times and ion chromatograms to the standards and validated by standard spikes. For monitoring potential background contamination, along with each batch of samples (n = 22), one procedural blank and one quality

Journal Pre-proof

control (spiked with 30 ng of native standard) were processed, using anhydrous sodium sulphate as a real sample. Multi-level calibrations were prepared in isooctane with good linearity ($r^2 > 0.99$) and used for quantification. Median recoveries (%) for each IS across the samples ranged between 79 and 123 %. Method limits of quantification (LOQs) were calculated using the 3σ approach, where σ represents the standard deviation of the mean value of the analyte in procedural blanks. A signal-to-noise ratio of 10 was used to estimate LOQs for analytes that were not detected in procedural blanks. The National Institute of Standards and Technology (NIST) indoor dust standard reference material (SRM 2585) was examined in duplicates (n = 4) to ensure method accuracy. Accuracy was within the acceptable % range (70-125%) except for a few PBDEs (BDE 153 (66 %), BDE 154 (57 %), and BDE 183 (139 %)), PCBs (CB 138 (68 %), CB 153 (57 %), CB 174 (62 %)), and *p,p'*-DDT (45 %). Due to a particularly low recovery of *p,p'*-DDT (< 50%), a correction factor was applied for this compound during data analysis. All compounds showed good precision, measured in terms of relative standard deviation (RSD) below 20 %, except anti-DP (38 %) and *γ*-HCH (32 %) (Table S3).

2.6 Statistical and Spatial Analysis

Statistical analyses were performed on Microsoft Excel (2016) and R version 4.2.2 for Windows. For samples with concentrations below the limit of quantification (LOQ), a value of detection frequency (DF) multiplied by LOQ was used for data analysis. Descriptive statistics was performed on Excel while t-test, analysis of variance (ANOVA), and principal component analysis (PCA) were performed using R. Our data were not normally distributed so non-parametric equivalents of the tests for difference were performed. The probability value of $p < 0.05$ was set as the level for statistical significance. Principal component analysis (PCA) was used to determine profiles, predict patterns, and identify sources of studied compounds in soil and dust samples. The first two principal components (PCs) with Eigen values above 1 were retained as the most significant factors, especially for biplot illustration. However, PC 3, with an Eigenvalue close to 1 (0.97), was also included in a discussion where needed. Factor loadings and factor scores were used to explain the patterns and profiles of the compounds.

Spatial distribution analysis was performed on ArcMap 10.3 using the Kriging spatial interpolation method. Kriging is a geostatistical interpolation technique that takes into account the degree of variation between known data points in establishing unbiased estimates in unknown regions (Thompson et al., 2012).

Journal Pre-proof

2.7 Exposure and risk assessments

Ingestion and dermal uptake of chemical compounds from the upper surface layer of soil and outdoor dust were the major identified pathways of non-dietary human exposure in the investigated e-waste sites. These two matrices (*i.e.,* surface soil and outdoor settled dust) are similar in the context of risk assessment (USEPA, 2017) and, as such, the same exposure and risk factors were employed for both matrices. The human health risks from ingestion and dermal uptake were assessed for adult e-waste workers considering both a 100% absorption fraction (worst-case scenario) and the absorption based on the calculated bio-accessible fraction of contaminants. The estimation of risk was proceeded by first determining the estimated daily intake (EDI) from exposure to contaminants in e-waste outdoor dust and soil samples followed by assessing the associated non-carcinogenic (hazard quotient, HQ) and carcinogenic (CR) health risks.

The EDI was calculated employing Eq. 1 and Eq. 2, modified from Ge et al. (2020), for dust and soil ingestion and dermal uptake, respectively.

$$EDI_{ingestion} = \frac{C_S \times IR \times CF \times ETF \times EF \times ED}{BW \times AT} \qquad \text{Eq.1}$$

$$EDI_{dermal} = \frac{C_S \times CF \times SA \times AF \times ABD \times ETF \times EF \times ED}{BW \times AT} \qquad \text{Eq. 2}$$

where C_S (mg/kg) was the concentration of the chemical in the sample (using median and the 95th percentile concentrations of the chemical to represent a medium and a worst-case scenario in studied e-waste sites); IR (mg/day) was the daily ingestion rate for soil/dust; EF (day/year) is the exposure frequency; ED (year) was the exposure duration; BW (kg) was the body weight; AT (day) was the average exposure time; ETF (hours/day), exposure time fraction, was the fraction of the day that an e-waste worker was exposed; ABD, as the fraction of contaminant absorbed dermally from soil; SA (cm^2) was the exposed skin surface area; AF (mg/cm^2/day) was the skin adherence factor; CF (dimensionless) was the conversion factor. Specific values of risk parameters employed are listed in Table S4 and Table S5.

The non-carcinogenic HQ and carcinogenic risk (CR) were estimated employing Eq. 3 and Eq. 4 respectively.

$$HQ = \frac{EDI}{RfD} \qquad \text{Eq. 3}$$

$$CR = EDI \times SFO \qquad \text{Eq. 4}$$

Journal Pre-proof

HQ was determined as the ratio between the calculated EDI and the reference dose factor (RfD) of selected compounds. HQ values equal to or greater than 1 indicate a potential exposure risk for the target population (USEPA 2017). CR was determined by multiplying the EDI by the oral slope factor (SFO), when available. Samples with CR value below 1.0×10^{-6} indicate negligible cancer risk, whereas a value between 1.0×10^{-6} and 1.0×10^{-4} suggests potential cancer risk, and a value above 1.0×10^{-4} indicates high-potential risk (EPA, 2000). Details of the selected compound bioaccessibility and their carcinogenic (SFO) and non-carcinogenic (RfD) risk factors are presented in Table S5.

3. Results and discussion

3.1 Concentrations and patterns of compounds in e-waste soil and settled outdoor dust samples

Five classes of persistent organic compounds were measured, *viz.,* PBDEs, DBDPE, DP, PCBs and OCPs. The flame retardants (PBDEs, DBDPE, and DP) were detected in almost all samples, with average DFs of 98%, 99%, and 99%, respectively, while the chlorinated POPs (PCBs and OCPs) had average DFs of 75% for PCBs and 38% for OCPs. The total concentration range of targeted classes of compounds was in the order: $\sum_{10}$PBDEs (44 - 12,300 ng/g) > DBDPE (4.9 - 3032 ng/g) > $\sum_{2}$DP (0.7 - 278 ng/g) > $\sum_{32}$PCBs (4.9 - 148 ng/g) > $\sum_{12}$OCPs (1.9 - 25 ng/g) for outdoor dust and DBDPE (4.9 - 9647 ng/g) > $\sum_{10}$PBDEs (90.3 - 7548 ng/g) > $\sum_{32}$PCBs (6.1 - 5025 ng/g) > $\sum_{12}$OCPs (1.9 - 250 ng/g) > $\sum_{2}$DP (2.1 - 142 ng/g) for soil. The percentage median contributions in dust samples were PBDEs (87%) > DBDPE (11%) > DP (0.8%) > PCBs (0.3%) > OCPs (0.1%). For soil, contributions were in the order: PBDEs (50%) > DBDPE (39%) > PCBs (8%) > DP (2%) > OCPs (1%). The median contribution of PBDEs exceeded those of other compounds for both dust and soil samples.

In the e-waste dismantling sites (sites 1, 2, 6, and 7), PBDEs exceeded other classes of compounds (Fig. 1a and 1b), whereas one of the other compounds predominated at the e-waste dumpsites (sites 3, 4 and 5). This indicates that samples from the e-waste dismantling and dumpsites significantly varied in terms of chemical compositions. A t-test was conducted to compare the concentrations of targeted compounds based on sampling location (Lagos versus Ogun), site activity (dismantling versus dumpsite), and sample type (soil versus dust). For the first descriptor (sampling location), it was observed that the concentrations of all studied compounds (except PBDEs) were significantly different, while the concentrations of PBDEs did not differ statistically between Lagos and Ogun ($p = 0.552$). As expected, e-waste samples from Lagos State, which is more densely populated and urbanized, were significantly more

Journal Pre-proof

polluted by studied compounds compared to samples from Ogun. For the second descriptor (site activity), all compounds but DP ($p = 0.504$) had significantly differnet in the concentrations between dismantling and dumpsite, confirming the variation in chemical composition in e-waste dismantling and dumpsites. Regarding sample type, the concentrations of DP and DBDPE were not statistically different between dust and soil samples, while PBDEs exhibited higher levels in dust ($p < 0.001$), and PCBs and OCPs showed higher concentrations in soil. Since the sampled outdoor dust might have been a lighter fraction of the soil redeposited on surfaces, compounds with higher volatility, like the lighter brominated flame retardants, might have volatilized and redeposited on outdoor surfaces. Furthermore, non-parametric one-way ANOVA performed to test the statistical difference in concentrations of targeted compounds in samples from all e-waste sites revealed significant concentration differences ($p < 0.05$) for DBDPE, PCBs, OCPs, PBDEs, and DP.

