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Halogenated flame retardants in atmospheric particles from a North African coastal city (Bizerte, Tunisia): Pollution characteristics and human exposure

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ABSTRACT

In the present study, atmospheric particle samples were collected between September 2015 and February 2016 from Bizerte city (Tunisia) to investigate the occurrence, potential sources and impacts of a range of flame retardants (FRs), including hexabromocyclododecane diastereoisomers (HBCDDs), new halogenated flame retardants (NHFRs), as well as methoxylated polybrominated diphenyl ethers (MeO-BDEs). Among 19 examined compounds, 9 congeners (α -HBCDD, β -HBCDD, γ -HBCDD, HBB, DBDPE, *syn*-DP, *anti*-DP, 2'-MeO-BDE-68 and 6-MeO-BDE-47) were detected in atmospheric particles at different levels and frequencies. Overall, the average concentration of NHFRs (1.53 pg m^{-3}) was 1.5 and 51 folds higher than that of HBCDDs (1.04 pg m^{-3}) and MeO-BDEs (0.03 pg m^{-3}), respectively. By comparison with other areas of the world, NHFRs and HBCDDs in Bizerte were at medium pollution level, while MeO-BDEs were at lower levels. No significant correlations were found between NHFR, HBCDD and MeO-BDE concentrations, suggesting different sources related on one hand to the biogenic origin of MeO-BDE, and on the other hand to various types and utilisations of imported NHFR- and HBCDD-containing products, as Tunisia does not manufacture FRs. DP and HBCDD diastereoisomer profiles appeared to be divergent from their commercial products, pointing out that a complex degradation or stereoselective transformation processes occurring in ambient air around Bizerte city. The estimated daily human exposure dose (DED) to particle-bound HBCDDs, NHFRs and MeO-BDEs via outdoor air inhalation was generally at low levels. Hence, this study reports for the first time the occurrence and potential impact of HBCDDs, NHFRs and MeO-BDEs in atmospheric particles from North Africa.

1. Introduction

Flame retardants (FRs) include a diverse group of chemicals, which are added to consumer and industrial products, such as furnitures, electronic and electrical equipments, textiles, plastics, antifoaming agents, hydraulic fluids, construction materials, to prevent and minimise fire hazards (Alaee et al., 2003; Covaci et al., 2011; Chen et al., 2019). Polybrominated diphenyl ethers (PBDEs), as well as 1,2,5,6,9,10-hexabromocyclododecane diastereoisomers (HBCDDs) (used mainly in building insulation) and tetrabromobisphenol A (TBBPA) have historically been the most widely used brominated flame-retardants (BFRs) (Covaci et al., 2011; UNEP, 2015; Rauert et al., 2018). However, PBDEs and HBCDDs have been banned worldwide and

added to the Stockholm Convention on Persistent Organic Pollutants (POPs) due to their persistence, bioaccumulation, and toxicity (Renner, 2004). Since then, a variety of new halogenated flame retardants (NHFRs) have been introduced as replacements. For example, the commercial Penta- and Octa-BDE formulations were primarily replaced by firemaster 550 and 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and Deca-BDE formulation by decabromodiphenylethane (DBDPE) (Covaci et al., 2011). In addition, Dechlorane Plus (DP), a nonregulated, highly chlorinated FR, was suggested by the European Union as a possible replacement for the insecticide Mirex (Hoh et al., 2006) and Deca-BDE formulation (Meire et al., 2012). A few monocyclic aromatic compounds, with lower production volumes, such as pentabromoethyl benzene (PBEB) and hexabromobenzene (HBB), have

also found new FR applications during this “FR revolution” (Ma et al., 2013). Large amounts of these NHFRs have been produced with growing annual demands due to the rapid economic development. Generally, they are used as additives rather than chemically bonded to the product matrix, which facilitates their release into the environment (Ali et al., 2016). As a result, NHFRs are consistently detected in different environmental media (Guerra et al., 2009; Zhao et al., 2013; Mekni et al., 2019; Reche et al., 2019). They are also detected regularly in Arctic (Liu et al., 2017; Vorkamp et al., 2015) and Antarctic (Aznar-Alemany et al., 2019a), indicating their potential to undergo long-range atmospheric transport. Although there are limited data about most NHFRs, especially production volumes, usages, toxicity, and physical-chemical properties, many of them show properties of persistency and toxicity (hormonal disruption, reproductive effects) leading to concerns over environmental levels (Abdelouahab et al., 2011; Zhang et al., 2016; Li et al., 2017).

Methoxylated brominated diphenyl ethers (MeO-BDEs), which are structurally related to PBDEs, may be transformation products of the latter (Zeng et al., 2008) or of natural (marine) origin, produced by sponges, mollusks, cyanobacteria and algae (Yu et al., 2013). MeO-BDEs have gained attention in recent years because they have toxic properties (effect on mRNA abundance of steroidogenic enzymes in the H295R cell line) and display a greater biomagnification potential than PBDEs in aquatic food webs (He et al., 2008; Wiseman et al., 2011).

There is no record of FR production in African countries and, therefore, the possible sources of these pollutants in the air are assumed to be the release from imported FR-containing products and the long-range atmospheric transport. Electrical and electronic e-waste recycling coupled with poor disposal techniques (such as open burning and dumping at poorly or non-constructed landfill sites, or even in surface water bodies) has demonstrated to be an important emission source of FRs in Africa (Robinson, 2009; Schluep et al., 2011; Katima et al., 2017). According to Baldé et al. (2014) the total electrical and electronic waste equipment generation in Africa was 1.9 Mt in 2014.

Africa is one of the least studied continents in the world with respect to air quality (Laakso et al., 2007). Previous works in the atmosphere of North Africa have been focused on PBDEs and organophosphate ester (OPE) flame retardants and plasticizers (Castro-Jiménez et al., 2017; Castro-Jiménez and Sempéré, 2018). However, until now, there have been no published studies on halogenated FRs (HFRs), i.e., NHFRs, HBCDDs and MeO-BDEs in North Africa atmosphere. Hence, the objectives of this study were first to investigate the occurrence and pollution levels of HFRs and MeO-BDEs in atmospheric particles from Bizerte (Tunisia), a coastal, industrial-port city of North Africa. Secondly, to assess their potential sources and make a comparison with the levels of regulated PBDEs, and thirdly, to estimate their atmospheric dry deposition and human exposure risk. To our knowledge, this is the first report of atmospheric concentrations of MeO-BDEs for the entire African continent.