3.1.1 PBDEs

All analysed PBDE congeners, except for BDE 28, were found in e-waste outdoor dust samples, while five congeners (BDE 47, BDE 99, BDE 153 and 154, and BDE 209) were present in all soil samples. The median $\sum_{10}$PBDE level in dust samples (n = 20) was 3680 ng/g. A median concentration of 3050 ng/g and a range of 31 to 11450 ng/g for BDE 209 (Fig. 2a) made it the most abundant congener among the 10 PBDEs that were analysed. The median BDE 209 concentration, which was more than 10 times the concentration of the second-highest BDE (BDE 99), corresponded to 84% of the total median PBDE concentration in all dust samples. The median BDE 209 concentration obtained equates to 72% of the total median PBDE concentration in the soil samples and was more than 5 times greater than the second highest congener (BDE 99). When comparing PBDE concentrations in dust and soil samples, it appears that the higher levels found in outdoor dust may be due to the redeposition of PBDEs from soil onto surfaces, as well as pre-existing PBDEs in certain stacked e-waste products. Samples were collected from settled dust on stacked car headlights, brake lights, hoods, doors, and dashboards. Considering site-specific concentrations, PBDEs contributed approx. 90% of the overall chemical concentrations at dust e-waste dismantling sites 2, 6, and 7 compared to 72% in dismantling site 1. Whereas, for sites 1 through 7, the percentage contributions of PBDEs in soil samples were 79%, 83%, 14%, 15%, 29%, 81%, and 79%, respectively (Fig. 1a and 1b). This showed the overall dominance of PBDEs in both dust and soil samples from e-waste dismantling sites (Table S6 and S7). Whereas in dumpsites (sites 3, 4, and 5), the percentage contributions of PBDEs were below 30%. The total median concentration of all

Journal Pre-proof

PBDEs measured in dust samples was 3880, 4460, 3720, and 1790 ng/g for e-waste dismantling sites 1, 2, 6 and 7, respectively. Site 2 had the highest median value and sample D8 (JK_03), which was a settled dust sample on stacked car inner doors and linings, venders, and dashboard components, contributed the highest total PBDE value of 11,300 ng/g in site 2. For site-specific soil concentrations, the total median values of all PBDEs were 4280, 1420, 580, 480, 1360, 3720, and 1720 ng/g for sites 1 to 7 respectively (Table S8 and S9). The trend in abundance of measured PBDE congeners was similar in all dust and soil samples from e-waste dismantling sites and BDE 28 consistently had the least value. Median congener concentrations across dumpsites exhibited a slightly different trend, consistently BDE 183 which was among the least dominant congeners in the dismantling sites was found to be one of the first four congeners in the dumpsites.

In a study conducted in South China (Zheng et al., 2015) BDE 209 was found to dominate e-waste indoor dust, contributing 84% to 90% of the sum of PBDEs, with reported concentrations that ranged from 146 to 232,000 ng/g. These levels were more than an order of magnitude greater than concentrations obtained in both outdoor dust and soil samples from this study. Another study in China on PBDEs in soil samples from e-waste sites reported levels of BDE 209 that ranged from 10 to 234,000 ng/g (Ge et al., 2020). Tue et al. (2013) reported that levels of PBDEs ranged from 30 to 7900 ng/g in indoor dust samples from Vietnamese informal e-waste recycling sites. These levels were about two times lower than the PBDE concentration range reported in this study. A study by Wang et al. (2011) measured the levels of PBDEs in soil samples collected near an e-waste recycling site in South China. BDE 209 concentration range (3.2 to 284 ng/g) lower than those reported in this study was obtained (Wang et al., 2011). A study in Ghana investigated the levels of PBDEs in soil samples from a major e-waste site in Agbogbloshie and reported BDE 209 concentrations that ranged from <LOQ to 8800 ng/g (Moeckel et al., 2020). These levels were within range compared to those in soil samples from the present study.

3.1.2 DBDPE and DP

Concentrations of DBDPE in dust samples ranged from 4.9 to 3030 ng/g, with a median value of 490 ng/g. This range is lower than that of e-waste soil samples, which had DBDPE that ranged from 4.9 to 9650 ng/g and a median value of 590 ng/g. The median concentrations of DBDPE in samples from e-waste dumpsites (sites 3, 4 and 5) were 3090, 495, and 3121 ng/g, respectively (Table S8). These values exceeded the median $\sum_{10}$PBDEs obtained in these dumpsites. Median DBDPE levels of all compounds measured in sites 3 and 5 were the highest

Journal Pre-proof

at both sites (Table S8, and Fig. 1b). The dominance of DBDPE in sites 3 and 5 could be because these dumpsites harbour e-wastes that could contain more novel FRs like TVs, TV motherboards, refrigerators, microwave, kettle heater and other kitchen electronic devices unlike dumpsite 4, which is dominated by old generators and motorcycles. The median DBDPE values in the dismantling sites (sites 1,2,6, and 7) were second to PBDEs in abundance both for dust samples and soil samples (Table S6 and S7, Fig. 1a and 1b). From the results obtained for DBDPE in this study, it is possible to speculate that DBDPE contamination at e-waste facilities will continue to rise in the future, as modern e-waste is being generated, dismantled, and dumped.

Also, DP has been produced and used as a replacement for PBDEs. The sum of these two major DP isomers (*syn*- and *anti*-DP) ranged from 0.7 to 278 ng/g, with a median value of 34 ng/g in all dust. For soil, a range of 2.1 to 142 ng/g and a median of 24.1 ng/g were obtained. Higher levels of the *syn-DP* isomer were observed in dust samples, while both isomers had about the same concentrations in soil samples. The highest concentration of DP in dust and soil samples from dismantling sites was recorded in samples from dismantling site 1, while a sample from site 5 had the highest concentration of DP in e-waste dumpsite soils.

Generally, the concentrations of DP were significantly lower than those of DBDPE in both dust and soil samples. Median DP concentrations in e-waste sites ranged from 18 ng/g (site 7) to 53 ng/g (site 1) for dust samples and 5.4 ng/g (site 1) to 43 ng/g (site 7) for soil samples. Comparison of results from this study with previous related works for dust and soil samples from e-waste sites revealed a similar concentration difference, where concentrations of DBDPE are about 5 to 10 times higher than those of DP (He et al., 2017; Hoang et al., 2022; Zheng et al., 2015).

3.1.3 *PCBs*

The levels of PCBs in settled surface dust samples from e-waste sites were generally low, with % composition of less than 1% of the total classes of compounds measured in this study (Fig. 1a). The range of $\sum_{32}$PCB in all dust samples was 4.9 to 148 ng/g. The maximum concentration of dust was found in site 1. Total median concentrations of PCBs in dust were 62 ng/g, 31 ng/g, 11 ng/g, and 10 ng/g for sites 1, 2, 6 and 7, respectively (Table S9). Interestingly, levels of PCBs in soil were significantly greater than in dust ($p < 0.001$). A range of $\sum_{32}$PCB in all soil samples was 6.1 to 5025 ng/g. It could therefore be deduced that soil samples were more impacted by PCBs compared to outdoor dust in the Nigerian outdoor e-waste environment, implying that PCBs adhere more to soil compared to finer dust particles.

Journal Pre-proof

The maximum level of $\sum_{32}$PCB in soil in this study is about six times higher than 830 ng/g for $\sum_{32}$PCB reported in soil samples collected from an e-waste recycling site in Agbogbloshie, Ghana (Moeckel et al., 2020) and two and half times higher than 1960 ng/g for $\sum_{38}$PCB in soils from e-waste region in South China (Liu et al., 2013). The total median concentration of PCBs in soil samples from sites 1 through 7 were 209, 33, 405, 790, 270, 20, and 15 ng/g respectively (Table S10), while the median concentrations of $\sum_{32}$PCB in soil from the seven sites were 216, 52, 416, 2060, 361, 37, and 16 ng/g for sites 1 to 7, respectively. These concentrations correspond to a range of 3% (site 2) to 66% (site 4) of the total compound composition in the seven sites (Fig. 1). A soil sample from site 4 had the maximum $\sum_{32}$PCB concentration (5025 ng/g). Site 4 is a dumpsite that predominantly harbours old generators and motorcycles, which is likely the reason for the dominance of PCBs in this site.

Overall, hexa-CBs (CB 138 and CB 153) and hepta-CB 180 were the most abundant congeners in outdoor dust, while penta-CB 110 and tetra-CB 66 were the most predominant in soil samples from all seven sites. The predominance of hexa-CBs in the outdoor dust samples is in accordance with PCB studies in outdoor dust from urban areas in China (Wang et al., 2013). Similarly, the abundance of tetra- and penta-CBs as observed in our soil samples was reported in soils from suburban cities in Kenya (Sun et al., 2016) and urban cities in India (Chakraborty et al., 2016). This trend differs from that observed in the e-waste recycling site in Agbogbloshie, Ghana (Moeckel et al., 2020) and electrical power station in Nigeria (Folarin, Abdallah, et al., 2018), where hexa-CBs dominated. Generally, the concentrations of PCBs in samples from the present study were up to 1 to 3 orders of magnitude greater than in other studies where e-waste activities were not conducted (Jiang et al., 2011; Melnyk et al., 2015). This reveals the pollution effects that may be associated with e-waste processes and their possible implications on environmental and human health.