2. Materials and methods

2.1. Atmospheric particle sampling

Seventeen atmospheric particle samples were collected from September 2015 to February 2016 on the roof of the Faculty of Sciences of Bizerte (37° 16' 0.5802" N, 9° 52' 49.875" E; 8 m above ground level), ~1 km far from the Bizerte city center, between the Mediterranean Sea and the Bizerte Lagoon (Fig. S1 in the supplementary information (SI)). Detailed descriptions of the sampling site, sample collection and pretreatment procedures have been given elsewhere (Barhoumi et al., 2018). Briefly, Bizerte is a medium-sized city (~127,000 inhabitants), with a humid climate and economic activity focused mainly on agriculture, fishing and operations of light and heavy industries (Barhoumi et al., 2018), inducing a considerable anthropogenic pressure. A high volume air sampler (Tisch Environmental Inc.,

OH, USA) equipped with a precombusted (450 °C, 6 h) quartz fiber filters (QFFs) (Whatman QMA grade, 20.3 × 25.4 cm) was used to collect samples for 48 h at an average flow rate of 0.66 m³ min⁻¹, resulting in a total sample volume of ~1900 m³ for each sample.

After collection, QFFs were individually wrapped in a clean aluminum foil, transported to the laboratory and stored in a freezer at -20 °C before processing. They were conditioned in a desiccator (25 °C) for 24 h, weighted using a microbalance, and then cut into two equal parts. One half was used for HFR and MeO-BDE analysis and the other half for the determination of total suspended particles (TSP), organic carbon (OC) and organic nitrogen (ON). Details regarding the sampling dates, meteorological conditions and collected air volumes, as well as TSP, OC and ON concentrations for each sample, are given in the SI (Table S1).

2.2. Analytical procedures

Details on analytical procedures (chemicals, extraction and instrumental analysis) are presented in the SI (Text S1). Briefly, QFF filters were cut into small pieces, spiked with a multi-standard mixture containing internal standards for PBDEs (¹³C-BDE-28, -47, -99, -100, -153, -154, -183 and -209), dechloranes (¹³C-*syn*-DP), and hexabromocyclododecane (d₁₈ α-HBCDD), and extracted using a fully automated accelerated solvent extraction system (ASE 350). The extracts were then purified using solid phase extraction (SPE), and depending on the analytes, the analysis of compounds was performed using:

- A liquid chromatography coupled to tandem mass spectrometry (LC-MS-MS) using electrospray ionisation (ESI), for HBCDDs.
- A gas chromatography coupled to tandem mass spectrometry (GC-MS-MS) working with negative ion chemical ionisation (NICI), for dechloranes.
- A gas chromatography coupled to mass spectrometry working with negative ion chemical ionisation (GC-NCI-MS), for DBDPE.
- And an agilent 7890 gas chromatography coupled to an Agilent 7000 A GC/MS triple quadrupole working with electron ionisation (EI) (GC-EI-MS-MS), for PBEB, HBB and MeO-BDEs.

The concentrations of TSP in the QFFs were determined according to Barhoumi et al. (2018) while OC and ON concentrations were determined by high temperature combustion (CHN analyzer) (Raimbault et al., 2008).

2.3. Quality assurance/quality control (QA/QC)

QA/QC was conducted by analysing field and laboratory blanks, calibrations of the high volume air sampler, and evaluation of the analytical performance of the instruments, which includes reproducibility, detection limits and standard spiked recoveries. Three field blanks were collected for the whole sampling period by placing a QFF in the air sampler and immediately removing without drawing air through the sampler. Laboratory and field blanks were processed in the same way as the samples to determine the contamination introduced during extraction and clean-up, and by handling, shipping and storage, respectively. Laboratory blanks were included with each batch of 5 samples. All target compounds measured in this study were detected in the blanks (field and laboratory blanks) with amounts ranging from 0.07 to 1.17 pg (Table S3). The air sampler was regularly calibrated (each month) following the manufacturer's manual (Tisch Environmental, HIGH VOL⁺). Multilevel calibration curves, covering the whole concentration ranges found in the samples, were used to quantify the analytes, and R² values > 0.95 were found for all of the analytes (Table S3). Quantification was carried out by isotopic dilution method based on the use of isotopically labeled standards. Table S2 shows the target compounds analysed in this study with each corresponding internal standard. A blank clean QFF was spiked with 50 µL of standards

(100 pg/ μL for each HFR and 50 pg/ μL for each MeO-BDEs), and processed as real samples. Recoveries from spiked QFF were in the range of 54–104% and 61–81% for HFRs and MeO-BDEs, respectively, being always within the range established as acceptable for isotopic dilution methods (40–120%). Reproducibility of the method was also satisfactory with relative standard deviations (RSD) < 20%. Method detection limits (MDLs) defined as mean blank value + 3 \times standard deviation (SD) (considering an average sampled air volume of 806 m^3), ranged from 0.1 to 1.5 fg m^{-3} (Table S3). For compounds that were not detected in blanks, instrument detection limits (IDLs), determined as a signal-to-noise ratio (S/N) of 3, were substituted. If the concentration of a given compound in a sample was below its MDL/IDL, thus this compound was considered as not detected in the sample, and was assumed zero for deriving sums and calculating fluxes. All data reported here were blank corrected.

2.4. Data handling

The targeted compounds analysed in this study were classified into two groups, the HFRs (PBEB, HBB, DBDPE, Dechlorane 602 (DDC-DBF), Dechlorane 603 (DDC-Ant), Dechlorane 604 (HCTBPH), *syn*-DP, *anti*-DP, α -HBCDD, β -HBCDD, γ -HBCDD) and MeO-BDEs (5-MeO-BDE-47, 6-MeO-BDE-47, 4'-MeO-BDE-49, 2'-MeO-BDE-68, 5'-MeO-BDE-99, 5'-MeO-BDE-100, 4'-MeO-BDE-101 and 4'-MeO-BDE-103), defined as Σ HFRs and Σ MeO-BDEs, respectively. Among HFRs, eight compounds (PBEB, HBB, DBDPE, DDC-DBF, DDC-Ant, HCTBPH, *syn*-DP, *anti*-DP) named new halogenated flame retardants are defined as Σ NHFRs (or NHFRs), and three compounds (α -HBCDD, β -HBCDD, γ -HBCDD) are defined as Σ HBCDDs (or HBCDDs), which are considered as discontinued FRs. Dechlorane Plus represents the sum of *syn*-DP and *anti*-DP, and is defined as Σ DPs (or DPs).

Box-and-whisker plots and Spearman rank order correlations were performed using graph prism 5 software. Mann-Whitney nonparametric tests (U-tests), conducted with Stat-View 5.0, were used to compare the distributions of two groups. The significance level for the result was set at $p \leq 0.05$. Principal component analysis (PCA) was performed using XLSTAT 2013.5.01.

The dry deposition fluxes (F $\text{pg m}^{-2} \text{day}^{-1}$) of HFRs and MeO-BDEs associated with particles were calculated as follows:

$$F = V_d \times C_{\text{PM}} \quad (1)$$

where V_d is the deposition velocity and C_{PM} is the volumetric concentration of HFRs and MeO-BDEs in atmospheric particles (pg m^{-3}). V_d is known to be variable, depending on particle size and meteorological conditions. There are no measured velocities available for these compounds for the Mediterranean Sea conditions. Based on recent works on the dry deposition of POPs and OPE (Castro-Jiménez et al., 2017; Barhoumi et al., 2018; Castro-Jiménez and Sempéré, 2018) we used in the present study a constant velocity of 0.2 cm s^{-1} . The results from this calculation only provide indicative estimation of fluxes that should be eventually validated by experimental measurements.