3.1.4 OCPs

The levels of OCPs in all soil and outdoor dust samples were generally low, with concentrations that ranged from 1.9 to 25 ng/g and 1.9 to 250 ng/g for dust and soil respectively. Results for site-specific concentrations of OCPs are presented in Tables S11 and S12. As observed for PCBs, levels of OCPs were significantly higher in soil samples ($p < 0.0001$) than in outdoor dust. PCBs and OCPs are among the earliest POPs and the availability of chemicals in soil has been reported to decrease over time (Wong et al., 2012). This may have resulted in the reduced volatility of PCBs and OCPs in this study, for soil-air exchange, and subsequently decreasing the levels of deposition of these compounds in settled outdoor dust.

Journal Pre-proof

The OCP concentrations in this study correspond to an average of approx. 0.1% and 1% of all compounds measured for dust and soil samples, respectively. The highest total median concentration of all studied OCPs per e-waste site was 113 ng/g, at site 5. Similarly, the maximum concentration of $\sum_{12}$OCP (250 ng/g) was found in a sample from site 5. DDT, followed by its transformation products (DDD > DDE), and HCB, were the OCPs that contributed the most to the $\sum_{12}$OCP in dust and soil samples. The dominance of DDT among the measured OCPs in e-waste samples could be due to its release from coated e-waste materials since the use of DDT as an antifouling agent in paints continued years after its ban (Lv et al., 2022). However, our results could not fully support this hypothesis, further studies to trace the source using isomer/congener ratios as identifiers may be warranted (Qiu and Zhu, 2010). The samples with the highest concentrations of HCB were soil samples from site 3, a dumpsite in Lagos State. The levels of HCB obtained in soil samples from this site could be associated with burning activities observed in some sessions of the dumpsite considering that HCB could be released as a by-product from combustion of e-waste materials (Weber et al., 2008).

3.2 Spatial distribution of investigated compounds in soil and settled dust

The measured concentrations of targeted compounds in outdoor dust and soil at each sampling site were analysed concerning geographic information obtained from the sampling points, including longitudes and latitudes. The interpolation method used in the spatial analysis predicted the spread of chemical concentrations in the areas adjacent to the sample sites in the two states where samples were collected, relative to known concentrations, given that these sites were representative of the region and similar sites exist throughout the region. (Fig. 3 and Fig. S2).

Significant spatial variations in compound concentrations were observed across longitudes and latitudes. This was depicted by the difference in the intensity of colours observed in the spatial maps. Overall, the concentration of targeted compounds in the north and northeast regions of Site 6 and Site 7 in Ogun State was lower than in other areas. The PBDE concentrations were predicted to be between moderately low to high concentrations in Ogun State, even though our sampling points were dominated by moderately high concentrations. In Lagos State, there were areas predicted to have very high, high, moderately high, and low concentrations of PBDEs (Fig. 3a). For DBDPE (Fig. 3b), a large part of Ogun State was predicted to have moderately low concentrations of DBDPE. In contrast, Lagos was predicted to have moderately high to very high concentrations of DBDPE. For PCBs (Fig. S2b), the spatial interpolation predictive

Journal Pre-proof

model revealed that, even though the highest concentration of PCBs was found in a dumpsite in the area surrounding Site 4, this did not translate to a significant spread of PCBs across neighbouring areas. Only a small portion of Lagos was predicted to have moderately low to moderately high concentrations of PCBs while other areas were typically predicted to be low. Concentrations of DP and OCPs were generally low in this study. However, relative to this low-concentration data, it was predicted that areas in Lagos State were dominated by higher concentrations of DP and OCPs compared to Ogun State (Fig. S2a and S2c). Similar spatial variations in the concentration of chemicals across investigated areas have been reported in previous studies (Hong et al., 2018; Liu et al., 2016; Vane et al., 2021; Zhu et al., 2018).

Among district areas, the highest concentration densities and spread of target compounds were found in Kosofe (sites 1 and 4), Ojo (site 3), and Surulere (site 5), which are urbanised and or industrialized regions in Lagos, Nigeria. POP contamination in dust tends to correlate with the level of urbanization in the sampling area (Akinrinade et al., 2020). Given the current and increasing demand for consumer goods, digital devices and consumables in African countries, it is foreseeable that these concentrations will increase shortly. Although based only on a limited number of sampling sites, the spatial results in this study could indicate that Nigeria's e-waste sites are point sources of POP emissions.

3.3 Source Apportionment

Four principal components (PCs) of the PCA could explain 100% of variations observed in the five classes of studied compounds (PBDEs, DBDPE, DP, PCBs, and OCPs), with the first two components explaining almost 70% of the total variations. Principal component 1 (PC 1) explained 48.2% while 20.4% was explained by principal component 2 (PC 2). In addition, the Eigenvalues obtained (Table S13) confirm the worth of the variability explained, with values of 2.4 for PC 1 and 1.02 for PC 2. This implies that PC 1 was able to explain close to half of the total variable worth. PBDEs accounted for the highest variability in PC 1, followed by DBDPE. For PC 2, DP, PCBs and DBDPE, in this order, accounted for over 95% of the total variation explained by PC 2. Consistently, DBDPE was among the first three contributing variables in PCs 1, 2 and 3. The high loadings of the BFRs in the PCs signify their incorporation into many e-waste products.

The PCA biplot for both observations (samples) and variables (compounds studied) are presented in Fig. 4a. The results revealed PBDEs as the most negatively correlated variable with PC 1 and DBDPE as the most positively correlated variable with PC 1. This implies that the loadings of flame retardants in the investigated e-waste environment could be associated

Journal Pre-proof

with the dismantling and dumping of materials containing PBDEs, followed by DBDPE and DP. In addition, PCBs were the most significant legacy chlorinated POPs contributor at studied e-waste sites.

To further explain the variations observed, a biplot of PC scores for both variables and samples were grouped. It was observed from grouping based on sample type (dust vs. soil, Fig. S3) that all dust samples formed a virtual cluster with PC2 values below 0, primarily driven by the dominant influence of PBDE concentrations on the observed variance. In addition, about 13 of the 20 dust samples were positively correlated with PC 2, just as PBDEs. Dust samples in this study, which were all from dismantling sites, could be said to be influenced more by PBDEs. For soil, there were no significant clusters. However, a large influence from DBDPE and partially PBDEs was observed.

There was a significant difference in the source of compounds when the samples were grouped based on activity conducted at dismantling or dumping sites (Fig. 4b). Most samples from e-waste dismantling sites were negatively correlated with PC 1, just as PBDEs, reflecting the influence of PBDEs in dismantling sites. Almost all samples from e-waste dumpsites were positively correlated with PC 1 just as PCBs, OCPs, and DBDPE, suggesting the contribution of these compounds in e-waste dumpsites. It is noteworthy that DBDPE showed a strong negative correlation with PC2 just as ca. 40% of samples from dismantling sites and 60% of samples from dumpsites, inferring a significant contribution to the sources of POPs by this compound at both e-waste dismantling and dumpsites.

For site-specific grouping (Fig. S4), it could be seen that only samples from site 4 were found to be significantly positively correlated with both PC 1 and 2, just as PCBs. The remaining two dumpsites (sites 3 and 5) showed some similarities in the source. Samples from these two sites formed a cluster with PC1 values above 0 (Fig. S5), just as PCBs, OCPs, and DBDPE. In addition, samples from both sites were negatively correlated with PC 2 (like DBDPE). This revealed that, in addition to PCBs, investigated dumpsites are majorly influenced by sources that emit DBDPE in the e-waste environment. Sites 1, 2, 6 and 7 (the dismantling sites) were found to be mostly negatively correlated with PC 1 like PBDEs, reflecting significant contributions of PBDEs in studied dismantling sites.

3.4 Effect of particle size fractionation

Previous studies indicated that concentrations may vary between different particle sizes of dust and soil samples which consequently may influence the extent of human exposure (Cao et al., 2012; Christia et al., 2021). This could be attributed to the larger surface area of the finer

Journal Pre-proof

particles compared to bigger ones. In this study, the concentrations of studied compounds were compared in seven soil samples, one sample per e-waste site, which were further sieved from 500 to 180 µm (Table S14). The results revealed significant differences between the concentrations in the two fractions for all classes of compounds, with the 180 µm fraction having a higher concentration in all seven samples. The 180 µm soil fraction was 82%, 80%, 72%, 69% and 87% of the total median concentrations of both fractions for PBDEs, DBDPE, DP, PCBs, and OCPs respectively. The results showed the significance of particle size fractionation on levels of pollutants and presumed toxic implications from exposure to contaminants in soils. Exposure and risk assessment associated with the intake of soil, presented in this study, were based on concentrations obtained using a 500 µm sieve. Therefore, there is a greater likelihood of higher risks if exposure were assessed using soil fractions with smaller particle sizes.

3.5 Human exposure and health risk assessment via oral ingestion and dermal uptake

Non-dietary exposure is important in explaining the body burden of POPs in an e-waste environment where soil and outdoor dust may have a significant impact on human exposure. The results of compound-specific daily intakes obtained in this present study are presented in Table S15 and S16 and site-specific EDIs are in Fig. 5a and b. Fig. 5c and d show the HQ levels at median concentrations and 95th percentile concentrations of studied contaminants at e-waste sites for dust and soil. A similar illustration is presented in Fig. 5d and e for CR.