The daily human exposure dose (DED, $\text{pg kg}^{-1} \text{bw day}^{-1}$) to particle-bound HFRs and MeO-BDEs via outdoor air inhalation was calculated using Eq. (2) proposed by the U.S. Environmental Protection Agency (USEPA) Exposure Factor Handbook (USEPA, 2011):

$$\text{DED} = C \times \text{IR} \times \text{ED} \times \text{AF}/\text{BW} \quad (2)$$

where C_{PM} is the measured concentration of particle-bound HFRs/MeO-BDEs in each sample (pg m^{-3}); IR is the inhalation rate ($\text{m}^3 \text{day}^{-1}$); ED is the exposure duration per day (h day^{-1}); AF is the absorption fraction (the inhalation fraction was assumed to be 100% bioavailable) and BW is the body weight of human (kg). A mean daily inhalation rate of 16.0 $\text{m}^3 \text{day}^{-1}$ was employed for adults and 7.6 $\text{m}^3 \text{day}^{-1}$ for children (Zhang et al., 2019). It was assumed that a person spends 6 h/day in an outdoor environment (i.e., 1/4 of the day) (Deng et al., 2018). The average body weight was considered to be 60 kg for adults and 16 kg

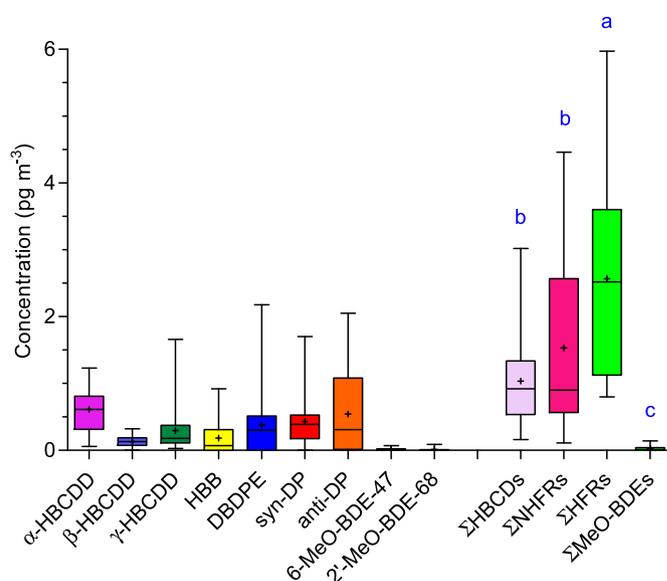


Fig. 1. Concentrations (pg m^{-3}) of HBCDDs, NHFRs and MeO-BDEs in atmospheric particles of Bizerte city as shown in box-and-whisker plots across the whole sampling period (September 2015 to February 2016). Boxes represent the interquartile range, bound by the 75th and 25th percentiles. Line and cross markers indicate medians and averages, respectively, whereas error bars show minimum and maximum concentrations. Comparison between mean total concentrations (U test, $p < 0.05$) is shown; the concentration distributions sharing the same letter are not statistically different at $p < 0.05$.

for children (Liu et al., 2016; Deng et al., 2018).

3. Results and discussion

From a total 19 target analytes, 3 HBCDDs (α -HBCDD, β -HBCDD, γ -HBCDD), 4 NHFRs (HBB, DBDPE, *syn*-DP, *anti*-DP) and 2 MeO-BDEs (2'-MeO-BDE-68, 6-MeO-BDE-47) were detected in samples with detection frequency ranging between 94 and 100% (Table S4). The concentrations of Σ HFRs and Σ MeO-BDEs ranged from 0.80 to 5.97 pg m^{-3} and from nq to 0.14 pg m^{-3} , with a mean (median) of 2.57 (2.52) pg m^{-3} and 0.03 (0.01) pg m^{-3} , respectively (Table S4, Fig. 1 and Fig. S2). Overall, the mean concentration of NHFRs was 1.5 and 51 times higher than that of HBCDDs and MeO-BDEs, respectively (Fig. 1).

3.1. Concentrations and composition profiles

3.1.1. Hexabromocyclododecanes

HBCDDs in air were largely particle-bound and rarely detected in the gas phase because of their low vapor pressure and high affinity for particles (Jo et al., 2017). In the present study, except for one sample for which β -HBCDD was not detected, the detection frequency of the three HBCDDs was 100% in all atmospheric particle samples (Table S4). The mean (median) concentrations of α -, β -, and γ -HBCDD were 0.60 (0.61), 0.13 (0.13), and 0.29 (0.18) pg m^{-3} , respectively (Table S4 and Fig. 1). Σ HBCDDs ranged from 0.16 to 3.02 pg m^{-3} with a mean (median) of 1.04 (0.92) pg m^{-3} , which was comparable to the values from Guangzhou and Shenzhen, China, and Central Brno, Czech Republic (Okonski et al., 2014; Yu et al., 2008a; Zhu et al., 2018). Our concentrations were lower than those from Beijing, Shanghai (Zhabei) and Dalian in China, but much higher than those from North-East Greenland, Denmark and Stockholm, Sweden (Table 1) (Hu et al., 2011; Li et al., 2012, 2018; Newton et al., 2015; Vorkamp et al., 2015).

The HBCDD composition profile along the whole sampling period is shown in Fig. 2. Overall, α - and γ -HBCDDs were the most abundant diastereomers, contributing on average about 59 and 29% to the

Table 1 Comparison of concentrations of Σ HBCDDs, Σ NHFRs and Σ MeO-BDEs (pg m^{-3}) in atmospheric particles of Bizerte city (present study) with those reported in other areas.