Comparing results obtained for the two exposure routes assessed, ingestion was found to be statistically significant, with intake values about 8 to 10 times higher than dermal exposure. The difference obtained in our study was in accordance with previous reports (An et al., 2022; Ge et al., 2020; Sohail et al., 2018). Total median EDI (summation of ingestion and dermal exposures) of selected contaminants in outdoor dust and soil ranged from 0.00018 to 2.69 ng/kg bw/day and 0.00018 to 2.25 ng/kg bw/day respectively for 100% absorption of contaminant. Considering that not all contaminants present in the samples are bioavailable for absorption by humans, exposure was also assessed based on the bio-accessible fractions. The bio-accessible median EDI obtained for outdoor dust and soil ranged from 0.00009 to 0.13 ng/kg bw/day and 0.00009 to 1.15 ng/kg bw/day respectively. At the 95th percentile, the highest values obtained for outdoor dust were 6.7 and 1.0 ng/kg bw/day for absolute and bio-accessible exposures, respectively. The corresponding values for soil were 4.2 and 1.2 ng/kg bw/day, respectively. Overall, the absolute and bio-accessible EDI values of outdoor dust were comparable with soil.

Journal Pre-proof

For compound-specific EDI values, it was observed that the PBDEs, with BDE 209 being the highest, exceeded all other compounds. A similar trend of EDI values was observed in both dismantling and dumpsites, except dumpsite 4, where $\sum_{24}$PCBs had the highest EDI value. The OCPs consistently had the least EDI values. The corresponding bio-accessible EDI values followed a similar pattern in all dismantling sites. However, the three dumpsites (sites 3, 4, and 5) all had EDI values for $\sum_{24}$PCBs exceeding other studied compounds, including BDE 209. This could be explained by the higher concentrations of PCBs observed in dumpsites compared to levels in dismantling sites coupled with the higher bio-accessibility values of PCBs compared to PBDEs.

The HQ of BDEs 47, 99 and 153 were considered in addition to BDE 209, since these PBDE congeners have RfD values. The overall median hazard quotient values were all below 1 and ranged from 0.002 (site 6) to 0.008 (site 2) for dust and 0.002 (site 7) to 0.05 (site 4) for soil. The HQ levels at the 95th percentile were 0.01 (site 7) to 0.04 (site 2) and 0.006 (site 6) to 0.13 (site 4) for dust and soil respectively. The corresponding bio-accessible values were about 2 to 4 times lower. As shown in Fig. 5c and d, the measured concentrations of micropollutants do not pose significant non-carcinogenic risks to humans. The HQs for exposure to contaminated outdoor dust and soil samples at e-waste dismantling sites were typically in the order: $\sum_{24}$PCBs > BDE 99 > BDE 47 > BDE 209 > BDE 153 > HCB > *p,p'*-DDT > *p,p'*-DDD > *p,p'*-DDE, while a trend of $\sum_{24}$PCBs > HCB > BDE 99 > BDE 47 > BDE 209 > BDE 153 > *p,p'*-DDT > *p,p'*-DDD > *p,p'*-DDE was observed at e-waste dumpsites. Consistently, PCBs had the highest HQ values in soil samples from all sites. However, while the PBDEs followed the PCBs at e-waste dismantling sites, HCB was in second place at e-waste dumpsites. This agrees with HCB's low RfD coupled with its higher concentration in dumpsites compared to dismantling sites.

The CR at median concentrations from exposure to contaminated outdoor dust ranged from 2.6×10^{-8} (for site 7) to 1.6×10^{-7} (for site 1) while at the 95th percentile values obtained ranged from 4.2×10^{-8} (for site 7) to 3.1×10^{-7} for site 1). The corresponding bio-accessible CR values were 2 to 4 times lower than the absolute CR values, with all bio-accessible CR values between 10^{-8} to 10^{-7}. The CR values obtained for exposure to contaminated dust were all below the lower USEPA limit (1.0×10^{-6}), implying that exposure to investigated contaminants in dust only, at the e-waste sites, is not likely to cause cancer. For soil, the overall cancer risk at median levels ranged from 4.7×10^{-8} (for site 7) to 1.1×10^{-6} (for site 4). The bio-accessible levels at median concentration ranged from 2.1×10^{-8} (for site 7) to 1.8×10^{-6} (for site 4). Noteworthy is the fact that a dismantling site (site 4) had CR, at both absolute and bio-accessible levels,

Journal Pre-proof

within the USEPA CR area of concern (1.0×10^{-6} - 1.0×10^{-4}), implying the possibility of cancer from exposure to studied contaminants in this e-waste site. At 95th percentile concentration CR levels were as high as 10^{-5}.

The results revealed that three dumpsites (sites 3, 4 and 5) and one dismantling site (site 1) had CR above the lower USEPA limit (Fig. 5 d and e). Even for bio-accessible CR at 95th percentile concentrations, CR values were as high as 10^{-6}, with two sites exceeding the lower USEPA CR limit. The cancer risks associated with exposure to contaminated samples at e-waste sites were typically in the order: PCBs > BDE 209 > HCB > *p,p'*-DDT > *p,p'*-DDD > *p,p'*-DDE. Generally, PCBs had the highest carcinogenic risk levels at all sites which conformed with PCBs' highest SFO amongst studied compounds. Overall, no site had CR levels above the USEPA upper limit (1.0×10^{-4}), thus with no indication of high-potential risk.

4. Conclusions

In this study, several persistent organic pollutants were found in outdoor dust and soil samples from seven e-waste sites in two Southwestern States in Nigeria. This study also provides the first report on DBDPE and DP in Nigeria. Spatial analysis conducted revealed e-waste sites as points of diffusion of POPs, with the prediction of low to high levels of organic compounds in areas not investigated previously. Pollution at dumpsites was found to be significantly associated with the legacy chlorinated POPs, PCBs and OCPs, while the greatest contribution from PBDEs was observed at dismantling sites, implying that pollutants associated with activities at dismantling and dumpsites are likely to be different. DBDPE was found to be a significant contributor to the contamination at both e-waste dismantling and dumpsites. The effect of particle size fractionation showed that finer particles might contain higher concentrations of compounds than the rougher ones, signifying the possibility of higher health risks from exposure to contaminants in finer particles. Daily intake of contaminants at investigated e-waste environments posed no non-carcinogenic adverse effects. However, the carcinogenic risk raises concern as more than half of the investigated e-waste sites had cancer risk levels that exceeded the USEPA lower threshold.

Acknowledgements

We appreciate Mr. Olatunde Aladegba for his assistance during sample collection. This work was supported by the INTERWASTE project (grant agreement 734522) funded by the European Commission (Horizon 2020) and by the Exposome Centre of Excellence of the University of Antwerp (BOF grant, Antigoon database number 41222). SSY acknowledges a

Journal Pre-proof

FWO junior post-doc scholarship (1270521N), Start-up Fund (2021R001) and Basic Scientific Research Special Funds of Zhejiang Shuren University (2021XZ017), and the National Natural Science Foundation of China (22276166).

Supplementary Materials

Additional data for this study are provided as supplementary information, including Table S1-16, and Fig. S1-4.

Conflicts of interest

The authors declare no conflicts of interest.

Journal Pre-proof

References

Ali, N., Shahzad, K., Nazar, E., Alhakamy, N. A., Ismail, I. M. I., Rashid, M. I., and Eqani, S. A. M. A. S. (2019). New Brominated Flame Retardants in the Environment of Developing Countries. In *Electronic Waste Pollution* (pp. 21–36). Springer.

Ali, N., Van den Eede, N., Dirtu, A. C., Neels, H., and Covaci, A. (2012). Assessment of human exposure to indoor organic contaminants via dust ingestion in Pakistan. *Indoor Air*, *22*(3), 200–211. https://doi.org/https://doi.org/10.1111/j.1600-0668.2011.00757.x

An, Q., Aamir, M., Mao, S., Liu, Y., Wang, Y., Zheng, P., and Liu, W. (2022). Current pollution status, spatial features, and health risks of legacy and emerging halogenated flame retardants in agricultural soils across China. *Science of The Total Environment*, *803*, 150043. https://doi.org/https://doi.org/10.1016/j.scitotenv.2021.150043

Akinrinade, O.E., Stubbings, W., Abou-Elwafa Abdallah, M., Ayejuyo, O., Alani, R., Harrad, S., 2020. Status of brominated flame retardants, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in air and indoor dust in AFRICA: A review. *Emerging Contaminants* 6, 405-420.

Awasthi, A. K., Wang, M., Awasthi, M. K., Wang, Z., and Li, J. (2018). Environmental pollution and human body burden from improper recycling of e-waste in China: A short-review. *Environmental Pollution*, *243*, 1310–1316.

Cao, Z.-G., Yu, G., Chen, Y.-S., Cao, Q.-M., Fiedler, H., Deng, S.-B., Huang, J., and Wang, B. (2012). Particle size: A missing factor in risk assessment of human exposure to toxic chemicals in settled indoor dust. *Environment International*, *49*, 24–30. https://doi.org/https://doi.org/10.1016/j.envint.2012.08.010

Chandra Yadav, I., Devi, N. L., Li, J., and Zhang, G. (2019). Examining the role of total organic carbon and black carbon in the fate of legacy persistent organic pollutants (POPs) in indoor dust from Nepal: Implication on human health. *Ecotoxicology and Environmental Safety*, *175*, 225–235. https://doi.org/https://doi.org/10.1016/j.ecoenv.2019.03.048

Chen, X., Chen, Y., Huang, C., Dong, Q., Roper, C., Tanguay, R. L., Zhu, Y., and Zhang, Y. (2019). Neurodevelopmental toxicity assessments of alkyl phenanthrene and Dechlorane Plus co-exposure in zebrafish. *Ecotoxicology and Environmental Safety*, *180*, 762–769. https://doi.org/https://doi.org/10.1016/j.ecoenv.2019.05.066

Christia, C., Poma, G., Caballero-Casero, N., and Covaci, A. (2021). From suspect screening to target analysis: Occurrence of six newly identified compounds in indoor dust from Belgium. *Environmental Research*, *197*, 111193. https://doi.org/https://doi.org/10.1016/j.envres.2021.111193

Journal Pre-proof

Journal Pre-proof

de Wit, C. A., Herzke, D., and Vorkamp, K. (2010). Brominated flame retardants in the Arctic environment—trends and new candidates. *Science of the Total Environment*, *408*(15), 2885–2918.

Delle Site, A. (2001). Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *Journal of Physical and Chemical Reference Data*, *30*(1), 187–439.

EPA, U. (2000). Risk-based concentration table. *Philadelphia PA: United States Environmental Protection Agency, Washington DC*.

Eze, C. T., Otitoloju, A. A., Eze, O. O., Ugochukwu, T. E., Onodugo, C., Ali, A. M., Lyche, J. L., Karlsen, O. A., and Goksøyr, A. (2023). West African e-waste-soil assessed with a battery of cell-based bioassays. *Science of The Total Environment*, *856*, 159068. https://doi.org/https://doi.org/10.1016/j.scitotenv.2022.159068

Folarin, B. T., Abdallah, M. A.-E., Oluseyi, T., Olayinka, K., and Harrad, S. (2018). Concentrations of polychlorinated biphenyls in soil and indoor dust associated with electricity generation facilities in Lagos, Nigeria. *Chemosphere*, *207*, 620–625.

Folarin, B. T., Oluseyi, T. O., Oyeyiola, A. O., Olayinka, K. O., and Alo, B. I. (2018). Distribution of Polychlorinated biphenyls in Environmental samples from an electrical power station in Lagos, Nigeria. *Journal of Taibah University for Science*, *12*(6), 852–857.

Ge, X., Ma, S., Zhang, X., Yang, Y., Li, G., and Yu, Y. (2020). Halogenated and organophosphorous flame retardants in surface soils from an e-waste dismantling park and its surrounding area: Distributions, sources, and human health risks. *Environment International*, *139*, 105741.

He, C.-T., Zheng, X.-B., Yan, X., Zheng, J., Wang, M.-H., Tan, X., Qiao, L., Chen, S.-J., Yang, Z.-Y., and Mai, B.-X. (2017). Organic contaminants and heavy metals in indoor dust from e-waste recycling, rural, and urban areas in South China: Spatial characteristics and implications for human exposure. *Ecotoxicology and Environmental Safety*, *140*, 109–115. https://doi.org/https://doi.org/10.1016/j.ecoenv.2017.02.041

Hoang, A. Q., Karyu, R., Tue, N. M., Goto, A., Matsukami, H., Suzuki, G., Takahashi, S., Viet, P. H., and Kunisue, T. (2022). Comprehensive characterization of halogenated flame retardants and organophosphate esters in settled dust from informal e-waste and end-of-life vehicle processing sites in Vietnam: Occurrence, source estimation, and risk assessment. *Environmental Pollution*, 119809.

Hong, W.-J., Jia, H., Ding, Y., Li, W.-L., and Li, Y.-F. (2018). Polychlorinated biphenyls

Journal Pre-proof

(PCBs) and halogenated flame retardants (HFRs) in multi-matrices from an electronic waste (e-waste) recycling site in Northern China. *Journal of Material Cycles and Waste Management*, *20*(1), 80–90. https://doi.org/10.1007/s10163-016-0550-8

Jayaraj, R., Megha, P., and Sreedev, P. (2016). Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology*, *9*(3–4), 90–100.

Jiang, Y., Wang, X., Zhu, K., Wu, M., Sheng, G., and Fu, J. (2011). Polychlorinated biphenyls contamination in urban soil of Shanghai: level, compositional profiles and source identification. *Chemosphere*, *83*(6), 767–773.

Kumar, J. M., Kumar, S. D., Kubendran, D., and Kalaichelvan, P. T. (2013). Hexachlorobenzene-sources, remediation and future prospects. *International Journal of Current Research and Review*, *5*(1), 1.

Li, B., Chen, J., Du, Q., Wang, B., Qu, Y., and Chang, Z. (2020). Toxic effects of dechlorane plus on the common carp (Cyprinus carpio) embryonic development. *Chemosphere*, *249*, 126481. https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.126481

Li, L., Chen, C., Li, D., Breivik, K., Abbasi, G., and Li, Y.-F. (2023). What do we know about the production and release of persistent organic pollutants in the global environment? *Environmental Science: Advances*, *2*(1), 55–68.

Liu, D., Lin, T., Shen, K., Li, J., Yu, Z., and Zhang, G. (2016). Occurrence and Concentrations of Halogenated Flame Retardants in the Atmospheric Fine Particles in Chinese Cities. *Environmental Science and Technology*, *50*(18), 9846–9854. https://doi.org/10.1021/acs.est.6b01685

Liu, M., Huang, B., Bi, X., Ren, Z., Sheng, G., and Fu, J. (2013). Heavy metals and organic compounds contamination in soil from an e-waste region in South China. *Environmental Science: Processes and Impacts*, *15*(5), 919–929. https://doi.org/10.1039/C3EM00043E

Lv, Y.-Z., Luo, X.-J., Li, Q.-Q., Yang, Y., Zeng, Y.-H., and Mai, B.-X. (2022). A new insight into the emission source of DDT in indoor environment from rural area of South China and comprehensive human health exposure assessment. *Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-022-24743-6

Mao, S., Zhang, G., Li, J., Geng, X., Wang, J., Zhao, S., Cheng, Z., Xu, Y., Li, Q., and Wang, Y. (2020). Occurrence and sources of PCBs, PCNs, and HCB in the atmosphere at a regional background site in east China: Implications for combustion sources. *Environmental Pollution*, *262*, 114267.

Melnyk, A., Dettlaff, A., Kuklińska, K., Namieśnik, J., and Wolska, L. (2015). Concentration

Journal Pre-proof

and sources of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in surface soil near a municipal solid waste (MSW) landfill. *Science of the Total Environment*, *530*, 18–27.

Moeckel, C., Breivik, K., Nøst, T. H., Sankoh, A., Jones, K. C., and Sweetman, A. (2020). Soil pollution at a major West African E-waste recycling site: Contamination pathways and implications for potential mitigation strategies. *Environment International*, *137*, 105563. https://doi.org/https://doi.org/10.1016/j.envint.2020.105563

Nakari, T., and Huhtala, S. (2010). In vivo and in vitro toxicity of decabromodiphenyl ethane, a flame retardant. *Environmental Toxicology*, *25*(4), 333–338.

Nnorom, I. C., and Odeyingbo, O. A. (2020). *14 - Electronic waste management practices in Nigeria* (M. N. V. Prasad, M. Vithanage, and A. B. T.-H. of E. W. M. Borthakur (eds.); pp. 323–354). Butterworth-Heinemann. https://doi.org/https://doi.org/10.1016/B978-0-12-817030-4.00014-0

Ohajinwa, C. M., Van Bodegom, P. M., Xie, Q., Chen, J., Vijver, M. G., Osibanjo, O. O., and Peijnenburg, W. J. G. M. (2019). Hydrophobic Organic Pollutants in Soils and Dusts at Electronic Waste Recycling Sites: Occurrence and Possible Impacts of Polybrominated Diphenyl Ethers. In *International Journal of Environmental Research and Public Health* (Vol. 16, Issue 3). https://doi.org/10.3390/ijerph16030360

Perkins, D. N., Drisse, M.-N. B., Nxele, T., and Sly, P. D. (2014). E-waste: a global hazard. *Annals of Global Health*, *80*(4), 286–295.

Qiu, X., Zhu, T., 2010. Using the o,p'-DDT/p,p′-DDT ratio to identify DDT sources in China. *Chemosphere* 81, 1033-1038.

Rautela, R., Arya, S., Vishwakarma, S., Lee, J., Kim, K.-H., and Kumar, S. (2021). E-waste management and its effects on the environment and human health. *Science of the Total Environment*, *773*, 145623.

Safder, U., Nam, K., Kim, D., Shahlaei, M., and Yoo, C. (2018). Quantitative structure-property relationship (QSPR) models for predicting the physicochemical properties of polychlorinated biphenyls (PCBs) using deep belief network. *Ecotoxicology and Environmental Safety*, *162*, 17–28.