Locations	Date of sampling	Sampling method	Type	Atmospheric particle	Congener numbers	Concentrations	References
ΣHBCDDs							
Shenzhen, China	2014/05	HVAS/GFF	Urban	PM	3	0.68 (0.42–1.07)	Zhu et al. (2018)
Central Brno, Czech Republic	2009/10–2010/10	HVAS/GFF	Urban	PM	3	0.64 (0.30–0.98)	Okonski et al. (2014)
North-East Greenland, Denmark	2012/01–2012/12	HVAS/GFF	Urban	PM	3	0.0057–0.13	Vorkamp et al. (2015)
Stockholm, Sweden	2012/02–2012/05	LVAS/GFF	Remote	PM	3	0.066 (< 0.026–0.58)	Newton et al. (2015)
Beijing, China	2008/10–2009/07	HVAS/GFF	Urban	PM	3	390 (20–1800)	Hu et al. (2011)
Shanghai (Zhabei), China	2006/02–2006/03	HVAS/GFF	Urban	PM	5	27.6 \pm 5.8	Li et al. (2012)
Dalian, China	2016/09–2017/08	HVAS/GFF	Urban	PM	3	24.32 (13.58–41.11)	Li et al. (2018)
Bizerte city, Tunisia	2015/09–2016/02	HVAS/GFF	Urban	PM	3	1.04 (0.16–3.02)	<i>This study</i>
ΣNHFRs							
Uganda, East Africa	2008/10–2010/07	HVAS/GFF	Urban	PM	5	1.7 (0.0–5.5)	Arinaitwe et al. (2014)
Loneyarbyen on Svalbard, European Arctic	2012/09–2013/05	HVAS/GFF	Arctic	PM	5	2.19	Salamova et al. (2014)
Central Brno, Czech Republic	2009/10–2010/10	HVAS/GFF	Urban	PM	4	0.04 (0.02–0.08)	Okonski et al. (2014)
East China Sea to the high Arctic	2009/06–2010/09	HVAS/GFF	Arctic	PM	3	0.15 (0.03–1.36)	Möller et al. (2010)
Great Lakes Basin (Point Petre), Canada	2013/03	HVAS/GFF	Urban	PM	3	4.54	Shunthirasingham et al. (2018)
Great Lakes Basin (Chicago and Cleveland), United States	2005/01–2009/12	HVAS/GFF	Urban	PM	4	5.1–15.3	Salamova and Hites (2011)
Tianjin, China	2014/06–2014/10	HVAS/GFF	Urban	PM	8	1.46.8	Li et al. (2017)
Bizerte city, Tunisia	2015/09–2016/02	HVAS/GFF	Urban	PM	4	1.53 (0.11–4.46)	<i>This study</i>
ΣMeO-BDEs							
Island Holmön, Northern Baltic	2012/05–2015/04	HVAS/GFF	Coastal	Gas-phase	2	0.03 (ND–0.10)	Bidleman et al. (2016)
Busan, Southeastern South Korea	2010/12–2011/01	HVAS/GFF	Urban-industrial	PM	6	6.9 (ND–46)	Kim et al. (2014)
Bizerte city, Tunisia	2015/09–2016/02	HVAS/GFF	Urban	PM	2	0.03 (nq–0.14)	<i>This study</i>

nq: below quantification limit, ND: not determined, HVAS: high-volume air sample, LVAS: low-volume air sample, GFF: glass fibre filter.

Σ HBCDD concentrations, respectively. β -HBCDD was the less abundant with an average contribution of \sim 13%. In the HBCDD technical formulation, the diastereomer contributions is generally 75–89% for γ -HBCDD with α - and β -accounting for 10–13% and 1–12%, respectively (Fig. 3) (Covaci et al., 2006). Therefore, the composition profile observed here is clearly divergent from that of the initial technical formulation (Fig. 3). The diastereomers can undergo thermal rearrangements at temperatures above 160 °C, resulting in profiles containing 78% α -HBCDD, 13% β -HBCDD and 9% γ -HBCDD (Covaci et al., 2006), which is more in line with the profile detected in Bizerte city (Fig. 3). Other authors (Newton et al., 2015; Drage et al., 2016; Rauer et al., 2018; Li et al., 2018; Yu et al., 2008a; Zhu et al., 2018) also found a similar profile with a predominance of α -HBCDD. By contrast, Abdallah et al. (2008), Hu et al. (2011) and Hoh and Hites (2005) reported higher γ -HBCDD contributions to Σ HBCDD levels in atmospheric samples from Birmingham (UK), Beijing (China) and Chicago (US) (89, 61 and 83%, respectively) (Fig. 3). In our study, the average ratio of the air concentration of α -HBCDD to γ -HBCDD (2.74) was comparable with that of decorative polystyrene ($\alpha/\gamma = 2.1$), but were not similar to those of the commercial mixtures, where the γ isomer is dominant, or construction polystyrene ($\alpha/\gamma = 0.07$) (Kukučka et al., 2013). These results suggest that thermal isomer conversion and photodegradation could be an explanation for the higher abundances of α -HBCDD encountered in the Bizerte urban air (Koppen et al., 2008; Covaci et al., 2011; Okonski et al., 2014), which is also supported by the significant positive correlation ($p < 0.001$) between the concentrations of γ -HBCDD and α -HBCDD or β -HBCDD (Table S5).

According to the Bizerte climatic conditions, the sampling period (autumn and winter) is considered as cold and humid (Barhoumi et al., 2018). Thereby, no clear seasonal differences or correlations with temperature were observed for Σ HBCDD concentrations (Fig. S2A and Table S5), which was consistent with the results reported by Drage et al. (2016) in Birmingham (UK) air.

3.1.2. Alternative/new FRs

From 8 NHFRs analysed, only 4 compounds were detected in all samples with the detection frequency of 100% (Table S4). Σ NHFRs ranged from 0.11 to 4.46 pg m^{-3} with a mean (median) concentrations of 1.53 (0.90) pg m^{-3} . *anti*-/*syn*-DP were the most predominating compounds (64% together, 0.54 and 0.43 pg m^{-3} , respectively) followed by DBDPE (25%, 0.38 pg m^{-3}) and HBB (12%, 0.18 pg m^{-3}) (Table S4, Figs. 1 and 2). In comparison to other studies, the average level of HBB reported here is close to that observed by Saini et al. (2019) in Toronto, Canada (0.24 pg m^{-3}), Khairy and Lohmann (2018) in Alexandria, Egypt (0.92 pg m^{-3}) and by Ma et al. (2013) in Chicago and Cleveland, US (0.67 and 0.81 pg m^{-3} , respectively). However, it was significantly lower than that reported by Kurt-Karakus et al. (2017) in Istanbul, Turkey (510 pg m^{-3}). DBDPE concentrations were similar to those measured in Eagle Harbor (1.0 pg m^{-3}) (Venier and Hites, 2008) and lower than that detected in Southern China (158 pg m^{-3}) (Tian et al., 2011). The mean DP concentrations in this study were similar to those observed in the atmosphere of the Canadian High Arctic (< 0.05–2.1 pg m^{-3}) (Möller et al., 2010), Spain (0.7 \pm 0.5 pg m^{-3}) (Reche et al., 2019) and in samples from Beijing (2.0 \pm 3.9 pg m^{-3}) and Dalian (3 \pm 6 pg m^{-3}) (Yu et al., 2011), but up to 10 times lower than those measured in air samples from 97 Chinese sites (15 \pm 15 pg m^{-3}) (Ren et al., 2008). As shown in Table 1, the Σ NHFR concentrations measured in this study generally fell within the lower-middle ranges of the levels reported in previous studies around the world.