Schuster, J. K., Harner, T., and Sverko, E. (2021). Dechlorane Plus in the Global Atmosphere. *Environmental Science and Technology Letters*, *8*(1), 39–45. https://doi.org/10.1021/acs.estlett.0c00758

Shamim, A., Mursheda, A. K., and Rafiq, I. (2015). E-waste trading impact on public health and ecosystem services in developing countries. *J Waste Resour*, *5*(4), 1–18.

Journal Pre-proof

Sindiku, O., Babayemi, J., Osibanjo, O., Schlummer, M., Schluep, M., Watson, A., and Weber, R. (2015). Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in e-waste polymers in Nigeria. *Environmental Science and Pollution Research*, *22*(19), 14489–14501. https://doi.org/10.1007/s11356-014-3266-0

Sohail, M., Eqani, S. A. M. A. S., Podgorski, J., Bhowmik, A. K., Mahmood, A., Ali, N., Sabo-Attwood, T., Bokhari, H., and Shen, H. (2018). Persistent organic pollutant emission via dust deposition throughout Pakistan: spatial patterns, regional cycling and their implication for human health risks. *Science of the Total Environment*, *618*, 829–837.

Sverko, E., Tomy, G. T., Reiner, E. J., Li, Y.-F., McCarry, B. E., Arnot, J. A., Law, R. J., and Hites, R. A. (2011). Dechlorane Plus and Related Compounds in the Environment: A Review. *Environmental Science and Technology*, *45*(12), 5088–5098. https://doi.org/10.1021/es2003028

Szabo, D.T., Loccisano, A.E., 2012. POPs and Human Health Risk Assessment, Dioxins and Health, pp. 579-618.

Thompson, J. A., Roecker, S., Grunwald, S., and Owens, P. R. (2012). *Chapter 21 - Digital Soil Mapping: Interactions with and Applications for Hydropedology* (H. B. T.-H. Lin (ed.); pp. 665–709). Academic Press. https://doi.org/https://doi.org/10.1016/B978-0-12-386941-8.00021-6

Tue, N. M., Takahashi, S., Suzuki, G., Isobe, T., Viet, P. H., Kobara, Y., Seike, N., Zhang, G., Sudaryanto, A., and Tanabe, S. (2013). Contamination of indoor dust and air by polychlorinated biphenyls and brominated flame retardants and relevance of non-dietary exposure in Vietnamese informal e-waste recycling sites. *Environment International*, *51*, 160–167. https://doi.org/https://doi.org/10.1016/j.envint.2012.11.006

Van den Eede, N., Dirtu, A. C., Ali, N., Neels, H., and Covaci, A. (2012). Multi-residue method for the determination of brominated and organophosphate flame retardants in indoor dust. *Talanta*, *89*, 292–300. https://doi.org/https://doi.org/10.1016/j.talanta.2011.12.031

Vane, C. H., Kim, A. W., Beriro, D., Cave, M. R., Lopes Dos Santos, R. A., Ferreira, A. M. P. J., Collins, C., Lowe, S. R., Nathanail, C. P., and Moss-Hayes, V. (2021). Persistent Organic Pollutants in Urban Soils of Central London, England, UK: Measurement and Spatial Modelling of Black Carbon (BC), Petroleum Hydrocarbons (TPH), Polycyclic Aromatic Hydrocarbons (PAH) and Polychlorinated Biphenyls (PCB). *Advances in Environmental and Engineering Research*, *2*(2).

Wang, W., Huang, M.-J., Wu, F.-Y., Kang, Y., Wang, H.-S., Cheung, K. C., and Wong, M. H.

Journal Pre-proof

(2013). Risk assessment of bioaccessible organochlorine pesticides exposure via indoor and outdoor dust. *Atmospheric Environment*, *77*, 525–533. https://doi.org/https://doi.org/10.1016/j.atmosenv.2013.04.071

Wang, X., Ling, S., Guan, K., Luo, X., Chen, L., Han, J., Zhang, W., Mai, B., and Zhou, B. (2019). Bioconcentration, biotransformation, and thyroid endocrine disruption of decabromodiphenyl ethane (Dbdpe), a novel brominated flame retardant, in zebrafish larvae. *Environmental Science and Technology*, *53*(14), 8437–8446.

Wang, X., Sheng, J., Gong, P., Xue, Y., Yao, T., and Jones, K. C. (2012). Persistent organic pollutants in the Tibetan surface soil: spatial distribution, air–soil exchange and implications for global cycling. *Environmental Pollution*, *170*, 145–151.

Wang, Y., Luo, C., Li, J., Yin, H., Li, X., and Zhang, G. (2011). Characterization of PBDEs in soils and vegetations near an e-waste recycling site in South China. *Environmental Pollution*, *159*(10), 2443–2448. https://doi.org/https://doi.org/10.1016/j.envpol.2011.06.030

Weber, R., Gaus, C., Tysklind, M., Johnston, P., Forter, M., Hollert, H., Heinisch, E., Holoubek, I., Lloyd-Smith, M., and Masunaga, S. (2008). Dioxin-and POP-contaminated sites—contemporary and future relevance and challenges. *Environmental Science and Pollution Research*, *15*(5), 363–393.

Wong, F., Kurt-Karakus, P., and Bidleman, T. F. (2012). Fate of Brominated Flame Retardants and Organochlorine Pesticides in Urban Soil: Volatility and Degradation. *Environmental Science and Technology*, *46*(5), 2668–2674. https://doi.org/10.1021/es203287x

Wu, Z. Y., Huang, L., Gao, Y. L., Guo, Q. H., and Sun, Y. Q. (2013). The Effects of Dechlorane Plus on Toxicity. *Applied Mechanics and Materials*, *380–384*, 4163–4166. https://doi.org/10.4028/www.scientific.net/AMM.380-384.4163

Xin, J., Liu, X., Liu, W., Jiang, L., Wang, J., and Niu, J. (2011). Production and use of DDT containing antifouling paint resulted in high DDTs residue in three paint factory sites and two shipyard sites, China. *Chemosphere*, *84*(3), 342–347.

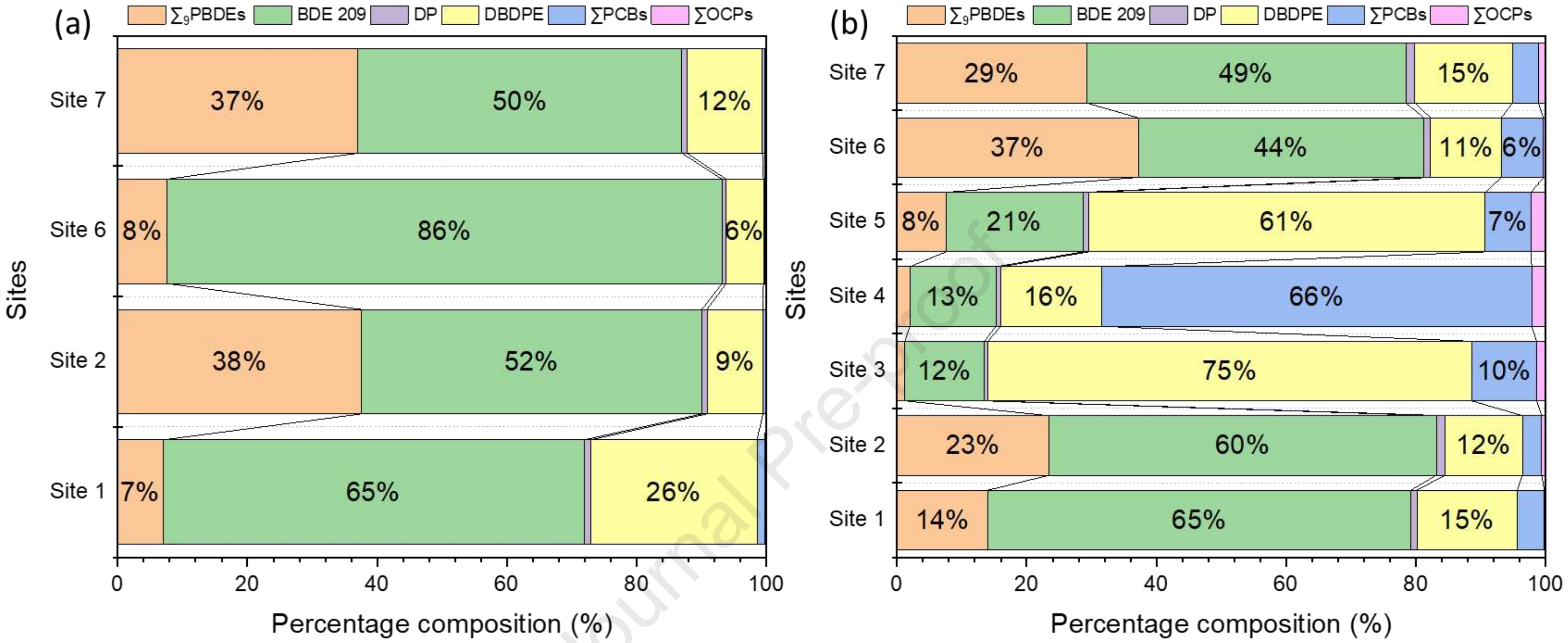
Zheng, X., Xu, F., Chen, K., Zeng, Y., Luo, X., Chen, S., Mai, B., and Covaci, A. (2015). Flame retardants and organochlorines in indoor dust from several e-waste recycling sites in South China: Composition variations and implications for human exposure. *Environment International*, *78*, 1–7. https://doi.org/https://doi.org/10.1016/j.envint.2015.02.006

Zhu, H., Sun, H., Yao, Y., Gan, Z., Wang, Y., and Kannan, K. (2018). Legacy and alternative brominated flame retardants in outdoor dust and pine needles in mainland China: Spatial

Journal Pre-proof

trends, dust-plant partitioning and human exposure. *Environmental Pollution*, *243*, 758–765. https://doi.org/https://doi.org/10.1016/j.envpol.2018.08.097

Journal Pre-proof



Journal Pre-proof

Fig. 1. Percentage composition of the investigated compounds in dust (a) and soil (b) collected from e-waste sites in Nigeria. In this figure, proportional contributions > 5% are labelled. In this figure, BDE 209 is considered to be a single component contributor to the total concentration in the samples.