The isomeric composition of DPs is a useful tool to track the transport and fate of these chemicals. The fractional abundance (f_{anti}) is defined as the amount of *anti*-DP divided by the total amount of both DP isomers. The f_{anti} values observed here ranged from nq to 0.79, with a mean of 0.41 \pm 0.28 (Fig. S3), which is lower than those in the commercial DP products Anpon and OxyChem (0.64–0.80 and 0.60,

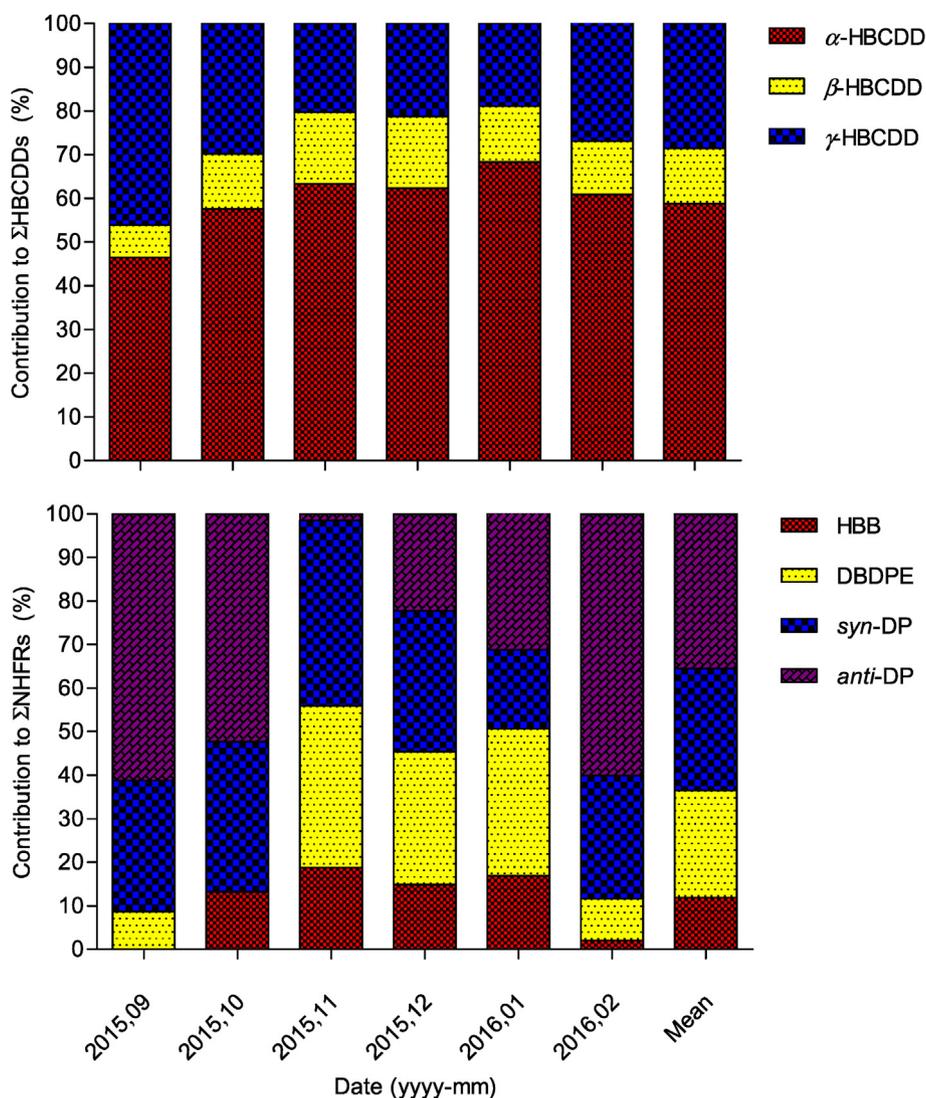


Fig. 2. Composition profiles of HBCDDs and NHFRs in atmospheric particle of Bizerte city from September 2015 to February 2016.

respectively) (Wang et al., 2010). Considering the preferential atmospheric photodegradation of the *anti*-isomer and its isomerisation over the *syn*-isomer, our f_{anti} values may reflect degradation/transformation processes that may occur during long- or short-range atmospheric transport (Möller et al., 2010; Yang et al., 2011).

Temporal variations of the Σ NHFR concentrations are showed in Fig. S2B. Like Σ HBCDDs, there were no notable seasonal (autumn versus winter) differences in levels of NHFRs. The highest Σ NHFR concentrations, recorded in December 2015 and January 2016, did not co-occur with HBCDD peak (September 2015). This emphasises differences in emission patterns and possibly source regions for NHFRs and HBCDDs (Vorkamp et al., 2015).

3.1.3. Methoxylated bromodiphenyl ethers

Two of the eight measured MeO-BDEs were detected in all atmospheric particle samples of Bizerte city, with concentrations ranging from nq to 0.14 pg m^{-3} and a mean (median) of 0.03 (0.01) pg m^{-3} (Table S4, Fig. 1 and Fig. S2D). In the same region, Ben Ameer et al. (2013), El Megdiche et al. (2017) and Mekni et al. (2019) have also detected 6-MeO-BDE-47 and 2'-MeO-BDE-68 are the most abundant MeO-BDEs in fishes (*Solea solea*), clams (*Ruditapes decussatus*) and sea urchins (*Paracentrotus lividus*) from the Bizerte Lagoon. These two compounds have also been the most frequently observed MeO-BDEs in marine environment (Barón et al., 2015; Aznar-Alemany et al., 2019b;

Routti et al., 2009), where those have been found to be naturally produced by the metabolic activities of marine sponges, bacteria or red algae in the presence of bromine, bromoperoxidase and hydrogen peroxide (Malmvarn et al., 2005; Nomiya et al., 2011). Interestingly, in the Baltic region, the highest levels of MeO-BDEs have been recorded in summer, and the lowest in winter (Löfstrand et al., 2011; Dahlberg et al., 2016), leading to the assumption that phytoplanktonic production is the main source of MeO-BDEs (Löfstrand et al., 2011). Barhoumi et al. (2018) also found that the highest levels of the biogenic *n*-alkanes in the atmospheric particle samples of Bizerte city were observed in spring and summer due to the algae bloom occurring at this period in Bizerte Lagoon (Grami et al., 2008). In the same way, the MeO-BDE peak in September 2015 (Fig. S2D) could be related to phytoplankton activity occurring in the Bizerte Lagoon and/or marine coastal waters in late summer. Since our samples were obtained in fall and winter, we may assume that higher levels of MeO-BDEs could be detected during spring and summer, which warrants further investigations.

Data on MeO-BDEs, especially in the atmosphere, are extremely limited. Kim et al. (2014) reported a higher mean concentration (6.9 pg m^{-3}) in atmospheric particle samples from Busan (South Korea). On the other side, Bidleman et al. (2016) determined comparable levels (mean of 0.03 pg m^{-3}) in Island Holmön (Northern Baltic) (Table 1). It is worth noting that the comparison of the HBCDD, NHFR and MeO-BDE concentrations recorded in this study with those reported

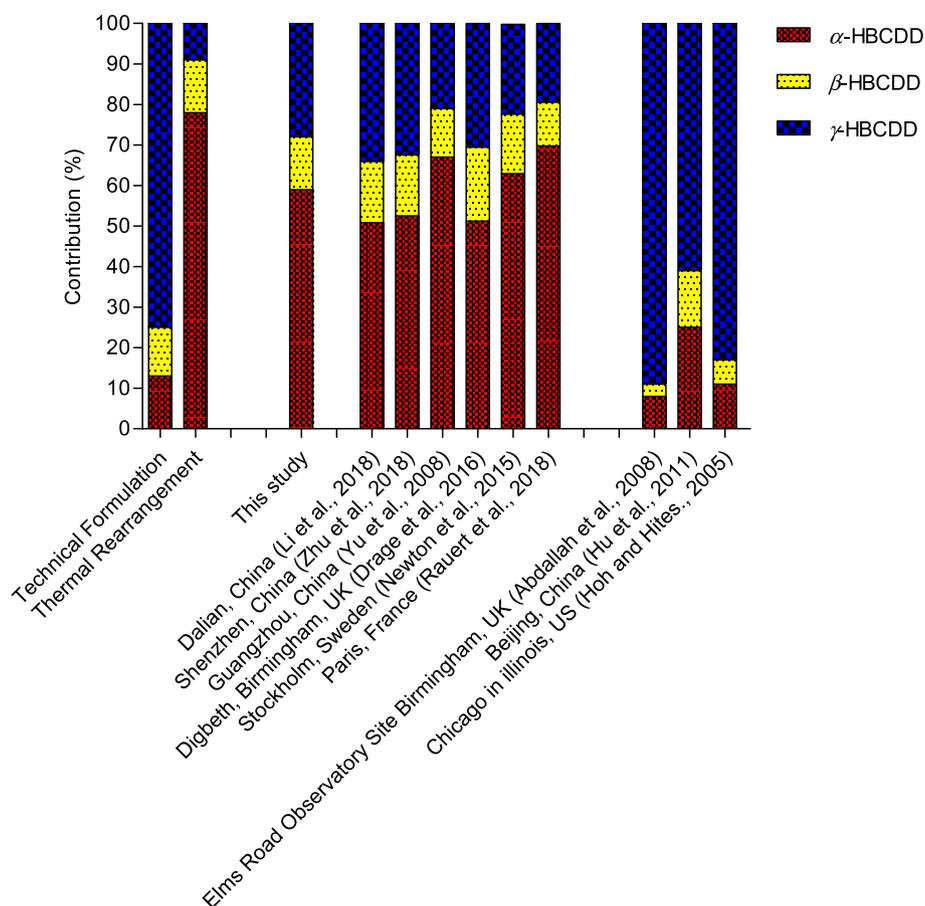


Fig. 3. Comparison between the HBCDD diastereomer profiles reported in Bizerte city (this work) with those of technical formulation, thermal rearrangements and other atmospheric studies.

in literature must be taken with caution, as the meteorological conditions, the number of samples collected, and the number of compounds analysed may not be the same.

3.2. Influence of air mass origin and meteorological parameters

The PCA loading and score plots of the whole dataset are shown in Fig. 4. The target chemicals were clearly separated into three clusters:

HBCDDs were clustered together in top right corner of the plot, while NHFRs and MeO-BDEs were clustered in lower-right and upper-left of the plot, respectively (Fig. 4a). This may suggest that HBCDD, NHFR and MeO-BDE individuals originated from different sources or have different fates (Deng et al., 2018). This result is consistent with that of the Spearman's rank correlation (Table S5). The weak correlation between HBCDDs, NHFRs and MeO-BDEs was expected due to their various physical-chemical properties and applications. The strong

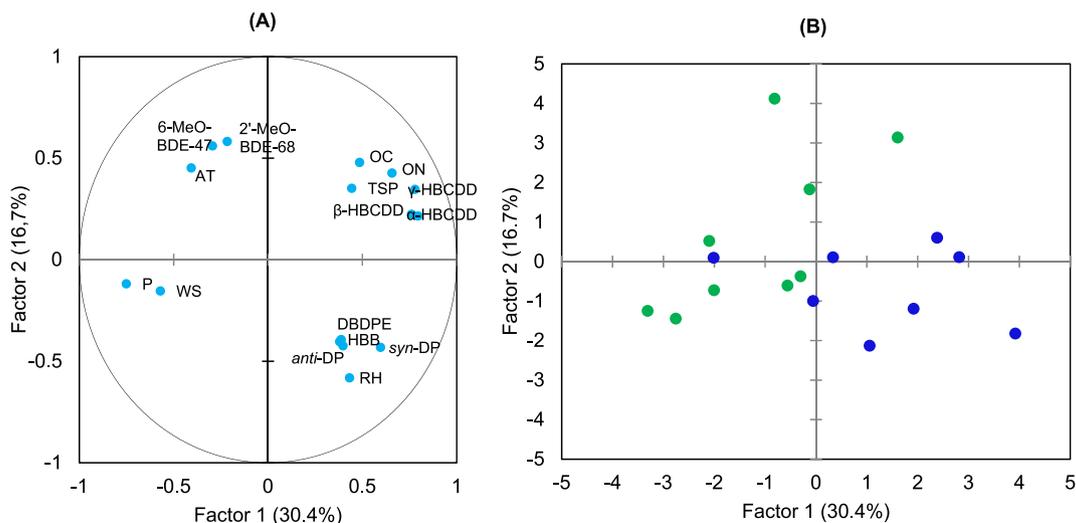


Fig. 4. Spearman principal component analysis loading (A) and scores (B) plots for the first two components of TSP, OC, ON, HBCDDs, NHFRs, MeO-BDEs and meteorological (AT, WS, RH, P) variables for the atmospheric particle samples of Bizerte city. Green and blue colors indicate autumn and winter seasons, respectively.

significant correlation between *syn*-DP and *anti*-DP ($r = 0.777$, $p < 0.001$) and between HBCDD diastereoisomers ($r = 0.820$ – 0.870 , $p < 0.001$) can be explained by their similar sources, which is obvious given their similar use, origin and chemical properties (Saini et al., 2019). No evident temporal separation was observed from PCA score plots for most of samples (Fig. 4b). Relatively high scores of PC1 were found in some samples collected in autumn and winter, indicating that HBCDDs and NHFRs were dominant during both seasons.