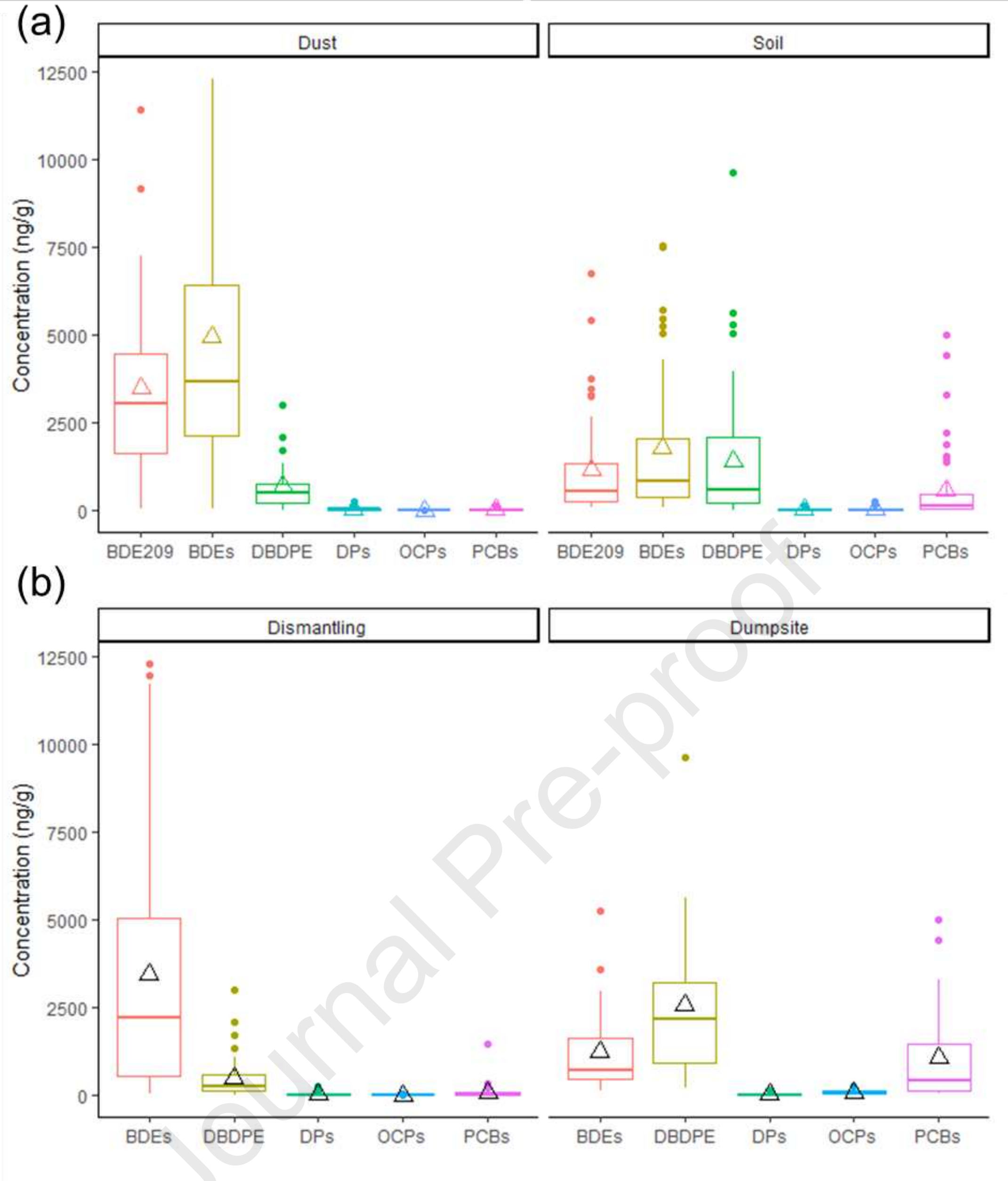


Fig. 2. Box plots of the investigated compounds in outdoor dust versus soil (a) and in dismantling sites versus dumpsites (b). In this figure, the boxplots represent the 25th to 75th percentiles of the concentrations, the triangle represents the mean of the data set, while the line in the box represents the median. The upper and lower whiskers represent the 5th and 95th percentiles of the concentrations in the data set, respectively.

Journal Pre-proof

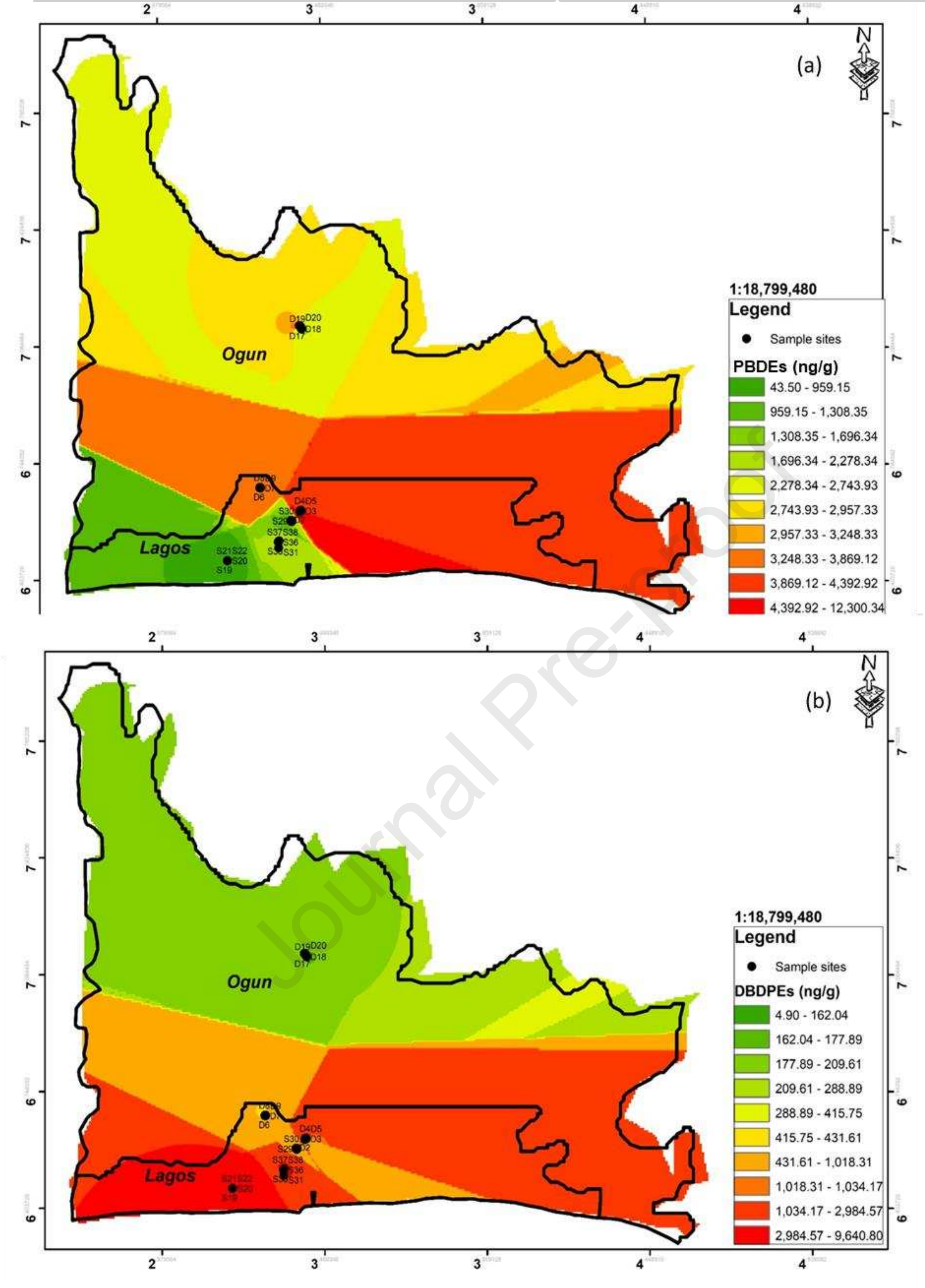
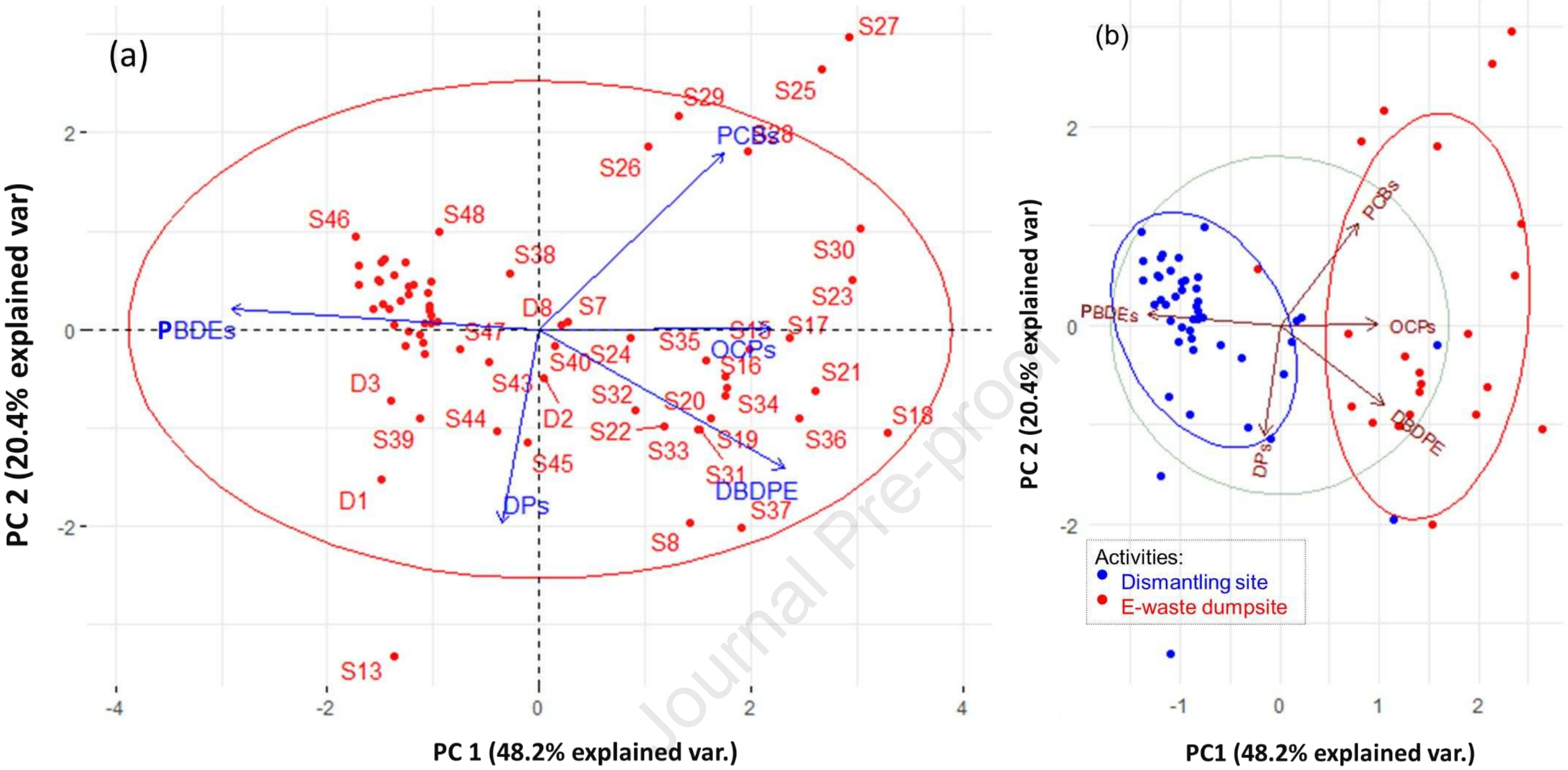