The influence of each meteorological parameter on the levels of HBCDDs, NHFRs and MeO-BDEs measured in this study was assessed. Individual HBCDDs and NHFRs exhibited negative correlations with ambient temperature (AT) and precipitation (P), and positive correlations with relative humidity (RH) (Table S5 and Fig. 4). Inversely, MeO-BDEs had positive correlations with AT, and significant negative correlations with RH, suggesting that HBCDDs and NHFRs had high affinity for particles, while MeO-BDEs had high affinity to gaseous phase. Similar results were highlighted by Jo et al. (2017) and Löfstrand et al. (2011). Masiol et al. (2013) shows that low temperatures may stimulate the transfer of pollutants from the gaseous to particulate phase, and inversely, while RH and precipitation promote pollutant condensation on particulate matter and deposition. Some positive and negative correlations appeared between individual HBCDDs/NHFRs/MeO-BDEs, and TSP, OC and ON (Table S5). This indicates that the levels of HBCDDs, NHFRs and MeO-BDEs in the Bizerte atmosphere were not driven by a single meteorological parameter, but by the combined effect of several meteorological conditions.

To investigate the influence of local atmospheric transport on atmospheric concentrations of HFRs and MeO-BDEs in Bizerte city, wind sector was applied (Fig. S4). As shown in Fig. S4, the dominant wind directions were from the West-North-West (WNW) and the North-West (NW) in autumn, and the South-East (SE) in winter. This suggests that local emissions from downtown Bizerte (high urbanisation), lead and cement factories, located NW of the site, and from Zarzouna city (municipal waste incineration) and Menzel Jemil city (mechanic and electronic factories, tire, plastic and textile industries), located SE of the site, are the most likely to influence the pollutant levels observed here. By using the NOAA HYSPLIT Backward Trajectory Model, Barhoumi et al. (2018) found that the influence of inter-continental atmospheric transport was minor in the same area and same period, since the air masses reaching the sampling site were of oceanic origin with limited passage through the European continent. Indeed, the clean nature of the oceanic air masses and high wind speeds above the Mediterranean Sea can disperse pollutants before they reach the sampling site. The negative correlations between wind speed (WS) and all individual HFRs and MeO-BDEs concentrations (Table S5), suggested the predominance of local sources, since strong winds flush pollutants out of the study area whereas weak winds allow pollutants to accumulate over time (Barhoumi et al., 2018).

The presence of HBCDDs in the air can be attributed to a variety of sources including, plastics, installed insulation boards in buildings, textiles, and municipal and hospital waste incineration (Lassen et al., 1999; Morf et al., 2008). DPs is mainly used for coating electrical wires and cables, connectors in computers, and plastic decoration materials (Qiu et al., 2007), which are widely used in urban areas. HBB is used mainly as an additive FR in papers, wood, textiles, electronics and plastics (Li et al., 2017). DBDPE is added to various polymeric materials, such as high-impact polystyrene, polypropylene and acrylonitrile butadiene styrene (ABS), which is used mainly in televisions, computers and cable boxes (Covaci et al., 2011; Pei, 2014). In Tunisia, there is no FR manufacturing plant. Therefore, based on these applications, we assumed that air transportation from local sources and release from FR-containing products are the most likely sources of particulate atmospheric HFRs in Bizerte city.

3.3. Comparison of atmospheric PBDE and NHFR concentrations

DBDPE was introduced to the market as alternative/replacement for the discontinued BDE-209 (Kierkegaard et al., 2004). In order to evaluate the PBDE response to their bans by the EU, we compared DBDPE concentrations measured in this study with those of BDE-209 measured by Castro-Jiménez et al. (2017) in atmospheric particles collected from the same area and same period (Fig. S5). BDE-209 concentration was significantly higher (U test, $p < 0.05$) than DBDPE concentration (10 times higher on average), and no significant correlation was found between these two compounds, pointing out that the use of DBDPE was still low in Bizerte city during the sampling period (2015–2016) compared to the use of BDE-209. Mekni et al. (2019) found a predominance of DBDPE over BDE-209 (BDE-209/DBDPE: $< \text{MDL}$ – 0.85) in sediment samples collected from the Bizerte Lagoon. The strongest degradation and debromination of BDE-209 in sediment relative to atmosphere can explain the predominance of DBDPE in sediments (Raff and Hites, 2007; Demirtepe and Imamoglu, 2019).

3.4. Estimation of particle dry deposition fluxes and human exposure via inhalation

Dry particle deposition is a continuous mechanism of the input of particle-bound contaminants into the global ocean during periods without precipitation (Dachs et al., 2002). For the study period, the dry deposition fluxes of ΣHBCDDs , ΣNHFRs and $\Sigma\text{MeO-BDEs}$ ranged from 28.4 to 521 $\text{pg m}^{-2} \text{day}^{-1}$, 18.5–771 $\text{pg m}^{-2} \text{day}^{-1}$ and from nq to 24.5 $\text{pg m}^{-2} \text{day}^{-1}$, with a mean (median) of 265 (155) $\text{pg m}^{-2} \text{day}^{-1}$, 179 (158) $\text{pg m}^{-2} \text{day}^{-1}$ and 5.01 (1.46) $\text{pg m}^{-2} \text{day}^{-1}$, respectively (Fig. 5 and Table S6). Dry deposition fluxes of ΣHBCDDs and ΣNHFRs were slightly higher in winter than in autumn, while $\Sigma\text{MeO-BDEs}$ were slightly higher in autumn. The seasonal fluctuation can be explained by the different ambient concentrations, phytoplankton activities and meteorological conditions (i.e., relative humidity, wind speed, temperature, and atmospheric stability) (Tasdemir and Holsen, 2005; Löfstrand et al., 2011). Very limited data are available for comparison with the HBCDDs, NHFRs and MeO-BDEs deposition fluxes measured in this study. Atmospheric dry deposition fluxes of ΣHBCDDs estimated in this work are similar to those reported in rural sites of Southern China (mean of 193 $\text{ng m}^{-2} \text{yr}^{-1}$) (Tian et al., 2011), but 12 times lower than those estimated in an urban site in central Brno, Czech Republic (mean of 2.1 $\text{ng m}^{-2} \text{day}^{-1}$) (Okonski et al., 2014). This may be due to

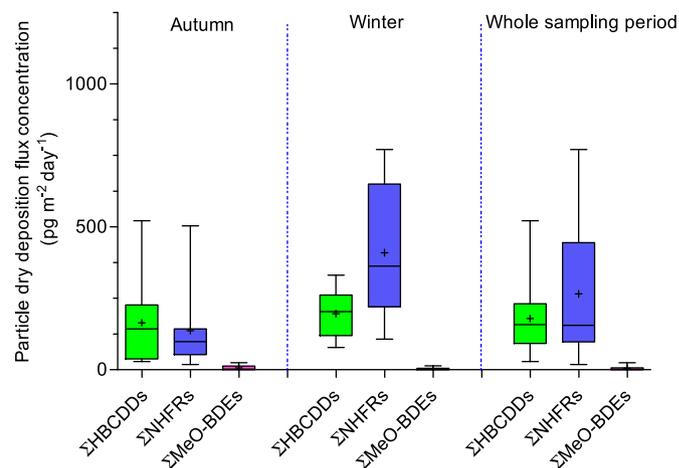


Fig. 5. Box-and-whisker plots of atmospheric particle dry deposition fluxes for ΣHBCDDs , ΣNHFRs and $\Sigma\text{MeO-BDEs}$ in Bizerte city at the two seasons and for the whole sampling period (September 2015 to February 2016). Boxes represent the interquartile range, bound by the 75th and 25th percentile. Line and cross markers indicate medians and averages, respectively, whereas error bars show minimum and maximum dry deposition fluxes.

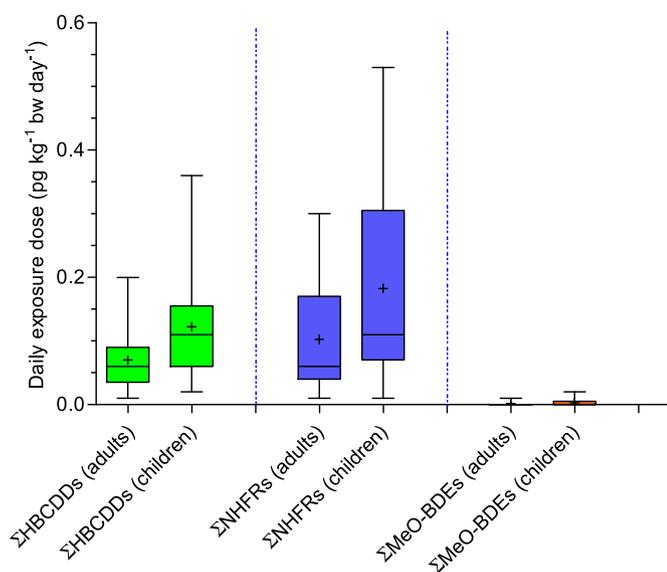


Fig. 6. Estimated daily exposure dose (DEDs) of adults and children to particle-bound HBCDDs, NHFRs and MeO-BDEs via inhalation ($\text{ng kg}^{-1} \text{bw day}^{-1}$). Boxes represent the interquartile range, bound by the 75th and 25th percentiles. Line and cross markers indicate medians and averages, respectively, whereas error bars show minimum and maximum daily exposure dose.

different particle-bound concentrations of HBCDDs and different V_d values used for the estimation. Xie et al. (2011) reported for the HBB a dry deposition flux of $0.5 \text{ pg m}^{-2} \text{ day}^{-1}$ (median value) in atmosphere of the Atlantic and the Southern Ocean, which was lower than that in the present study (median value of $12.49 \text{ pg m}^{-2} \text{ day}^{-1}$). Dry deposition flux of DBDPE (mean of $65.25 \text{ pg m}^{-2} \text{ day}^{-1}$) in Bizerte city was significantly lower than those measured in rural sites of Southern China (mean of $850 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Tian et al., 2011). The total dry deposition fluxes of DPs were in the range of $28.32\text{--}485.22 \text{ pg m}^{-2} \text{ day}^{-1}$, with an average value of $178.80 \pm 149.30 \text{ pg m}^{-2} \text{ day}^{-1}$, which is close to those observed by Okonski et al. (2014) in central Brno, Czech Republic (mean of $0.07 \text{ ng m}^{-2} \text{ day}^{-1}$), but significantly lower than that detected in urban areas of Southern China ($14.5\text{--}83.77 \text{ ng m}^{-2} \text{ day}^{-1}$) (Tian et al., 2011; Wu et al., 2017). Additionally, *anti*-DP was usually the less abundant isomer, contributing to 43% of the total DP deposition fluxes, suggesting that the *anti*-isomer is less persistent in the atmosphere than the *syn*-isomer. Considering the surface of the Bizerte Lagoon as $1.28 \times 10^8 \text{ m}^2$ (Barhoumi et al., 2016), approximately 0.01 kg yr^{-1} of $\Sigma\text{HBCDDs}/\Sigma\text{NHFRs}$ and $2.34 \times 10^{-4} \text{ kg yr}^{-1}$ of $\Sigma\text{MeO-BDEs}$ can be deposited to surface waters through atmospheric particles.

The human body can be exposed to FRs through various exposure pathways, of which breathing is thought to be important (Li et al., 2018). Therefore, the daily exposure doses of children and adults to particle-bound HFRs and MeO-BDEs via outdoor air inhalation were estimated and are summarised in Fig. 6 and Table S7. The mean DED values for HBCDDs, NHFRs and MeO-BDEs were 0.07, 0.10 and $0.002 \text{ pg kg}^{-1} \text{bw day}^{-1}$ for adults, respectively, and 0.12, 0.18 and $0.003 \text{ pg kg}^{-1} \text{bw day}^{-1}$ for children, respectively. When the estimated exposures of DBDPE and 2'-MeO-BDE-68 were compared with corresponding reference dose (RfD) (Ali et al., 2012), they were several orders of magnitude lower than the RfD for both children and adults (Table S7), indicating insignificant risk to local population. Limited data of DED are available in literature for particle-bound FRs. Reche et al. (2019) found DED values for adults ranging from $2 \times 10^{-4}\text{--}8 \times 10^{-4}$, and from $\text{nd}\text{--}9 \times 10^{-4} \text{ ng kg}^{-1} \text{bw day}^{-1}$ for DP and DBDPE, respectively; which were 5–15 folds higher than the DED values reported here. It is worth noting that DED values were calculated based on outdoor sources only. However HFRs are known to have higher concentrations in indoor than outdoor environments (Melymuk

et al., 2016). Therefore the estimated DED must be taken with caution.

4. Conclusion

This study provided valuable baseline data on the occurrence, potential sources and impacts of HBCDDs, NHFRs and MeO-BDEs in a North African coastal city (Bizerte). Nine compounds (α -HBCDD, β -HBCDD, γ -HBCDD, HBB, DBDPE, *syn*-DP, *anti*-DP, 2'-MeO-BDE-68 and 6-MeO-BDE-47) were detected in all of the air samples. Tunisia does not manufacture FRs, therefore, their occurrence may have come from imported FR-containing products, which end up in landfills after their utilisation. Wind sector and air mass backward trajectories suggested that the sources of most FRs were mainly originated from local emissions. No obvious autumn/winter variations were observed for most of the compounds and the estimated DED indicating insignificant risk to local population as a result of their exposure to these pollutants through inhalation. Further research is needed to elucidate precisely the potential sources and impacts of these new organic contaminants in the study area.

CRedit author statement

Badreddine Barhoumi: Conceptualization, Methodology, Writing-Original draft preparation, Writing-Reviewing and Editing; **Marc Tedetti:** Writing-Reviewing and Editing, finalizing the paper content; **Andrea Peris and Oscar Aznar-Alemany:** Data curation, Software and Methodology; **Catherine Guigue:** Initial data analysis; **Soufiane Touil and Mohamed Ridha Driss:** Supervision; **Ethel Eljarrat:** Funding acquisition, Methodology, Writing-Reviewing and Editing, Supervision and Validation.

Declaration of competing interest

All authors declare no competing financial interest.

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