Fig. 3. Spatial maps of PBDEs (a) and DBDPE (b) in dust and soil samples

Journal Pre-proof



Journal Pre-proof

Fig. 4. PCA Biplot (a) e-waste samples and variables (b) e-waste sample grouped based on activity.

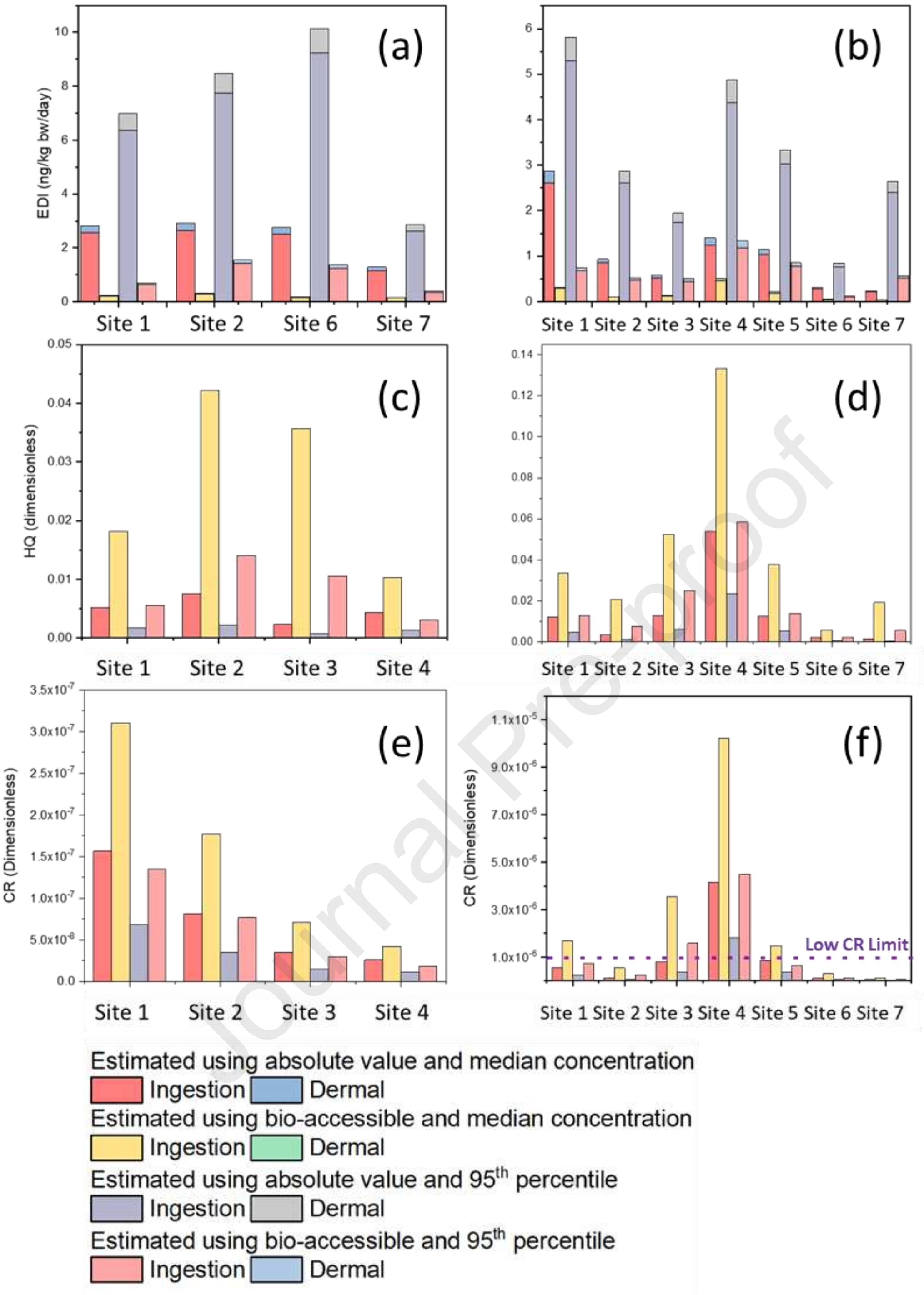


Fig. 5. Estimated daily intake (EDI) (ng/kg bw/day) (a) dust (b) soil; HQs in (c) dust (d) soil; CR in (e) dust (f) soil at absolute and bio-accessible median & 95th percentile concentrations for studied contaminants in investigated e-waste sites.

Journal Pre-proof

Highlights

- First report on DBDPE and DPs in dust and soil from Nigeria.
- POPs composition varies at dismantling and dumpsites.
- Results indicated that e-waste sites are points for diffusion of POPs.
- Particle size fractionation of soil affects POPs concentration.
- Cancer risk levels exceeded the lower USEPA threshold at some e-waste sites.

Journal Pre-proof

CRediT author statement

Bilikis Folarin: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Visualization.

Giulia Poma: Conceptualization, Methodology, Writing - Original Draft, Writing - Review & Editing.

Shanshan Yin: Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization, Funding acquisition.

Jorgelina Altamirano: Methodology, Writing - Review & Editing.

Temilola Oluseyi: Conceptualization, Writing - Review & Editing.

Gbolahan Badru: Formal analysis, Writing –Review and editing.

Adrian Covaci: Conceptualization, Methodology, Resources, Writing - Review & Editing, Supervision, Project Administration, Funding acquisition.

Journal Pre-proof

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof