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Legacy and novel flame retardants from indoor dust in Antarctica: sources and human exposure

Simonetta Corsolini[1*], América Metzdorff[1], Davide Baroni[1], Jose L. Roscales[2], Begoña Jiménez[2], Elena Cerro-Gálvez[3~~2~~], Jordi Dachs[3], Cristóbal Galbán-Malagón[4,5], Ondřej Audy[6], Jiří Kohoutek[6], Petra Přibylova[6], Matias Poblete-Morales[7], Ruben Avendaño-Herrera[7,8], Elisa Bergami[1], Karla Pozo[6,9]

[1] Department of Physical, Earth and Environmental Sciences, Via P. A. Mattioli 4, University of Siena 53100, Italy

[2] Department of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, (IQOG-CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

[3] Department of Environmental Chemistry, IDAEA-CSIC-Jordi Girona 18-26, Barcelona, 08034, ~~Barcelona,~~ Catalunya, Spain

[4] Centre for Genomics, Ecology & Environment, Universidad Mayor, Camino La Pirámide 5750, Huechuraba, Santiago, Chile

[5] Departamento de Ciencias de la Vida, Facultad de Ciencias de la Vida, Universidad Andrés Bello, Avda. República 252, Santiago, Chile

[6] Masaryk University, Faculty of Science, Research Centre for Toxic Compounds in the Environment (RECETOX), Kamenice 753/5, 625 00, Brno, Czech Republic

[7] Universidad Andrés Bello, Laboratorio de Patología de Organismos Acuáticos y Biotecnología Acuícola, Facultad de Ciencias de la Vida, Quillota # 980, 2520000 Viña del Mar, Chile

[8] Interdisciplinary Center for Aquaculture Research (INCAR), 2520000 Viña del Mar, Chile

[9] Facultad de Ingeniería y Tecnología, Universidad San Sebastián, Lientur #1457, Concepción, Chile

*Corresponding author: Simonetta Corsolini

Department of Physical, Earth and Environmental Sciences, Via P. A. Mattioli 4, University of Siena 53100, Italy. E-mail: simonetta.corsolini@unisi.it

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Abstract

The air humidity in Antarctica is very low and this peculiar weather parameter make the use of flame retardants in research facilities highly needed for safety reasons, as fires are a major risk. Legacy and novel flame retardants (nFRs) including polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), Dechlorane Plus (DP), and other nFRs were measured in indoor dust samples collected at research Stations in Antarctica: Gabriel de Castilla, Spain (GCS), Julio Escudero, Chile (JES), and onboard the RRS James Clark Ross, United Kingdom (RRS JCR). The GC-HRMS and LC-MS-MS ~~gas chromatography~~ analyses of dust samples revealed $\sum_7$PBDEs of 41.5 ± 43.8 ng/g in rooms at GCS, 18.7 ± 11.6 ng/g at JES, and 27.2 ± 37.9 ng/g onboard the RRS JCR. PBDE pattern was different between the sites and most abundant congeners were BDE-183 (40%) at GCS, BDE-99 (50%) at JES, and BDE-153 (37%) onboard the RRS JCR. The $\sum_{(4)}$HBCDs were 257 ± 407 ng/g, 14.9 ± 14.5 ng/g, and 761 ± 1043 ng/g in indoor dust collected in rooms at GCS, JES, and RRS JCR, respectively. The $\sum_9$nFRs were 224 ± 178 ng/g at GCS, 14.1 ± 13.8 ng/g at JES, and 194 ± 392 ng/g on the RRS JCR. Syn- and anti-DP were detected in most of the samples and both isomers showed the highest concentrations at GCS: 163 ± 93.6 and 48.5 ± 61.1 ng/g, respectively. The laboratory and living room showed the highest concentration of HBCDs, DPs, BTBPE. The wide variations in FR levels in dust from the three research facilities and between differently used rooms reflect the different origin of furnishing, building materials and equipment. The potential health risk associated to a daily exposure via dust ingestion was assessed for selected FRs: BDEs 47, 99, and 153, α-, β-, and γ-HBCD, BTBPE, syn- and anti-DP. Although the estimated exposures are below the available reference doses, caution is needed given the expected increasing use of novel chemicals without a comprehensive toxicological profile.

Keywords: PBDEs, HBCDs, novel FRs, DPs, Antarctic research facilities, dust

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1. Introduction

Antarctica is the most remote continent on Earth and its climate is considered one of the most extreme: ~~very~~ severe limited liquid water availability, very low atmospheric humidity, temperatures, ~~atmospheric humidity~~ and strong winds are limiting factors that contribute to render the continent inhospitable and then ~~un~~inhabited. In spite of that, harmful persistent organic pollutants (POPs) ~~can~~ reach Antarctica and the Southern Ocean. ~~and t~~The long-range atmospheric transport (LRAT) and deposition has been identified as ~~their~~ POP main path to reach polar regions (Wania 2003; Cabrerizo et al., 2017; Casal et al. 2019). In addition~~Moreover~~, climate change has been suggested to influence the global distribution of POPs~~climate change has been suggested to influence contaminant global and polar distribution~~ (Bengtson Nash, 2011), as well remobilization of historical polar reservoirs (Cabrerizo et al. 2013).~~.~~

Research stations are the only land-based settlements in the Antarctic continent and, as a consequence, they have been identified as the source of locally derived pollutants due to daily activities and research logistics (Wild et al., 2015; Chen et al., 2015; Casal et al. 2017). Tourism is another emergent pollution source as it is increasing during recent years (Corsolini, 2019).

The Stockholm Convention on Persistent Organic Pollutants (SC-POPs~~, http://chm.pops.int/~~) was adopted ~~i~~on 22 May 2001 and entered into force on 17 May 2004 to protect human health and the environment from POPs (http://chm.pops.int/) since they~~-~~ are ~~—~~persistent, bioaccumulative, and toxic~~-~~ substances ~~(PBTs)~~. Among POPs, flame retardants (FRs) are compounds applied to consumer products and materials to slow down or to hinder their ignition or combustion (de Wit, 2002). Particularly, brominated flame retardants (BFRs) are commonly used in consumer products such as furniture, plastics, textiles, clothing, electrical and electronic equipment (EEE). These chemicals have attracted scientific interest because they can be dispersed into the environment during production, use and disposal (de Wit, 2002), and show environmental concern and potential risk for humans (Besis and Samara, 2012; Johnson-Restrepo and Villa, 2016; Kodavanti and Loganathan, 2016~~)~~). The most extensively used BFRs have been the polybrominated diphenyl ethers (PBDEs) and the hexabromocyclododecanes (HBCDs), among others (Alaee et al., 2003). PBDEs have been used since 1970s and their production has continued until recently. During the last decade, PBDEs have been progressively regulated~~–~~: ~~according to their bromination degree. I~~ in 2009 their commercial formulations known as PentaBDE (containing tetra- and penta-BDE congeners) and OctaBDE (containing hexa- and hepta-BDE) were included in the Annex A (eliminate production and use) ~~of POPs under~~to the Stockholm Convention; ~~–~~DecaBDE (containing deca-BDE 97-98%, nona-BDE 2.5%, octa-BDE 0.04%) was added in May 2017 and implemented by the European Commission (EU Regulation, 2017). PBDE regulation has led to an increase in the manufacture and use of replacement products such as novel flame retardants (nFRs) (SC-POPs, 2017; McGrath et al., 2017). Hexabromocyclododecanes (HBCDs) are brominated aliphatic cyclic hydrocarbons used as flame retardants in thermal insulation building materials, upholstery textiles, and electronics devices (Loganathan et al., 2020~~Covaci et al., 2006~~); they are replaced by nFRs since 2011 (Kajiwara et al., 2011) and since May 2013 are listed in the Annex A ~~of~~to the SC-POPs (SC-POPs, 2017), with specific exemptions for production and use in expanded and extruded polystyrene used in building material (UNEP, 2013). To date, as many as 75 nFRs have been manufactured (McGrath et al., 2017); these chemicals are considered priority contaminants with respect to their production volume, distribution in the environment, bioaccumulation and toxic potential (de Wit et al., 2010; Covaci et al., 2011). Among nFRs: hexabromobenzene (HBB), mainly produced in China and historically used in polymers, plastics, textiles, wood, and paper (Covaci et al., 2011); pentabromotoluene (PBT), mostly used in textiles, polyester resins, paint emulsions, plastics, and rubbers (De Wit et al., 2011); 2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), recently detected in the environment, has been produced since the mid-1970s and is now being used as a replacement for Octa-BDE (Ali et al., 2012); 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), commercialized in a technical mixture of α- and β- diastereoisomers that can be thermally isomerized to γ-TBECH and δ-TBECH (de Wit et al., 2010; Covaci et al., 2011). These compounds are mainly applied in polyurethane products and expandable polystyrene beads used in thermal insulation for housing (Tomy et al., 2008). Dechlorane plus (DP) is an important chlorinated FR developed to replace the banned Mirex (Xian et al., 2011) and proposed as possible alternative to the now restricted DecaBDE (Sverko et al., 2011). Commercial products contain a mixture of syn- and anti-DP stereoisomers (UNEP, 2019) and are used in many applications such as cable coatings, electrical wires, plastic roofing materials, and computer and television connectors (Kim et al., 2014). In 2019, DP was proposed to be included in the SC-POP list (UNEP, 2019).

~~Indoor dust has been identified as an important source of f~~Flame retardants in home and public buildings are released from many household products and building materials and are adsorbed on indoor dust that has been identified as an important FR source (e.g. Jones-Otazo et al., 2005, Wu et al., 2010; Kim et al., 2019)~~ because they are released from many household products and building materials~~. Previous studies ~~on the presence~~ of flame retardants in indoor dust have indicated that a variety of factors, including the number of household appliances, building age and cleaning rate can influence the concentration of PBDEs and other contaminants in indoor environment (Harrad et al., 2009; Wu et al., 2010). Due to the remoteness of the Antarctic~~a~~ continent and Southern Ocean and to the fact that all materials used in the scientific stations are transported there from other continents (no local production exists), the indoor presence of FRs in research stations should be ascribed mainly to those sources. Moreover, FRs can also be transported by LRAT (Möller et al., 2012; Kim et al., 2018) and fell by wet and dry depositions, which amplify their concentrations by snow scavenging of contaminants in air (Casal et al. 2019, Khairy et al. 2016). However, such LRAT has a limited potential to affect directly indoor air contamination, since outdoor atmospheric concentrations of FR are low (Khairi et al. 2016)~~and then contributing to indoor contamination~~. Legacy and novel FRs have already been ~~already~~ detected in abiotic and biotic environmental compartments (e.g. ~~Chen et al., 2012; Wolschke~~Loganathan et al., 20~~15~~20), and their ~~distribution~~ presence in ecosystems from Antarctica and Southern Ocean has been ~~largely~~ reported in the scientific literature (e.g.: Corsolini et al., 2006; Borghesi et al., 2009; Wolschke et al., 2015; AMAP, 2017; Roscales et al., 2016; Mello et al., 2016; Corsolini et al., 2017; Kim et al., 2018; Gao et al., 2018; Corsolini et al., 2019).

The main aims of the present study were: to evaluate the levels of legacy FRs (PBDE IUPAC nos. 28, 47, 66, 85, 99, 100, 153, 154, 183, and α-, β-, γ- and δ-isomers of HBCD) and nFRs (HBB, PBT, PBBZ, PBEB, BTBPE, α- and β-TBECH, syn- and anti-DP) in indoor dust from different rooms in two Antarctic research stations (Gabriel de Castilla and Julio Escudero), and on board of the RRS James Clark Ross sailing from Punta Arenas, Chile, to the Drake Passage and Bransfield Strait; to estimate the human exposure to FRs via dust ingestion during a research expedition in Antarctica.

2. Materials and Methods

2.1 Collection of samples

Dust samples (n = 23) were collected in two Antarctic research stations, Julio Escudero Station, Chile (JES, 62°12′57″S 58°57′35″W) and Gabriel de Castilla Station, Spain (GCS, 62°58′38″S; 60°40′33″W), and on board the Royal Research Ship James Clark Ross (RRS JCR) of the British Antarctic Survey, UK, (Figure SM1) using a commercial ARIETE Model 2735 vacuum cleaner; control samples and field blanks were conducted at each sampling site using the sampling vacuum and carefully stored and transported in individual sealed bags to avoid cross contaminations.

~~.~~Samples were collected in December 2016 –January 2017 onboard ~~RRS JCR~~RRS James Clark Ross and in January 2017 at ~~GCS~~Gabriel de Castilla Station and ~~JES~~Julio Escudero Station. Ten dust samples were collected at ~~GCS~~Gabriel de Castilla Station in two laboratories, two igloos, a living room, and five bedrooms. Six dust samples were collected at ~~JES~~Julio Escudero Station from the meeting room, one laboratory, two rooms, hall, corridor. Seven dust samples were collected on board the ~~RRS JCR~~RRS James Clark Ross from the sample storage room (with freezers), one laundry room (n =2), one laboratory, one cabin (n =2), one computer room. The collection of samples was carried out according to a strict standard protocol: in each room, one squared meter of carpet was vacuumed for 2 minutes and, in case of bare floor, four squared meters were vacuumed for four minutes (Harrad et al., 2008). The dust samples were collected using specially designed sampling socks (313 x 175 x 254 mm) made by craft paper which were closed, sealed in a plastic bag and stored at -20 °C; they ~~that~~ were mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie~~., sealed in a plastic bag and stored at -20 °C.~~

2.2 Sample preparation and analysis

Solvents used for analysis (n-hexane, dichloromethane, and nonane) were purchased from LGC Promochem (LGC Standards GmbH, Wesel, Germany) and J.T. Baker (Avantor Performance Materials, Gliwice, Poland).

Samples were spiked before extraction with a mixture of surrogate chemicals consisted of 50 µL of ^{13}C PBDEs (IUPAC nos. 28, 47, 66, 85, 99, 100, 153, 154, 183) (20 pg/µL); ^{13}C γ-HBCD (50 ng/mL); ^{13}C-labelled nFRs (20 pg/µL) contained ^{13}C-BTBPE, ^{13}C-PBT; ^{13}C-PBEB, ^{13}C-PBBZ, ^{13}C-HBB, ^{13}Cα-TBECH; ^{13}C-β-TBECH (Cambridge Isotope Laboratory); ^{13}C-syn-DP, ^{13}C-anti-DP (Wellington Lab).

Each sample was passed through a mesh size sieve (500 µm) in order to separate the dust from the other materials of larger size. Finally, they were weighed (~ 1 g) (Sartorius AG Germany, model MSA 125P-000-DU).

The samples were extracted ~~i~~by~~n~~ ultrasonic assisted extraction (UAE, Banderlin Sonorex) three times (3 x 15 minutes) with 10 mL hexane, in order to increase the diffusion and desorption rate of analytes from the sample matrix. After the extraction, the sample volume was reduced under a gentle stream of nitrogen at ambient temperature. Sample clean-up was achieved by mixing 3 mL of sulphuric acid with the sample (Covaci et al., 2007). Then samples were eluted with 40 mL hexane/dihloromethane (DCM 1/1, v/v) in a chromatographic column packed with 1 g active silica gel, 8 g of 44% sulphuric acid-impregnated silica gel, and 1 g active silica gel on the top, then micro-concentrated by a stream of nitrogen in a TurboVap II concentrator unit (Caliper Life Sciences, USA) and finally transferred into a mini vial and filled with nonane to the final volume of 50 µL.

After the instrumental analyses of nFRs and PBDEs, ~~were measured using GC-HRMS, then~~ the used final extracts were evaporated and solvent exchange to acetonitrile ~~was done~~ for HBCD measurement~~ using LC-MS/MS~~.

2.3 Instrumental analysis

nFRs and PBDEs -

In this study FRs were identified and quantified using~~ a~~ gas chromatography - high resolution mass spectrometry (GC-HRMS); the 7890A GC (Agilent, USA) was equipped with a 15 m x 0.25 mm x 0.10 um RTX-1614 column (Restek, USA) coupled with an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at > 10000 resolution (10% valley definition). The injection volume was 2 µL and injection was splitless at 280°C, with He as carrier gas at 1 mL/min. The GC temperature program was 80°C (1 min hold), then 20°C/min to 250°C, followed by 1.5°C/min to 260°C (2 min hold) and 25°C/min to 320°C (4.5 min hold). Further details on GC-MS analysis are reported in Venier et al. (2016).

HBCDs -

Analysis of ~~HBCD~~α-, β-, γ- and δ-isomers of HBCD ~~s~~ was done using liquid chromatography coupled to a Qtrap mass spectrometer ~~the HP~~(LC-MS/MS); ~~apparatus~~ an Agilent 1290 series apparatus (Agilent Technologies,~~ Waldbronn,~~ Germany) consisting of a vacuum degasser, a binary pump, a thermostated autosampler (10°C), and a thermostated column compartment kept at 30°C was used. The column was Phenomenex Luna C-18 endcapped (3 µm) 100 x 2 mm i.d., equipped with Phenomenex SecureGuard C18 guard column (Phenomenex, Torrance, CA, USA) and the mass spectrometer was an AB Sciex Qtrap 5500 (AB Sciex, Concord, ON, Canada) with electrospray ionization (ESI). Ions were detected in negative ion mode.

Concentrations of chemical residue in dust samples are given in ng/g dry weight throughout the manuscript.

2.4 Quality Assurance and Quality Control (QA/QC)

The method for quality control (QC) (Harrad et al., 2008) -was performed by analyzing laboratory (n=2), trip and ~~several~~ field blanks~~ blank evaluation~~. To track cross contamination, one blank was taken per room category at each station (n=4).~~:~~ ~~i) s~~Sodium sulfate (Na2SO4) was extracted before sampling with DCM for 18 hours and then used in the trip and field blanks~~prepared during sampling, and ii)~~. ~~procedural blanks (Na2SO4 prepared before sample extraction prepared before sample extraction).~~ Na2SO4 was deposited inside the bags to keep a record of the potential contamination of the zip bag itself. Thus the field blanks consisted in vacuum bags with Na2SO4; these plastic bags were transported to the research station with the rest of materials and, once there, they were placed into de vacuum system (deactivated). The trip blanks were analysed and quantified and levels were 5 times lower in magnitude. The recoveries of ^{13}C-labeled compounds were within an acceptable range according to EPA method 1614 (25-150%).

The limit of detection (LOD) was calculated from the lowest calibration point as an amount producing a signal to noise 3; the LODs of the analyzed chemicals were: 2.07-36.4 pg/g for PBDEs, 0.6-1.8 ng/g for HBCDs, 0.02-23.0 pg/g for nFRs (Table SM1). The limits of quantification (LOQs) were set as the mean value of target compounds detected in procedural blanks plus ten times of standard deviations. For the undetectable compounds in blanks, the LOQs were set as a signal to noise ratio of 10. The LOQs ranged from 6.22 to 109 pg/g for PBDEs, 2.0 to 6.0 ng/g for HBCDs and 0.07 to 69.2 pg/g for nFRs (Table SM1). Three solvent blanks were used to evaluate contamination from the laboratory procedures. The FR ~~peaks~~ concentrations in all procedural and field blank samples were low (maximum value: <11.2 pg/g for PBDEs; 1350 pg/g for nFRs) and no correction was necessary.

2.5 Calculation of estimated daily exposure to FRs

Three PBDEs (BDE-47, BDE-99 and BDE-153), HBCDs (stereoisomers α-, β-, and γ-HBCD), and two nFRs i.e. BTBPE and syn- and anti-DP were selected to estimate the estimated daily exposure (EDE) via dust ingestion. The estimated daily exposure (ng/kg$_{bw}$/day) to FRs was calculated as:

~~EsEx~~ EDE = $\sum$(C x E~~F~~FT x DI)/BW [1]

where: ~~*EsEx*~~ *EDE* is the estimated exposure; *C* is the concentration (ng/g) of FRs in dust samples from different rooms (average concentration was taken into account for two or more rooms with same use); *EFT* is the estimated fraction of time spent in each room during the day (see Table SM2); *DI* is the daily dust ingestion rate, which was assumed to be 20 mg/day and 50 mg/day for adults to take into account a mean and high dust ingestion scenarios, respectively (Jones-Otazo et al., 2005; Abdallah et al., 2008); *BW* is the body weight assumed for adults (70 kg) (EFSA, 2012). Given the uncertainties about the bioavailability of these substances, a conservative approach has been chosen in exposure assessment considering 100% absorption after their oral ingestion (McGrath et al., 2018).

2.6 Statistical analysis

The software Microsoft Office Excel 2010 (Microsoft, Redmond, WA) and SPSS (V17, Statistical Product and Service Solutions, Chicago, USA) were used to perform the statistical analysis of the data. The concentrations below LOD were assigned a value equal to LOD/2.

The Shapiro-Wilk (S-W) and the Kolmogorov-Smirnov (K-S) tests were used to test if data were normally distributed (Tables SM3-5). As some data sets were not normally distributed, concentrations were $\log_{10}$-tranformed. Data were then analyzed again by S-W and K-S and ~~were~~ normal~~ly~~ distribution was ~~ed~~confirmed ($p>0.05$). A one-~~-~~way ANOVA (software SPSS version 22) was applied (Tables SM6-8) to evaluate concentration differences among the three facilities for all studied contaminants. After ANOVA, the post-hoc Tukey test was run in order to assess pairwise comparisons~~verify differences between sampling sites~~ (Tables SM9-11). All comparisons were based on a confidence interval of ~~All contaminants were considered using~~ 95% and a ~~confidence interval with statistical~~ significance level of $p<0.05$. ~~The concentrations below LOD were assigned a value equal to LOD/2.~~

3. Results and Discussion

The following FRs were detected in the dust samples collected indoor of the research facilities in Antarctica: BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, α-, β-, and γ-HBCD, HBB, PBT, BTBPE, α-TBECH, β-TBECHs, syn- and anti-DPs. The BDEs 66 and 85, PBEB and PBBZ were detected in eight, one, thirteen, and eight out of 23 samples, respectively; δ-

HBCD was below LOD in all samples. The percentage of detection of BDE congeners, HBCD isomers and nFR compounds was 58%, 58%, and 78%, respectively. The concentrations of the detected FRs are summarized by research facility in ~~the~~ Table 1 and detailed by sampling room in ~~the~~ Table ~~SM1~~2. The sum of PBDE congeners and HBCD isomers are reported as $\sum_{(7)}$PBDEs and $\sum_{(4)}$HBCDs, respectively.

3.1 Concentrations of legacy and novel FRs

The concentrations of FRs in the research stations and vessel showed different patterns of abundance: HBCDs made up most of the total FR residue in rooms at ~~GCS~~Gabriel de Castilla Station and ~~RRS JCR~~RRS James Clark Ross (50% and 87%, respectively), while PBDEs were the most abundant at ~~JES~~Julio Escudero Station (40%) (Figure 1a).

3.1.1 PBDEs

The $\sum_{(7)}$PBDEs concentrations in the dust samples collected ~~in the rooms~~ at the research facilities were higher in the rooms of ~~GCS~~Gabriel de Castilla Station > RRS James Clark Ross ~~and~~> ~~JES~~Julio Escudero Station ~~were 41.5 ± 43.8 ng/g (7.08 – 131 ng/g) and 18.7 ± 11.6 ng/g (7.67 – 35.7 ng/g), respectively, and 27.2 ± 37.9 ng/g (7.99 – 106 ng/g) onboard RRS JCR~~ (Table 1). Among congeners, o~~O~~nly BDE-28 levels ~~significantly~~ differed between research facilities ($p<0.05$; Tables SM3, SM6). The PBDE congener abundance varied between the research facilities: BDE-183 (40%) > BDE-99 (23%) > BDE-153 (14%) at ~~GCS~~Gabriel de Castilla Station; BDE-99 (50%) > BDE-47 (35%) at ~~JES~~Julio Escudero Station; BDE-153 (37%) > BDE-99 (22%) > BDE-183 (21%) on ~~RRS JCR~~RRS James Clark Ross (Figure 1b). The BDE-183 showed the highest concentrations in the laboratory of ~~GCS~~Gabriel de Castilla Station (68.6 ng/g) and in the computer room of the ~~RRS JCR~~RRS James Clark Ross (15.0 ng/g) (Table ~~SM1~~2). This congener made up 13–42% of the Octa-BDE and it is considered a marker of its use (Alaee et al., 2003). This formulation has been mainly used in hard plastic (e.g. acrilonitrile-butadiene-stirene and high impact polystyrene) which in turn are used for EEE (Yogui and Sericano, 2009). It was reported that DecaBDE transfer to indoor dust is linked to polymer weathering and abrasion (Webster et al., 2009): the same process might be the reason why OctaBDE is abundant in rooms where EEE are in use.

The $\sum_{(3)}$BDEs (BDEs 47, 99, 100) made up >40% of the BDE residue in rooms at ~~GCS~~Gabriel de Castilla Station and on ~~RRS JCR~~RRS James Clark Ross, and 90% at ~~JES~~Julio Escudero Station (Figure 1b); these congeners are the main components of the PentaBDE mixture used in polyurethane foam. As PentaBDE was banned in 2009 (SC-POPs, 2017), its presence in indoor dust of remote research facilities may suggest old furniture, carpets or upholstery are still in use in these rooms. Nonetheless, higher BDE concentrations have been reported in other Antarctic sites, e.g. the $\sum_{(4)}$PBDEs (BDE-47, BDE-99, BDE-183, BDE-209) was 9560 ng/g and 2240 ng/g at McMurdo Station and Scott Base (Ross Sea), respectively (Hale et al., 2008).

Our results showed that PBDEs were higher in laboratory, sample storage room and living rooms respect to bedrooms (Figure ~~SM~~2) in agreement with the Σ_9PBDE concentration detected in home ~~office~~ and office ~~home~~ dust samples in an urban area of South Africa (~~30.9 – 205 ng/g and 73.8 – 625 ng/g, respectively;~~ Kefeni & Okonkwo, 2014). Overall, PBDE concentrations found in our samples~~here~~ were ~~comparable to the~~lower than the lowest average ~~lowest~~ concentrations ~~o~~found in~~f~~ ~~Σ_8PBDE in~~ dust samples from rural regions (e.g. ~~reviewed worldwide by Fromme et al. (2014) and found in rural~~ Pakistan and Kuwait) ~~, 22.4 ng/g and 90.02 ng/g, respectively~~(Table SM12). One or more order of magnitude higher levels ~~Four to ten times higher PBDE concentrations~~ were reported in ~~others~~ urban areas compared to those measured here (e.g. ~~: $\sum_{(10)}$PBDEs = 179 ± 3.2 ng/g in~~ U.K., ~~(Harrad et al., 2008), $\sum_{(27)}$PBDE = 400 ng/g in Guangzhou,~~ China ~~(Wang et al., 2014), and $\sum_{(10)}$PBDE = 1600 ng/g in~~ , ~~Texas~~Canada, USA ~~(Harrad et al., 2008).~~) (Table SM12).

~~Except for the igloo 2, the HBCDs were detected in all dust samples at GCS with 257 ± 407 ng/g (12 - 1321 ng/g), in the meeting room and in room 3 at JES with 14.9 ± 14.5 ng/g (4.66 - 25.2 ng/g), and in all rooms on board the RRS JCR with 761 ± 1043 ng/g (80.6 - 2459 ng/g) (Tables 1, SM12).~~

3.1.2 HBCDs

The HBCDs were detected in all dust samples at Gabriel de Castilla Station except for the igloo 2, in the meeting room and in room 3 at Julio Escudero Station, and in all rooms on board the RRS James Clark Ross (Tables 1-2). ~~The α- and γ-HBCD were significantly different between the sampling sites ($F>3.39$, $p<0.05$; β-HBCD: $p>0.05$), namely between JES and GCS, and between JES and RRS JCR (Tables SM4, SM7, SM10).~~

High HBCD concentrations were ~~reported~~ detected in UK house dust (Abdallah et al., 2013) in agreement with our findings. HBCDs ~~are~~ were reported to be extensively used in textiles made in Japan (Kajiwara et al., 2009), and their emissions from textiles were ~~reported~~ observed also at room temperature of 20°C suggesting them as a potential source of these chemicals and other BFRs to indoor dust (Kajiwara et al., 2009; Lucattini et., 2018).

The ~~HBCD~~ isomer abundance varied between Stations ~~(δ-HBCDs <LOD in all samples)~~ and was: γ-HBCD > α-HBCD > β-HBCD at ~~JES~~Julio Escudero Station; α-HBCD > β-HBCD > γ-HBCD at ~~GCS~~Gabriel de Castilla Station and onboard the ~~RRS JCR~~RRS James Clark Ross (Figure 1c). The α- and γ-HBCD were both higher at RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station and differed between the sampling sites ($F>3.39$, $p<0.05$; β-HBCD: $p>0.05$), namely between Julio Escudero Station and Gabriel de Castilla Station, and between Julio Escudero Station and RRS James Clark Ross (Tables SM4, SM7, SM10). The α-HBCD isomer was ~~reported to be~~ the most abundant also in house dust of UK (Abdallah et al., 2013), suggesting the indoor dust reflects the levels and profile of home and office dust in the country of origin, being them likely built and furnished with the same materials. The highest ∑HBCD concentrations found in indoor dust from Antarctic Stations were of the same order of magnitude than values reported for urban areas in Belgium ~~(160 ± 170 ng/g, 33-770 ng/g)~~ (Roosens et al., 2009) and USA ~~(810 ± 1100 ng/g,79 - 2000 ng/g)~~ (Abdallah et al., 2008) (Table SM13).

3.1.3 novel FRs

Among the nFRs, β-TBECH, syn-DP, anti-DP were detected in all samples (Tables 1, SM3). HBB, PBT, and DPs w~~as~~ere higher at RRS James Clark Ross > ~~2.03 ± 4.36 ng/g in rooms at GCS~~Gabriel de Castilla Station > ~~, 1.95 ± 2.54 ng/ at JES~~Julio Escudero Station~~, and 7.67 ± 14.4 ng/g on RRS JCR; PBT was 1.14 ± 1.78 ng/g at GCS, 0.09 ± 0.04 ng/g at JES, and 1.78 ± 2.29 ng/g on RRS JCR;~~, BTBPE~~BTBPE~~ was higher onboard the ~~8.02 ± 17.2 ng/g in rooms at GCS, 148 ± 336 ng/g on RRS JCR~~RRS James Clark Ross > Gabriel de Castilla Station~~,~~ and it was <LOD in all rooms at ~~JES~~Julio Escudero Station except the corridor (~~0.71 ng/g,~~ Table ~~SM1~~2);~~. The~~ the TBECH~~s~~ highest concentrations were found in dust samples of ~~lower at~~ RRS James Clark Ross > Julio Escudero Station > Gabriel de Castilla Station~~GCS (α-TBECH: 0.21 ± 0.14 ng/g; β-TBECH: 0.16 ± 0.11 ng/g) than at JES (α-TBECH: 0.51 ± 0.75 ng/g; β-TBECH: 0.34 ± 0.59 ng/g), and on RRS JCR (α-TBECH: 1.05 ± 1.04 ng/g; β-TBECH: 0.93 ± 0.96 ng/g). The sum of DP isomers was 212 ±140 ng/g at GCS, 7.22 ± 9.27 ng/g at JES, and 33.94 ±35.39 ng/g on RRS JCR~~ (Table 1). BTBPE and DPs made up most of the total nFR residue being together >-95% ca. of the nFR burden (Figure 1d); t.~~ T~~he levels of BTBPE, anti-DP, syn-DP, α-TBECH, β-TBECH significantly differed between research facilities ($p<0.05$; HBB, PBT: $p>0.05$; Tables SM5, SM8, SM11).

3.1.3.1 BTBPE

~~BTBPE and DPs made up most of the total nFR residue being together > 95% ca. of the nFR burden (Figure 1d).~~The physical-chemical properties of several nFRs allow them to remain mostly in the gaseous phase (Li et al., 2015), but in the case of BTBPE, 50% ca. was reported to be trapped in the particle respect to the gaseous phase (Zhao et al., 2020). In the case of DP and other nFRs with relative low volatility, it is thought that they are mainly associated with atmospheric particulate which allow their transport and deposition (ECHA, 2017), hence from surface media they can be dispersed with dust, being the reason why they were detected in indoor dust.

Previous studies have detected nFRs in remote regions including the Antarctic atmosphere (Zhao et al., 2020) and concentrations can be up to tens of pg/m^3 (ECHA, 2017). BTBPE concentrations in indoor house dust in the UK ~~median and average value~~ were of the same order of magnitude of our values ~~5.6 and 0.01-110 ng/g, respectively, in indoor dust in the UK~~ (Tao et al., 2016)~~, thus being of the same order of magnitude of our values (4.52 and 2.97–905 ng/g, respectively~~(~~;~~ Table 1). This chemical i~~wa~~s a replacement for OctaBDE (Covaci et al., 2011) and it was reported it could be widely used in the UK after the Furniture and Furnishings (Fire Safety) Regulations 1988 (Tao et al., 2016). These findings suggest the use of materials made in the country of origin, as previously suggested for HBCDs. The BTBPE detection frequency was 100% at ~~GCS~~Gabriel de Castilla Station and on ~~RRS JCR~~RRS James Clark Ross suggesting its presence in indoor dust likely due to the use of BTBPE-containing materials; the highest level was found in the sample storage room (Table 2).~~,~~ ~~17% at JES suggesting its presence in indoor dust in the first case, where BTBPE-containing materials are likely used.~~ At ~~JES~~Julio Escudero Station it was detected only in the corridor (~~,~~detection frequency = 17%); Zhao et al. (2020) also ~~suggesting its presence due to LRAT, in agreement with finding~~ reported BTBPE low~~by Zhao et al. (2020) regarding the~~ detection frequency and preferential distribution through LRAT in air samples collected at the Great Wall Station, China, 2 km South of Julio Escudero Station (detection frequencies = 30% ca., concentrations: n.d. - 0.021 ng/g) (Zhao et al., 2020). Interestingly, in the Arctic BTBPE was detected in 0% of air samples and in 45% of organisms from Station Nord (81°N, 16°E, NE Greenland) and E and W Greenland, respectively (Vorkamp et al. 2015), suggesting a different transport and/or use of BTBPE-containing products in the Arctic and Antarctic regions.

3.1.3.2 DPs

~~Mean concentration of~~The syn-DP anti-DP ~~in GCS was 163 ± 93.6 ng/g (68-388 ng/g) and~~ made up 73% and 22% of nFR residue at Gabriel de Castilla Station~~. Mean for anti-DP was 48.5 ± 61.1 ng/g (3.36-170 ng/g) representing 22% nFRs~~. Accordingly, ∑DPs represented at least 50% of the concentrations of all studied flame retardants in the bedrooms, igloos, and laboratories (Figure ~~SM~~2);~~. A~~ at ~~JES~~Julio Escudero Station, ~~the~~ anti-DP was higher than syn-DP~~-~~ and they represented 45% and ~~was 3.60 ± 2.43 ng/g (2.00-8.14 ng/g,~~ 24% of nFRs~~)~~ ~~and the anti-DP was 6.95 ± 7.50 ng/g (2.86-22.1 ng/g, 45% of nFRs)~~ (Tables 1-~~, SM1~~2; Figure SM~~3~~2). T~~, and t~~he ΣDP ~~ir~~concentration was~~ sum was~~ highest~~r~~ in the hall (≈ 80%, Figure ~~SM~~2). The DP is used in a range of products, e.g. electronic wiring and cables, automobiles, plastic roofing materials, and hard plastic connectors in televisions and computer monitors, wire coatings, and also in furniture (Zhang et al., 2015) and building material (Hou et al., 2018). Moreover, as ∑DPs was detected in the Southern Ocean atmosphere at concentration of 0.31 pg/m^3 (Möller et al., 2012), future work will need to elucidate the relative contributions of LRAT and local sources to this atmospheric occurrence.~~. Therefore, it is not surprising it represents most of the nFR residue in the research stations.~~

3.2 Assessment of human exposure to FRs via dust ingestion

Inadvertent indoor dust ingestion is considered a major human exposure pathway to FRs, alongside dietary intake (Jones-Otazo et al. 2005; Besis and Samara, 2012; Kim et al., 2016; McGrath et al., 2018; Bu et al., 2019). For the~~se~~ PBDEs, the USEPA provided a reference dose value (RfD), defined as “an estimate of a daily oral exposure of the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime” (USEPA, 2008). To our knowledge, no health-based guidance value has currently been adopted by USEPA or other regulatory authorities for the remaining compounds investigated in this study. However, HBCDs, BTBPE and DPs were also considered for assessing the human exposure via dust ingestion in view of their high levels measured in the dust samples. The ~~formula 1 (section 2.6) was applied and the~~ values and percentage contribution of estimated daily exposure are showed in the Table ~~2~~ 3 and Figure 3, respectively. ~~The higher exposure scenario with an ingestion of 50 mg/day to selected PBDEs returned~~ Overall, the highest exposure was ascribed to α- > β- > γ-HBCDs isomer ~~values of 0.007 ng/kg_{bw}/day for BDE-99 at the GCS > 0.005 ng/kg_{bw}/day at JES > 0.003 ng/kg_{bw}/day on board the RRS JCR. These estimated values for each chemical were far below their corresponding RfD (Table 2)~~(RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station), and to syn- and anti-DP (Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station) (Figure 3).~~.~~

3.2.1 $\sum_3$BPDEs

In the Antarctic facilities, the higher exposure scenario for each congener with an ingestion of 50 mg/day to selected PBDEs returned exposure values far below their corresponding RfD: the exposure to BDE-47, -99, -153 was < 0.017 ng/kg_{bw}/day and highest values were calculated in samples from Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table 3). Exposure to $\sum_3$BPDEs in Antarctic research facilities was generally much lower than the expected intake via dust ingestion to tri- to hexa-BDEs in indoor environments ~~,~~ reported in different countries across Europe, North America, Asia and Australia (Besis and Samara, 2012). Besis and Samara (2012)~~.~~ reported that for human exposure both in house and office, the intake through diet~~-~~ likely prevails in countries where the use of PBDEs is high.

3.2.2 HBCDs

~~In the case of $\sum$(4)HBCDs, the higher exposures were calculated at the high dust ingestion rate (50 mg/day) on board the RRS JCR and at the GCS with 0.61 and 0.26 ng/kg_{bw}/day respectively, consistent with the literature data ranging from 0.03-1.3 ng/kg_{bw}/day (Ali et al., 2012; Fromme et~~

~~al., 2016; Sun et al., 2018).~~ Over the past years, some guidance values had been derived to assess the health implication of human exposure to ∑HBCDs~~HBCDs (NRC, 2000, RfD = 0.2 mg/kg$_{bw}$/day; UBA, 2001, TDI = 139 µg/kg$_{bw}$/day), but no protective reference value as RfD, tolerable daily intake (TDI) or minimal risk level (MRL) is currently adopted by the competent institutions.~~. For instance, the US National Research Council Subcommittee on Flame-Retardant Chemicals reported a HBCD Reference Dose (RfD) of 0.2 mg/kg$_{bw}$/day for rats (NRC, 2000). -The Panel on Contaminants in the Food Chain (CONTAM) of the European Food Safety Authority (EFSA) recognized that neurodevelopmental effects on behavior are the ''critical endpoint'' and then proposed a method based ~~Starting by~~on a benchmark dose (lower confidence~~ limit~~) limit for a benchmark response of 10% (BMDL$_{10}$) of 0.79 mg/kg body weight; the database showed limitations and uncertainties, thus the CONTAM Panel concluded that this BMDL is inadequate to establish a health-based guidance value (EFSA, 2011). Moreover, the Panel observed that HBCD elimination in humans and animals are different and alternatively used a margin of exposure (MOE) method based on body burden (EFSA, 2011):~~, the CONTAM Panel derived~~ a chronic ∑HBCD human dietary intake ~~for ∑HBCDs of 0.003 mg/kg$_{bw}$/day~~ is associated with the body burden at the BMDL$_{10}$ to use for ~~the~~a MOE calculation ~~of a MOE~~of~~ =~~ 0.003 mg/kg$_{bw}$/day/estimated dietary intake; a MOE higher than 8 indicates that there is no health concern due to the dietary intake of these chemicals (EFSA, 2011).

The ∑HBCD exposure values at the high dust ingestion rate (50 mg/day) showed the following order: RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station (Table 3), and they were consistent with the literature data, ranging from 0.03-1.3 ng/kg$_{bw}$/day (Ali et al., 2012; Fromme et al., 2016; Sun et al., 2018). According to Barghi et al. (2016), we alternatively used the ~~margin of exposure (~~MOE~~)~~ approach introduced by the ~~Panel on Contaminants in the Food Chain~~ EFSA ~~(~~CONTAM Panel~~) of the European Food Safety Authority (EFSA)~~. ~~Starting by a benchmark dose (lower confidence limit) for a benchmark response of 10% (BMDL$_{10}$), the CONTAM Panel~~

~~derived a chronic human dietary intake for ∑HBCDs of 0.003 mg/kg$_{bw}$/day associated with the body burden at the BMDL$_{10}$ to use for the calculation of a MOE = 0.003 mg/kg$_{bw}$/day/estimated dietary intake; a MOE higher than 8 indicates that there is no health concern due to the dietary intake of these chemicals (EFSA, 2011).~~ Applying this ~~model~~ approach to our exposure assessments ~~from~~ to dust estimated ingestion, ~~estimated on RRS JCR and at the GCS,~~ we obtained a MOE of 4900 units on RRS James Clark Ross and 11500 ca.~~,~~ at the Gabriel de Castilla Station, ~~respectively,~~ showing that the exposure to HBCDs is below levels of health concern.

3.2.3 BTBPE

Although BTBPE is commonly detected in indoor dust, ~~international studies~~the scientific literature have generally reported lower levels than other nFRs, probably due to low production volumes in the USA and EU (McGrath et al., 2018). Mean or median concentrations (ng/g) reach double-digit levels in North America, while in the other continents they are generally lower (Stapleton et al., 2008; Ali et al., 2012; Fromme et al., 2016; Venier et al., 2016; McGrath et al., 2018; Bu et al., 2019; De la Torre et al., 2020); the corresponding median exposure values, when calculated, were always <0.01 ng/kg$_{bw}$/day (Ali et al., 2012; Bu et al., 2019; De la Torre et al., 2020). On board the RRS James Clark Ross, a high concentration was measured in dust collected in the sample storage room (Table 2) and the exposure values at the high dust ingestion rate in the Antarctic facilities were lower than the RfD$_{BTBPE}$ (243000 ng/kg$_{bw}$/day) proposed by Hardy et al. (2008). ~~On board the RRS JCR, a mean value of 148 ng/g of BTBPE was obtained, due to the particularly high level measured in dust collected in the sample storage room (905 ng/g). The exposures at the high dust ingestion rate were: 0.041 ng/kg$_{bw}$/day for RRS JCR > 0.009 ng/kg$_{bw}$/day for GCS > 1.7E-05 ng/kg$_{bw}$/day for JES, thus significantly lower than the RfD$_{BTBPE}$ proposed by Hardy et al. (2008) of 243000 ng/kg$_{bw}$/day.~~ The RfD values proposed by Hardy (2008) and Wang (2013), several orders of magnitude higher than our results, may not be appropriate given the shortcomings of toxicological data supporting them. In this respect, it should be noted that this RfD value was derived on the basis of old toxicological studies and little is known about chronic toxicity of brominated nFRs (Ali et al., 2012); furthermore, Hardy and coll. ~~the authors~~ added to their paper ~~(Hardy et al., 2008)~~ a disclosure of conflicts of interest as three of them were employed by brominated FRs manufacturers (Hardy et al., 2008).

3.2.4 DPs

The estimated exposure to ∑DPs at the high dust ingestion rate ~~to DP~~ was 0.182 ng/kg$_{bw}$/day at the ~~GCS~~Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table 3); this value was higher with respect to 1.4 ng/day, i.e. 0.02 ng/kg$_{bw}$/day (based on median concentrations; 100 mg/day of dust ingestion rate) in dust samples collected in 2002-2003 from 69 residential homes in Ottawa, Canada (Zhu et al., 2007). Li et al. (2015) reported median exposures to ∑DPs of 0.08 and 0.2 ng/day for the Chinese population, corresponding to 0.001 and 0.003 ng/kg$_{bw}$/day at mean and high dust ingestion rates. In a more recent work, Sun et al. (2018) estimated 0.010 (syn-DP) and 0.033 (anti-DP) ng/kg$_{bw}$/day in homes and 0.008 (syn-DP) and 0.044 (anti-DP) ng/kg$_{bw}$/day in offices from Hangzhou, East China. Higher median levels were reported by Zheng et al. (2015) in three e-waste recycling regions in Guangdong Province, South China, where indoor exposures to ∑DPs in five villages ranged 0.07–~~-~~2.47 ng/kg$_{bw}$/day at the dust ingestion rate of 50 mg/day. For these chemicals Wang et al. (2013) provided a considerable RfD equal to 5 mg/kg$_{bw}$/day.

~~5~~4. Conclusions

In this study PBDEs, HBCDs, and nFRs were detected in indoor dust collected in research facilities in the Antarctic Region, providing an evidence of their role as ~~n~~FRs local source in Antarctica. Buildings and technical cloth and gear may be ascribed as a local source for indoor environments in research stations and ships, and LRAT may be an additional source of legacy and novel FRs in the Antarctic atmosphere~~, while buildings and technical cloth and gear may be ascribed as an additional local source for indoor environments in research stations and ships~~. The highest levels of FRs were found in common areas in all facilities, like laboratories/storage room, hall/corridor, and living room, perhaps because of the presence of electric and electronic equipment and other furniture. The concentration and relative abundance of legacy and ~~novel flame retardants~~nFRs (e.g. HBCDs, BTBPE) in indoor dust can reflect the levels and profile of dust in home and office in the country of origin, being these materials transported from the country of origin. Except DPs at ~~GCS~~Gabriel de Castilla Station, levels we~~a~~re low when compared to relatively populated regions~~when compared to anthropized regions~~, and similar or lower to concentrations reported in remote regions (Tables ~~SM13~~SM12-~~15~~14).

Taking into account the toxicological relevance of our finding, no adverse effect on human health is expected from the exposure via dust ingestion to PBDEs and HBCD; HBCD isomers, and syn- and anti-DP contributed mostly to the exposure. As far as ~~novel~~ nFRs, the exposures to BTBPE on board the RRS James Clark Ross and to DPs at the Gabriel de Castilla Station were higher than the available literature data~~; in the latter case exposure reached a value comparable to the levels estimated for residents in one of the most DP-polluted areas in the world (Wang et al., 2013)~~. Since these chemicals are PBTs, an exhaustive characterization of their toxicity should be performed before adopting health-based guidance values. As banned flame retardants continue to be replaced, further studies should be conducted to assess the human exposure to nFRs in Antarctic facilities, even because the use of flame retardants in Antarctic facilities ~~can be considered~~is highly needed for safety reasons ~~as~~ since the very low air humidity makes fires a major risk.

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CRediT authorship contribution statement

S. Corsolini: Conceptualization, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision; A. Metzdorff: Formal analysis, Data Curation, Writing PhD thesis (this research derives from it); D. Baroni: Formal analysis, Writing - Original Draft, Visualization; J.L. Roscales: Sampling design support, collection of samples, writing, review and editing; B. Jiménez: Acquisition of the financial support, review and editing; E. Cerro-Gálvez: collection of samples at Gabriel de Castilla; J. Dachs: Acquisition of the financial support and review; C. Galbán-Malagón: Acquisition of financial support for sampling, Review and Editing; O. Audy: Sample analysis for PBDEs, nFRs; Jiří Kohoutek: Sample analysis for HBCDs; P. Přibylová: Data management and analytical part writing; M. Poblete Morales: collection of samples; R. Avendaño-Herrera: Acquisition of financial support for sampling, review; E. Bergami: collection of samples; K. Pozo: Conceptualization, Supervision, Acquisition of the financial support for the project leading to this publication.

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Table 1: Concentrations (ng/g) of flame retardants (mean ± standard deviation, minimum - maximum, median) found in dust samples from the different research facilities in Antarctica (nd = not detected; [a] detected in three rooms at each site; [b] detected in two rooms; [c] detected in a room).

	Gabriel de Castilla			Julio Escudero			RRS James Clark Ross		
	~~M~~mean ± SD	~~M~~min - ~~M~~max	~~M~~median	~~M~~mean ± SD	~~M~~min - ~~M~~max	~~M~~median	~~M~~mean ± SD	~~M~~min - ~~M~~max	~~M~~median
BDE-28	1.09 ± 3.03	0.04 - 9.70	0.06	0.08 ± 0.04	0.03 - 0.12	0.09	0.14 ± 0.12	<LOD-0.34	0.16
BDE-47	4.58 ± 2.96	1.22 - 10.6	3.91	5.98 ± 4.56	2.53 - 13.8	4.30	2.91±3.05	<LOD-9.12	2.75
BDE-66	0.07[a] ± 0.02	0.05-0.09	-	0.35[b] ± 0.15	-	-	0.22 ± 0.16[b]	-	-
BDE-85	0.68[c]			nd	-	-	nd	-	-
BDE-99	9.62 ± 6.55	1.80 - 16.5	10.9	8.57 ± 5.60	4.37 - 18.2	7.25	5.07 ± 3.81	2.70 - 11.8	3.84
BDE-100	1.98 ± 1.17	0.59 - 3.60	2.23	1.99 ± 1.49	0.74 - 3.64	1.59	1.07 ± 1.04	0.55 - 2.93	0.62
BDE-153	5.65 ± 5.42	0.69 - 16.5	4.27	-	-	-	10.2 ± 21.6	0.55 - 58.8	0.83
BDE-154	1.85 ± 1.76	0.33 - 4.83	1.05	0.33[c]	-	-	1.88 ± 3.04	0.24 - 8.56	0.30
BDE-183	16.3 ± 22.6	2.41 - 68.6	5.15	nd	-	-	4.74 ± 5.52	1.39 - 15.0	1.66
$\sum_{(7)}$*PBDEs*	*41.5 ± 43.5*	*7.08 - 131*	*27.6*	*18.7 ± 11.6*	*7.67 ± 35.7*	*13.2*	*27.2 ± 37.9*	*7.99 - 106*	*10.4*
α-HBCD	138 ± 197	4.76 - 648	74.6	5.78 ± 4.41	2.67 - 8.90	5.78	384 ± 501	46.3 - 1150	106
β-HBCD	76.0 ± 166	0.97 - 517	19.6	1.75 ± 0.65	1.29 - 2.21	1.75	275 ± 434	9.79 - 1020	34.2
γ-HBCD	43.1 ± 44.6	6.29 - 156	34.9	7.40 ± 9.46	<LOD-14.1	7.40	102 ± 108	24.5 - 289	50.2
δ-HBCD	nd	-	nd	nd	-	-	nd	-	-
∑*HBCDs*	*257 ± 407*	*12.0 - 1321*	*129*	*14.9 ± 14.5*	*4.66 - 25.2*	*14.9*	*761 ± 1043*	*80.6 - 2459*	*190*
HBB	2.03 ± 4.36	0.19 - 11.9	0.42	1.95 ± 2.54	0.16 - 6.07	0.52	7.67 ± 14.4	0.24 - 29.2	0.63
PBT	1.14 ± 1.78	0.08 - 4.97	0.17	0.09 ± 0.04	0.06 - 0.13	0.08	1.78 ± 2.29	0.22 - 5.81	0.81
PBBZ[a]	0.08 ± 0.21	<LOD-0.69	-	0.24 ± 0.48	<LOD-1.32	-	0.08 ± 0.17	<LOD-0.46	-
PBEB[a]	0.05 ± 0.09	<LOD-0.27	-	0.30 ± 0.70	<LOD-2.15	0.07	0.04 ± 0.05	<LOD-0.12	-
BTBPE	8.02 ± 17.2	0.42 - 56.1	2.02	0.71[c]	-	-	148 ± 336	2.97 - 905	4.52
α-TBECH	0.21 ± 0.14	0.06 - 0.49	0.19	0.51 ± 0.75	0.12 - 1.63	0.15	1.05 ± 1.04	0.22 - 2.72	0.42
β-TBECH	0.16 ± 0.11	0.05 - 0.38	0.16	0.34 ± 0.59	0.05 - 1.54	0.11	0.93 ± 0.96	0.17 - 2.52	0.34
∑*TBECHs*	*0.37 ± 0.24*	*0.11-0.87*	*0.35*	*0.45 ± 1.03*	*<LOD-3.17*	*0.10*	*1.98 ± 1.99*	*0.39-5.24*	*0.76*
syn-DP	163 ± 93.6	68.0 - 388	147	3.60 ± 2.43	2.00 - 8.14	2.40	12.2 ± 17.3	0.98 - 46.7	1.89
anti-DP	48.5 ± 61.1	3.36 - 170	22.2	6.95 ± 7.50	2.86 - 22.1	3.98	21.8 ± 20.3	4.52 - 58.3	15.60
∑*DPs*	*212 ±140*	*78-542*	*169*	*7.22 ± 9.27*	*<LOD-30.24*	*5*	*33.94 ±35.39*	*5.58-87-4*	*17.16*
$\sum_{(7)}$*NBFRs*	*224 ± 178*	*72.2 - 632*	*172*	*14.1 ± 13.8*	*5.97 ± 40.3*	*7.94*	*194 ± 392*	*9.30 - 1050*	*24.2*

Table 2: Concentration (ng/g) of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDs) and novel flame retardants (~~NFRs~~nFRs) including Dechlorane Plus (DP) from the different research facilities in Antarctica (nd = not detected; GCS: Lab 1-2 = laboratories, LR = living room, Bed 1-5 = bedrooms; JES: MRoom = meeting room, Lab = laboratory, Room 3-4 = bedrooms; RRS JCR: SS Room = sample storage room, LR A and LR B = laundry room, Lab 1B = laboratory, Cab A and Cab B = cabin; C Room = computer room; N.B.: A and B are refereed to sample replicates in the same room on board RRS JCR).

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	Lab 1	Lab 2	Igloo 1	Igloo 2	LR	Bed 1	Bed 2	Bed 3	Bed 4	Bed 5	MRoom	Lab	Room 3	Room 4	Hall	Corridor	SS Room	LR A	LR B	Lab 1B	Cab A	Cab B	C Room
PBDEs																							
BDE-28	9.70	0.21	0.06	0.18	0.54	0.04	0.06	0.04	0.04	0.04	<LOD	0.12	0.09	0.09	<LOD	0.04	<LOD	0.14	0.16	<LOD	0.17	0.16	0.34
BDE-47	nd	6.46	1.22	6.13	10.6	1.97	5.75	3.92	2.35	2.80	13.8	4.30	3.27	6.03	<LOD	2.54	<LOD	2.42	2.75	<LOD	3.05	3.03	9.12
BDE-66	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.09	0.06	0.05	0.45	<LOD	<LOD	0.24	<LOD	<LOD	<LOD	0.12	0.14	<LOD	<LOD	<LOD	0.41
BDE-85	nd	0.68	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE-99	nd	10.9	1.80	15.0	16.5	<LOD	<LOD	<LOD	3.90	<LOD	18.2	7.25	4.92	8.10	<LOD	4.37	<LOD	2.70	2.85	<LOD	4.15	3.84	11.8
BDE-100	nd	2.23	0.59	2.37	3.60	<LOD	<LOD	<LOD	1.12	<LOD	3.64	1.59	<LOD	<LOD	<LOD	0.74	<LOD	0.55	0.62	<LOD	0.58	0.69	2.93
BDE-153	nd	16.5	6.39	<LOD	4.95	3.59	1.69	0.69	10.3	1.12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	58.8	0.65	0.55	2.66	0.58	0.83	7.27
BDE-154	nd	4.83	0.66	<LOD	2.21	4.21	0.93	0.33	1.17	0.45	<LOD	<LOD	<LOD	<LOD	<LOD	0.33	8.56	0.24	0.27	1.28	0.30	0.29	2.26
BDE-183	nd	68.6	4.51	<LOD	17.7	24.3	3.29	2.41	5.79	3.57	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.66	1.39	7.25	1.47	1.66	15.0
HBCDs																							
α-HBCD	74.4	76.5	4.76	nd	648	74.6	78.6	49.5	179	52.9	2.67	nd	8.90	nd	nd	nd	1150	76.8	46.3	1080	60.7	170	106
β-HBCD	25.6	17.9	0.97	nd	517	19.6	22.4	11.2	55.1	14.5	1.29	nd	2.21	nd	nd	nd	1020	19.2	9.79	784	10.4	45.4	34.2
γ-HBCD	34.9	35.9	6.29	nd	156	19.3	27.1	17.9	55.7	35.1	<LOD	nd	14.1	nd	nd	nd	289	45.2	30.9	224	24.5	50.2	51.5
δ-HBCD	<LOD	<LOD	<LOD	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	nd	<LOD	nd	nd	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NFRs																							
HBB	0.26	0.52	0.65	<LOD	11.9	<LOD	0.19	<LOD	0.42	0.25	0.23	0.27	6.02	0.16	4.25	0.76	<LOD	0.24	0.33	0.93	<LOD	<LOD	29.2
PBT	1.55	0.97	0.07	<LOD	4.97	<LOD	0.09	<LOD	0.16	0.17	<LOD	<LOD	0.13	0.06	<LOD	0.08	<LOD	0.64	5.81	0.81	<LOD	0.21	1.44
PBBZ	0.88	0.07	<LOD	<LOD	0.69	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	<LOD	0.55	<LOD	1.32	<LOD	<LOD	<LOD	<LOD	0.77	<LOD	<LOD	0.46
PBEB	0.14	0.09	<LOD	<LOD	0.27	<LOD	0.01	<LOD	<LOD	<LOD	0.24	0.17	0.07	<LOD	2.15	0.08	<LOD	0.02	0.07	0.88	<LOD	<LOD	0.12
BTBPE	2.86	56.1	0.42	2.03	11.4	1.14	2.25	1.14	2.01	0.87	<LOD	<LOD	<LOD	<LOD	<LOD	0.71	905	4.15	2.97	108	3.44	4.52	9.30
α-TBECH	0.06	0.07	0.11	0.27	0.32	0.23	0.49	0.16	0.08	0.29	0.14	<LOD	1.63	<LOD	0.15	0.12	2.25	0.22	0.25	1.14	0.42	0.34	2.72
β-TBECH	0.05	0.06	0.08	0.19	0.26	0.18	0.38	0.14	0.07	0.23	0.11	0.10	1.54	0.05	0.12	0.09	1.94	0.17	0.17	1.06	0.34	0.30	2.52
syn-DP	134	194	85.8	174	388	222	160	81.9	68.0	127	2.00	2.40	4.64	2.40	8.14	2.04	46.7	1.06	1.56	23.2	0.98	1.89	9.89
anti-DP	18.2	30.8	3.36	170	154	13.8	26.2	45.6	10.4	12.9	3.00	4.42	5.76	3.54	22.1	2.86	40.7	4.52	15.6	58.3	5.46	9.21	18.5

Table 3: Estimated human exposure to FRs via dust ingestion and RfD values (ng/kg$_{bw}$/day) ingestion at mean (20 mg/day = ing-20) and high (50 mg/day = ing-50) ingestion rate in adults ($^{a-}$USEPA, 2008; $^{b-}$NRC, 2000. Not adopted by any regulatory authority; see MOE approach by EFSA, 2011; $^{c-}$RfD - Hardy et al., 2008. Not adopted by any regulatory authority; $^{d-}$RfD - Wang et al., 2013, not adopted by any regulatory authority).

	Gabriel de Castilla		Julio Escudero		RRS James Clark Ross		RfD
	ing-20	ing-50	ing-20	ing-50	ing-20	ing-50	
BDE-47	0.002	0.004	0.001	0.003	0.001	0.003	100^{a}
BDE-99	0.003	0.007	0.002	0.005	0.001	0.003	100^{a}
BDE-153	0.002	0.006	<5.6E-06	<1.4E-05	0.001	0.003	200^{a}
∑PBDEs	0.007	0.017	0.003	0.008	0.003	0.009	
α-HBCD	0.054	0.135	0.001	0.002	0.128	0.321	n.a.
β-HBCD	0.035	0.088	0.0003	0.001	0.085	0.213	n.a.
γ-HBCD	0.016	0.039	0.001	0.003	0.031	0.077	n.a.
∑HBCDs	0.105	0.262	0.002	0.005	0.244	0.611	200,000^{b}
BTBPE	0.004	0.009	<6.9E-06	<1.7E-05	0.017	0.041	243,000^{c}
syn-DP	0.056	0.140	0.001	0.003	0.003	0.009	n.a.
anti-DP	0.017	0.042	0.002	0.006	8E-06	0.020	n.a.
∑DPs	0.073	0.182	0.003	0.008	0.003	0.029	5,000,000^{d}

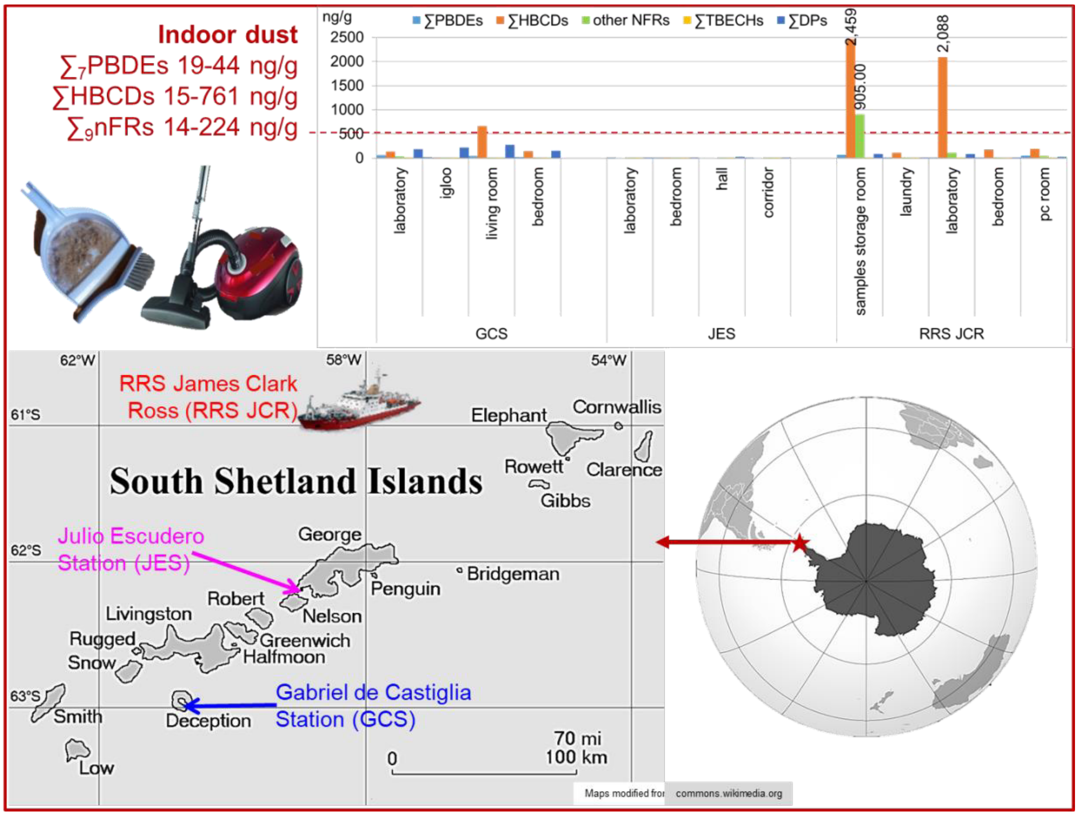
Figure legend

Figure 1: Percentage contribution of FRs in the research stations and vessel: a) ∑PBDEs, ∑HBCDs and ∑NFRs; b) BDE congeners; c) HCBD isomers (δ-HBCD always < LOD); d) novel FRs.

Figure 2: Percentage contribution of ∑PBDEs, ∑HBCDs, other NFRs, ∑TBECHs, and ∑DPs in rooms with different use (at GCS: living room and meeting room).

Figure 3: Estimated human exposure to FRs via indoor dust ingestion at mean (20 mg/day) and high (50 mg/day) ingestion rate (percentage contribution).

GRAPHICAL ABSTRACT



Legacy and novel flame retardants from indoor dust in Antarctica: sources and human exposure

Simonetta Corsolini[1*], América Metzdorff[1], Davide Baroni[1], Jose L. Roscales[2], Begoña Jiménez[2], Elena Cerro-Gálvez[3], Jordi Dachs[3], Cristóbal Galbán-Malagón[4,5], Ondřej Audy[6], Jiří Kohoutek[6], Petra Přibylova[6], Matias Poblete-Morales[7], Ruben Avendaño-Herrera[7,8], Elisa Bergami[1], Karla Pozo[6,9]

[1] Department of Physical, Earth and Environmental Sciences, Via P. A. Mattioli 4, University of Siena 53100, Italy

[2] Department of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, (IQOG-CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

[3] Department of Environmental Chemistry, IDAEA-CSIC-Jordi Girona 18-26, Barcelona, 08034, Catalunya, Spain

[4] Centre for Genomics, Ecology & Environment, Universidad Mayor, Camino La Pirámide 5750, Huechuraba, Santiago, Chile

[5] Departamento de Ciencias de la Vida, Facultad de Ciencias de la Vida, Universidad Andrés Bello, Avda. República 252, Santiago, Chile

[6] Masaryk University, Faculty of Science, Research Centre for Toxic Compounds in the Environment (RECETOX), Kamenice 753/5, 625 00, Brno, Czech Republic

[7] Universidad Andrés Bello, Laboratorio de Patología de Organismos Acuáticos y Biotecnología Acuícola, Facultad de Ciencias de la Vida, Quillota # 980, 2520000 Viña del Mar, Chile

[8] Interdisciplinary Center for Aquaculture Research (INCAR), 2520000 Viña del Mar, Chile

[9] Facultad de Ingeniería y Tecnología, Universidad San Sebastián, Lientur #1457, Concepción, Chile

*Corresponding author: Simonetta Corsolini

Department of Physical, Earth and Environmental Sciences, Via P. A. Mattioli 4, University of Siena 53100, Italy. E-mail: simonetta.corsolini@unisi.it

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Abstract

The air humidity in Antarctica is very low and this peculiar weather parameter make the use of flame retardants in research facilities highly needed for safety reasons, as fires are a major risk. Legacy and novel flame retardants (nFRs) including polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), Dechlorane Plus (DP), and other nFRs were measured in indoor dust samples collected at research Stations in Antarctica: Gabriel de Castilla, Spain (GCS), Julio Escudero, Chile (JES), and onboard the RRS James Clark Ross, United Kingdom (RRS JCR). The GC-HRMS and LC-MS-MS analyses of dust samples revealed $\sum_7$PBDEs of 41.5 ± 43.8 ng/g in rooms at GCS, 18.7 ± 11.6 ng/g at JES, and 27.2 ± 37.9 ng/g onboard the RRS JCR. PBDE pattern was different between the sites and most abundant congeners were BDE-183 (40%) at GCS, BDE-99 (50%) at JES, and BDE-153 (37%) onboard the RRS JCR. The $\sum_{(4)}$HBCDs were 257 ± 407 ng/g, 14.9 ± 14.5 ng/g, and 761 ± 1043 ng/g in indoor dust collected in rooms at GCS, JES, and RRS JCR, respectively. The $\sum_9$nFRs were 224 ± 178 ng/g at GCS, 14.1 ± 13.8 ng/g at JES, and 194 ± 392 ng/g on the RRS JCR. Syn- and anti-DP were detected in most of the samples and both isomers showed the highest concentrations at GCS: 163 ± 93.6 and 48.5 ± 61.1 ng/g, respectively. The laboratory and living room showed the highest concentration of HBCDs, DPs, BTBPE. The wide variations in FR levels in dust from the three research facilities and between differently used rooms reflect the different origin of furnishing, building materials and equipment. The potential health risk associated to a daily exposure via dust ingestion was assessed for selected FRs: BDEs 47, 99, and 153, α-, β-, and γ-HBCD, BTBPE, syn- and anti-DP. Although the estimated exposures are below the available reference doses, caution is needed given the expected increasing use of novel chemicals without a comprehensive toxicological profile.

Keywords: PBDEs, HBCDs, novel FRs, DPs, Antarctic research facilities, dust

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1. Introduction

Antarctica is the most remote continent on Earth and its climate is considered one of the most extreme: severe limited liquid water availability, very low atmospheric humidity, temperatures, and strong winds are limiting factors that contribute to render the continent inhospitable and then inhabited. In spite of that, harmful persistent organic pollutants (POPs) reach Antarctica and the Southern Ocean. The long-range atmospheric transport (LRAT) and deposition has been identified as POP main path to reach polar regions (Wania 2003; Cabrerizo et al., 2017; Casal et al. 2019). In addition, climate change has been suggested to influence the global distribution of POPs (Bengtson Nash, 2011), as well remobilization of historical polar reservoirs (Cabrerizo et al. 2013).

Research stations are the only land-based settlements in the Antarctic continent and, as a consequence, they have been identified as the source of locally derived pollutants due to daily activities and research logistics (Wild et al., 2015; Chen et al., 2015; Casal et al. 2017). Tourism is another emergent pollution source as it is increasing during recent years (Corsolini, 2019).

The Stockholm Convention on Persistent Organic Pollutants (SC-POPs) was adopted on 22 May 2001 and entered into force on 17 May 2004 to protect human health and the environment from POPs (http://chm.pops.int/) since they are persistent, bioaccumulative, and toxic substances. Among POPs, flame retardants (FRs) are compounds applied to consumer products and materials to slow down or to hinder their ignition or combustion (de Wit, 2002). Particularly, brominated flame retardants (BFRs) are commonly used in consumer products such as furniture, plastics, textiles, clothing, electrical and electronic equipment (EEE). These chemicals have attracted scientific interest because they can be dispersed into the environment during production, use and disposal (de Wit, 2002), and show environmental concern and potential risk for humans (Besis and Samara, 2012; Johnson-Restrepo and Villa, 2016; Kodavanti and Loganathan, 2016). The most extensively used BFRs have been the polybrominated diphenyl ethers (PBDEs) and the hexabromocyclododecanes (HBCDs), among others (Alaee et al., 2003). PBDEs have been used since 1970s and their production has continued until recently. During the last decade, PBDEs have been progressively regulated: in 2009 their commercial formulations known as PentaBDE (containing tetra- and penta-BDE congeners) and OctaBDE (containing hexa- and hepta-BDE) were included in the Annex A (eliminate production and use) to the Stockholm Convention; DecaBDE (containing deca-BDE 97-98%, nona-BDE 2.5%, octa-BDE 0.04%) was added in May 2017 and implemented by the European Commission (EU Regulation, 2017). PBDE regulation has led to an increase in the manufacture and use of replacement products such as novel flame retardants (nFRs) (SC-POPs, 2017; McGrath et al., 2017). Hexabromocyclododecanes (HBCDs) are brominated aliphatic cyclic hydrocarbons used as flame retardants in thermal insulation building materials, upholstery textiles, and electronics devices (Loganathan et al., 2020); they are replaced by nFRs since 2011 (Kajiwara et al., 2011) and since May 2013 are listed in the Annex A to the SC-POPs (SC-POPs, 2017), with specific exemptions for production and use in expanded and extruded polystyrene used in building material (UNEP, 2013). To date, as many as 75 nFRs have been manufactured (McGrath et al., 2017); these chemicals are considered priority contaminants with respect to their production volume, distribution in the environment, bioaccumulation and toxic potential (de Wit et al., 2010; Covaci et al., 2011). Among nFRs: hexabromobenzene (HBB), mainly produced in China and historically used in polymers, plastics, textiles, wood, and paper (Covaci et al., 2011); pentabromotoluene (PBT), mostly used in textiles, polyester resins, paint emulsions, plastics, and rubbers (De Wit et al., 2011); 2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), recently detected in the environment, has been produced since the mid-1970s and is now being used as a replacement for Octa-BDE (Ali et al., 2012); 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), commercialized in a technical mixture of α- and β-diastereoisomers that can be thermally isomerized to γ-TBECH and δ-TBECH (de Wit et al., 2010; Covaci et al., 2011). These compounds are mainly applied in polyurethane products and expandable polystyrene beads used in thermal insulation for housing (Tomy et al., 2008). Dechlorane plus (DP) is an important chlorinated FR developed to replace the banned Mirex (Xian et al., 2011) and proposed as possible alternative to the now restricted DecaBDE (Sverko et al., 2011). Commercial products contain a mixture of syn- and anti-DP stereoisomers (UNEP, 2019) and are used in many applications such as cable coatings, electrical wires, plastic roofing materials, and computer and television connectors (Kim et al., 2014). In 2019, DP was proposed to be included in the SC-POP list (UNEP, 2019).

Flame retardants in home and public buildings are released from many household products and building materials and are adsorbed on indoor dust that has been identified as an important FR source (e.g. Jones-Otazo et al., 2005, Wu et al., 2010; Kim et al., 2019). Previous studies of flame retardants in indoor dust have indicated that a variety of factors, including the number of household appliances, building age and cleaning rate can influence the concentration of PBDEs and other contaminants in indoor environment (Harrad et al., 2009; Wu et al., 2010). Due to the remoteness of the Antarctic continent and Southern Ocean and to the fact that all materials used in the scientific stations are transported there from other continents (no local production exists), the indoor presence of FRs in research stations should be ascribed mainly to those sources. Moreover, FRs can also be transported by LRAT (Möller et al., 2012; Kim et al., 2018) and fell by wet and dry depositions, which amplify their concentrations by snow scavenging of contaminants in air (Casal et al. 2019, Khairy et al. 2016). However, such LRAT has a limited potential to affect directly indoor air contamination, since outdoor atmospheric concentrations of FR are low (Khairi et al. 2016). Legacy and novel FRs have already been detected in abiotic and biotic environmental compartments (e.g. Loganathan et al., 2020), and their presence in ecosystems from Antarctica and Southern Ocean has been reported in the scientific literature (e.g.: Corsolini et al., 2006; Borghesi et al., 2009; Wolschke et al., 2015; AMAP, 2017; Roscales et al., 2016; Mello et al., 2016; Corsolini et al., 2017; Kim et al., 2018; Gao et al., 2018; Corsolini et al., 2019).

The main aims of the present study were: to evaluate the levels of legacy FRs (PBDE IUPAC nos. 28, 47, 66, 85, 99, 100, 153, 154, 183, and α-, β-, γ- and δ-isomers of HBCD) and nFRs (HBB, PBT, PBBZ, PBEB, BTBPE, α- and β-TBECH, syn- and anti-DP) in indoor dust from different rooms in two Antarctic research stations (Gabriel de Castilla and Julio Escudero), and on board of the RRS James Clark Ross sailing from Punta Arenas, Chile, to the Drake Passage and Bransfield Strait; to estimate the human exposure to FRs via dust ingestion during a research expedition in Antarctica.

2. Materials and Methods

2.1 Collection of samples

Dust samples (n = 23) were collected in two Antarctic research stations, Julio Escudero Station, Chile (JES, 62°12′57″S 58°57′35″W) and Gabriel de Castilla Station, Spain (GCS, 62°58′38″S; 60°40′33″W), and on board the Royal Research Ship James Clark Ross (RRS JCR) of the British Antarctic Survey, UK, (Figure SM1) using a commercial ARIETE Model 2735 vacuum cleaner; control samples and field blanks were conducted at each sampling site using the sampling vacuum and carefully stored and transported in individual sealed bags to avoid cross contaminations.

Samples were collected in December 2016 –January 2017 onboard RRS James Clark Ross and in January 2017 at Gabriel de Castilla Station and Julio Escudero Station. Ten dust samples were collected at Gabriel de Castilla Station in two laboratories, two igloos, a living room, and five bedrooms. Six dust samples were collected at Julio Escudero Station from the meeting room, one laboratory, two rooms, hall, corridor. Seven dust samples were collected on board the RRS James Clark Ross from the sample storage room (with freezers), one laundry room (n =2), one laboratory, one cabin (n =2), one computer room. The collection of samples was carried out according to a strict standard protocol: in each room, one squared meter of carpet was vacuumed for 2 minutes and, in case of bare floor, four squared meters were vacuumed for four minutes (Harrad et al., 2008). The dust samples were collected using specially designed sampling socks (313 x 175 x 254 mm) made by craft paper which were closed, sealed in a plastic bag and stored at -20 °C; they were mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie.

2.2 Sample preparation and analysis

Solvents used for analysis (n-hexane, dichloromethane, and nonane) were purchased from LGC Promochem (LGC Standards GmbH, Wesel, Germany) and J.T. Baker (Avantor Performance Materials, Gliwice, Poland).

Samples were spiked before extraction with a mixture of surrogate chemicals consisted of 50 μL of ^{13}C PBDEs (IUPAC nos. 28, 47, 66, 85, 99, 100, 153, 154, 183) (20 pg/μL); ^{13}C γ-HBCD (50 ng/mL); ^{13}C-labelled nFRs (20 pg/μL) contained ^{13}C-BTBPE, ^{13}C-PBT; ^{13}C-PBEB, ^{13}C-PBBZ, ^{13}C-HBB, ^{13}Cα-TBECH; ^{13}C-β-TBECH (Cambridge Isotope Laboratory); ^{13}C-syn-DP, ^{13}C-anti-DP (Wellington Lab).

Each sample was passed through a mesh size sieve (500 μm) in order to separate the dust from the other materials of larger size. Finally, they were weighed (~ 1 g) (Sartorius AG Germany, model MSA 125P-000-DU).

The samples were extracted by ultrasonic assisted extraction (UAE, Banderlin Sonorex) three times (3 x 15 minutes) with 10 mL hexane, in order to increase the diffusion and desorption rate of analytes from the sample matrix. After the extraction, the sample volume was reduced under a gentle stream of nitrogen at ambient temperature. Sample clean-up was achieved by mixing 3 mL of sulphuric acid with the sample (Covaci et al., 2007). Then samples were eluted with 40 mL hexane/dihloromethane (DCM 1/1, v/v) in a chromatographic column packed with 1 g active silica gel, 8 g of 44% sulphuric acid-impregnated silica gel, and 1 g active silica gel on the top, then micro-concentrated by a stream of nitrogen in a TurboVap II concentrator unit (Caliper Life Sciences, USA) and finally transferred into a mini vial and filled with nonane to the final volume of 50 μL.

After the instrumental analyses of nFRs and PBDEs, the used final extracts were evaporated and solvent exchange to acetonitrile for HBCD measurement.

2.3 Instrumental analysis

nFRs and PBDEs - In this study FRs were identified and quantified using gas chromatography - high resolution mass spectrometry (GC-HRMS); the 7890A GC (Agilent, USA) was equipped with a 15 m x 0.25 mm x 0.10 um RTX-1614 column (Restek, USA) coupled with an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at > 10000 resolution (10% valley definition). The injection volume was 2 μL and injection was splitless at 280°C, with He as carrier gas at 1 mL/min. The GC temperature program was 80°C (1 min hold), then 20°C/min to 250°C, followed by 1.5°C/min to 260°C (2 min hold) and 25°C/min to 320°C (4.5 min hold). Further details on GC-MS analysis are reported in Venier et al. (2016).

HBCDs - Analysis of α-, β-, γ- and δ-isomers of HBCD was done using liquid chromatography coupled to a Qtrap mass spectrometer (LC-MS/MS); an Agilent 1290 series apparatus (Agilent Technologies, Germany) consisting of a vacuum degasser, a binary pump, a thermostated autosampler (10°C), and a thermostated column compartment kept at 30°C was used. The column was Phenomenex Luna C-18 endcapped (3 μm) 100 x 2 mm i.d., equipped with Phenomenex SecureGuard C18 guard column (Phenomenex, Torrance, CA, USA) and the mass spectrometer was an AB Sciex Qtrap 5500 (AB Sciex, Concord, ON, Canada) with electrospray ionization (ESI). Ions were detected in negative ion mode.

Concentrations of chemical residue in dust samples are given in ng/g dry weight throughout the manuscript.

2.4 Quality Assurance and Quality Control (QA/QC)

The method for quality control (QC) (Harrad et al., 2008) was performed by analyzing laboratory (n=2), trip and field blanks. To track cross contamination, one blank was taken per room category at each station (n=4). Sodium sulfate (Na2SO4) was extracted before sampling with DCM for 18 hours and then used in the trip and field blanks. Na2SO4 was deposited inside the bags to keep a record of the potential contamination of the zip bag itself. Thus the field blanks consisted in vacuum bags with Na2SO4; these plastic bags were transported to the research station with the rest of materials and, once there, they were placed into de vacuum system (deactivated). The trip blanks were analysed and quantified and levels were 5 times lower in magnitude. The recoveries of ^{13}C-labeled compounds were within an acceptable range according to EPA method 1614 (25-150%). The limit of detection (LOD) was calculated from the lowest calibration point as an amount producing a signal to noise 3; the LODs of the analyzed chemicals were: 2.07-36.4 pg/g for PBDEs, 0.6-1.8 ng/g for HBCDs, 0.02-23.0 pg/g for nFRs (Table SM1). The limits of quantification (LOQs) were set as the mean value of target compounds detected in procedural blanks plus ten times of standard deviations. For the undetectable compounds in blanks, the LOQs were set as a signal to noise ratio of 10. The LOQs ranged from 6.22 to 109 pg/g for PBDEs, 2.0 to 6.0 ng/g for HBCDs and 0.07 to 69.2 pg/g for nFRs (Table SM1). Three solvent blanks were used to evaluate contamination from the laboratory procedures. The FR concentrations in all procedural and field blank samples were low (maximum value: <11.2 pg/g for PBDEs; 1350 pg/g for nFRs) and no correction was necessary.

2.5 Calculation of estimated daily exposure to FRs

Three PBDEs (BDE-47, BDE-99 and BDE-153), HBCDs (stereoisomers α-, β-, and γ-HBCD), and two nFRs i.e. BTBPE and syn- and anti-DP were selected to estimate the estimated daily exposure (EDE) via dust ingestion. The estimated daily exposure (ng/kg$_{bw}$/day) to FRs was calculated as:

$$EDE = \sum(C \times EFT \times DI)/BW \qquad [1]$$

where: *EDE* is the estimated exposure; *C* is the concentration (ng/g) of FRs in dust samples from different rooms (average concentration was taken into account for two or more rooms with same use); *EFT* is the estimated fraction of time spent in each room during the day (see Table SM2); *DI* is the daily dust ingestion rate, which was assumed to be 20 mg/day and 50 mg/day for adults to take into account a mean and high dust ingestion scenarios, respectively (Jones-Otazo et al., 2005; Abdallah et al., 2008); *BW* is the body weight assumed for adults (70 kg) (EFSA, 2012). Given the uncertainties about the bioavailability of these substances, a conservative approach has been chosen in exposure assessment considering 100% absorption after their oral ingestion (McGrath et al., 2018).

2.6 Statistical analysis

The software Microsoft Office Excel 2010 (Microsoft, Redmond, WA) and SPSS (V17, Statistical Product and Service Solutions, Chicago, USA) were used to perform the statistical analysis of the data. The concentrations below LOD were assigned a value equal to LOD/2. The Shapiro-Wilk (S-W) and the Kolmogorov-Smirnov (K-S) tests were used to test if data were normally distributed (Tables SM3-5). As some data sets were not normally distributed, concentrations were log$_{10}$-tranformed. Data were then analyzed again by S-W and K-S and normal distribution was confirmed ($p>0.05$). A one-way ANOVA (software SPSS version 22) was applied (Tables SM6-8) to evaluate concentration differences among the three facilities for all studied contaminants. After ANOVA, the post-hoc Tukey test was run in order to assess pairwise comparisons (Tables SM9-11). All comparisons were based on a confidence interval of 95% and a significance level of $p<0.05$.

3. Results and Discussion

The following FRs were detected in the dust samples collected indoor of the research facilities in Antarctica: BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, α-, β-, and γ-HBCD, HBB, PBT, BTBPE, α-TBECH, β-TBECHs, syn- and anti-DPs. The BDEs 66 and 85, PBEB and PBBZ were detected in eight, one, thirteen, and eight out of 23 samples, respectively; δ-HBCD was below LOD in all samples. The percentage of detection of BDE congeners, HBCD isomers and nFR compounds was 58%, 58%, and 78%, respectively. The concentrations of the detected FRs are summarized by research facility in Table 1 and detailed by sampling room in Table 2. The sum of PBDE congeners and HBCD isomers are reported as $\sum_{(7)}$PBDEs and $\sum_{(4)}$HBCDs, respectively.

3.1 Concentrations of legacy and novel FRs

The concentrations of FRs in the research stations and vessel showed different patterns of abundance: HBCDs made up most of the total FR residue in rooms at Gabriel de Castilla Station and RRS James Clark Ross (50% and 87%, respectively), while PBDEs were the most abundant at Julio Escudero Station (40%) (Figure 1a).

3.1.1 PBDEs

The $\sum_{(7)}$PBDEs concentrations in the dust samples collected at the research facilities were higher in the rooms of Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table 1). Among congeners, only BDE-28 levels differed between research facilities ($p<0.05$; Tables SM3, SM6). The PBDE congener abundance varied between the research facilities: BDE-183

(40%) > BDE-99 (23%) > BDE-153 (14%) at Gabriel de Castilla Station; BDE-99 (50%) > BDE-47 (35%) at Julio Escudero Station; BDE-153 (37%) > BDE-99 (22%) > BDE-183 (21%) on RRS James Clark Ross (Figure 1b). The BDE-183 showed the highest concentrations in the laboratory of Gabriel de Castilla Station (68.6 ng/g) and in the computer room of the RRS James Clark Ross (15.0 ng/g) (Table 2). This congener made up 13–42% of the Octa-BDE and it is considered a marker of its use (Alaee et al., 2003). This formulation has been mainly used in hard plastic (e.g. acrilonitrile-butadiene-stirene and high impact polystyrene) which in turn are used for EEE (Yogui and Sericano, 2009). It was reported that DecaBDE transfer to indoor dust is linked to polymer weathering and abrasion (Webster et al., 2009): the same process might be the reason why OctaBDE is abundant in rooms where EEE are in use.

The $\sum_{(3)}$BDEs (BDEs 47, 99, 100) made up >40% of the BDE residue in rooms at Gabriel de Castilla Station and on RRS James Clark Ross, and 90% at Julio Escudero Station (Figure 1b); these congeners are the main components of the PentaBDE mixture used in polyurethane foam. As PentaBDE was banned in 2009 (SC-POPs, 2017), its presence in indoor dust of remote research facilities may suggest old furniture, carpets or upholstery are still in use in these rooms. Nonetheless, higher BDE concentrations have been reported in other Antarctic sites, e.g. the $\sum_{(4)}$PBDEs (BDE-47, BDE-99, BDE-183, BDE-209) was 9560 ng/g and 2240 ng/g at McMurdo Station and Scott Base (Ross Sea), respectively (Hale et al., 2008).

Our results showed that PBDEs were higher in laboratory, sample storage room and living rooms respect to bedrooms (Figure 2) in agreement with the Σ_9PBDE concentration detected in home and office dust samples in an urban area of South Africa (Kefeni & Okonkwo, 2014). Overall, PBDE concentrations found in our samples were lower than the lowest average concentrations found in dust samples from rural regions (e.g. Pakistan and Kuwait) (Table SM12). One or more order of magnitude higher levels were reported in urban areas compared to those measured here (e.g. U.K., China, Canada, USA) (Table SM12).

3.1.2 HBCDs

The HBCDs were detected in all dust samples at Gabriel de Castilla Station except for the igloo 2, in the meeting room and in room 3 at Julio Escudero Station, and in all rooms on board the RRS James Clark Ross (Tables 1-2). High HBCD concentrations were detected in UK house dust (Abdallah et al., 2013) in agreement with our findings. HBCDs were reported to be extensively used in textiles made in Japan (Kajiwara et al., 2009), and their emissions from textiles were observed also at room temperature of 20°C suggesting them as a potential source of these chemicals and other BFRs to indoor dust (Kajiwara et al., 2009; Lucattini et., 2018).

The isomer abundance varied between Stations and was: γ-HBCD > α-HBCD > β-HBCD at Julio Escudero Station; α-HBCD > β-HBCD > γ-HBCD at Gabriel de Castilla Station and onboard the RRS James Clark Ross (Figure 1c). The α- and γ-HBCD were both higher at RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station and differed between the sampling sites ($F>3.39$, $p<0.05$; β-HBCD: $p>0.05$), namely between Julio Escudero Station and Gabriel de Castilla Station, and between Julio Escudero Station and RRS James Clark Ross (Tables SM4, SM7, SM10). The α-HBCD isomer was the most abundant also in house dust of UK (Abdallah et al., 2013), suggesting the indoor dust reflects the levels and profile of home and office dust in the country of origin, being them likely built and furnished with the same materials. The highest ∑HBCD concentrations found in indoor dust from Antarctic Stations were of the same order of magnitude than values reported for urban areas in Belgium (Roosens et al., 2009) and USA (Abdallah et al., 2008) (Table SM13).

3.1.3 novel FRs

Among the nFRs, β-TBECH, syn-DP, anti-DP were detected in all samples (Tables 1, SM3). HBB, PBT, and DPs were higher at RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero

Station, BTBPE was higher onboard the RRS James Clark Ross > Gabriel de Castilla Station and it was <LOD in all rooms at Julio Escudero Station except the corridor (Table 2); the TBECH highest concentrations were found in dust samples of RRS James Clark Ross > Julio Escudero Station > Gabriel de Castilla Station (Table 1). BTBPE and DPs made up most of the total nFR residue being together >95% ca. of the nFR burden (Figure 1d); the levels of BTBPE, anti-DP, syn-DP, α-TBECH, β-TBECH significantly differed between research facilities ($p<0.05$; HBB, PBT: $p>0.05$; Tables SM5, SM8, SM11).

3.1.3.1 BTBPE

The physical-chemical properties of several nFRs allow them to remain mostly in the gaseous phase (Li et al., 2015), but in the case of BTBPE, 50% ca. was reported to be trapped in the particle respect to the gaseous phase (Zhao et al., 2020). In the case of DP and other nFRs with relative low volatility, it is thought that they are mainly associated with atmospheric particulate which allow their transport and deposition (ECHA, 2017), hence from surface media they can be dispersed with dust, being the reason why they were detected in indoor dust.

Previous studies have detected nFRs in remote regions including the Antarctic atmosphere (Zhao et al., 2020) and concentrations can be up to tens of pg/m^3 (ECHA, 2017). BTBPE concentrations in indoor house dust in the UK were of the same order of magnitude of our values (Tao et al., 2016) (Table 1). This chemical is a replacement for OctaBDE (Covaci et al., 2011) and it was reported it could be widely used in the UK after the Furniture and Furnishings (Fire Safety) Regulations 1988 (Tao et al., 2016). These findings suggest the use of materials made in the country of origin, as previously suggested for HBCDs. The BTBPE detection frequency was 100% at Gabriel de Castilla Station and on RRS James Clark Ross suggesting its presence in indoor dust likely due to the use of BTBPE-containing materials; the highest level was found in the sample storage room (Table 2). At Julio Escudero Station it was detected only in the corridor (detection frequency = 17%); Zhao et al.

(2020) also reported BTBPE low detection frequency and preferential distribution through LRAT in air samples collected at the Great Wall Station, China, 2 km South of Julio Escudero Station (detection frequencies = 30% ca., concentrations: n.d. - 0.021 ng/g) (Zhao et al., 2020). Interestingly, in the Arctic BTBPE was detected in 0% of air samples and in 45% of organisms from Station Nord (81°N, 16°E, NE Greenland) and E and W Greenland, respectively (Vorkamp et al. 2015), suggesting a different transport and/or use of BTBPE-containing products in the Arctic and Antarctic regions.

3.1.3.2 DPs

The syn-DP anti-DP made up 73% and 22% of nFR residue at Gabriel de Castilla Station. Accordingly, ∑DPs represented at least 50% of the concentrations of all studied flame retardants in the bedrooms, igloos, and laboratories (Figure 2); at Julio Escudero Station, anti-DP was higher than syn-DP and they represented 45% and 24% of nFRs (Tables 1-2; Figure SM2). The ΣDP concentration was highest in the hall (≈ 80%, Figure 2). The DP is used in a range of products, e.g. electronic wiring and cables, automobiles, plastic roofing materials, and hard plastic connectors in televisions and computer monitors, wire coatings, and also in furniture (Zhang et al., 2015) and building material (Hou et al., 2018). Moreover, as ∑DPs was detected in the Southern Ocean atmosphere at concentration of 0.31 pg/m^3 (Möller et al., 2012), future work will need to elucidate the relative contributions of LRAT and local sources to this atmospheric occurrence.

3.2 Assessment of human exposure to FRs via dust ingestion

Inadvertent indoor dust ingestion is considered a major human exposure pathway to FRs, alongside dietary intake (Jones-Otazo et al. 2005; Besis and Samara, 2012; Kim et al., 2016; McGrath et al., 2018; Bu et al., 2019). For the PBDEs, the USEPA provided a reference dose value (RfD), defined as “an estimate of a daily oral exposure of the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime" (USEPA, 2008). To our knowledge, no health-based guidance value has currently been adopted by USEPA or other regulatory authorities for the remaining compounds investigated in this study. However, HBCDs, BTBPE and DPs were also considered for assessing the human exposure via dust ingestion in view of their high levels measured in the dust samples. The values and percentage contribution of estimated daily exposure are showed in the Table 3 and Figure 3, respectively. Overall, the highest exposure was ascribed to α- > β- > γ-HBCDs isomer (RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station), and to syn- and anti-DP (Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station) (Figure 3).

3.2.1 $\sum_3$BPDEs

In the Antarctic facilities, the higher exposure scenario for each congener with an ingestion of 50 mg/day to selected PBDEs returned exposure values far below their corresponding RfD: the exposure to BDE-47, -99, -153 was < 0.017 ng/kg$_{bw}$/day and highest values were calculated in samples from Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table 3). Exposure to $\sum_3$BPDEs in Antarctic research facilities was generally much lower than the expected intake via dust ingestion to tri- to hexa-BDEs in indoor environments reported in different countries across Europe, North America, Asia and Australia (Besis and Samara, 2012). Besis and Samara (2012) reported that for human exposure both in house and office, the intake through diet likely prevails in countries where the use of PBDEs is high.

3.2.2 HBCDs

Over the past years, some guidance values had been derived to assess the health implication of human exposure to ∑HBCDs. For instance, the US National Research Council Subcommittee on Flame-Retardant Chemicals reported a HBCD Reference Dose (RfD) of 0.2 mg/kg$_{bw}$/day for rats

(NRC, 2000). The Panel on Contaminants in the Food Chain (CONTAM) of the European Food Safety Authority (EFSA) recognized that neurodevelopmental effects on behavior are the ‘’critical endpoint’’ and then proposed a method based on a benchmark dose (lower confidence) limit for a benchmark response of 10% ($BMDL_{10}$) of 0.79 mg/kg body weight; the database showed limitations and uncertainties, thus the CONTAM Panel concluded that this BMDL is inadequate to establish a health-based guidance value (EFSA, 2011). Moreover, the Panel observed that HBCD elimination in humans and animals are different and alternatively used a margin of exposure (MOE) method based on body burden (EFSA, 2011): a chronic ∑HBCD human dietary intake is associated with the body burden at the $BMDL_{10}$ to use for a MOE calculation of 0.003 mg/kg_{bw}/day/estimated dietary intake; a MOE higher than 8 indicates that there is no health concern due to the dietary intake of these chemicals (EFSA, 2011).

The ∑HBCD exposure values at the high dust ingestion rate (50 mg/day) showed the following order: RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station (Table 3), and they were consistent with the literature data, ranging from 0.03-1.3 ng/kg_{bw}/day (Ali et al., 2012; Fromme et al., 2016; Sun et al., 2018). According to Barghi et al. (2016), we alternatively used the MOE approach introduced by the EFSA CONTAM Panel. Applying this approach to our exposure assessment to dust estimated ingestion, we obtained a MOE of 4900 units on RRS James Clark Ross and 11500 ca. at the Gabriel de Castilla Station, showing that the exposure to HBCDs is below levels of health concern.

3.2.3 BTBPE

Although BTBPE is commonly detected in indoor dust, the scientific literature have generally reported lower levels than other nFRs, probably due to low production volumes in the USA and EU (McGrath et al., 2018). Mean or median concentrations (ng/g) reach double-digit levels in North America, while in the other continents they are generally lower (Stapleton et al., 2008; Ali et al., 2012; Fromme et al., 2016; Venier et al., 2016; McGrath et al., 2018; Bu et al., 2019; De la Torre et al., 2020); the corresponding median exposure values, when calculated, were always <0.01 ng/kg$_{bw}$/day (Ali et al., 2012; Bu et al., 2019; De la Torre et al., 2020). On board the RRS James Clark Ross, a high concentration was measured in dust collected in the sample storage room (Table 2) and the exposure values at the high dust ingestion rate in the Antarctic facilities were lower than the RfD$_{BTBPE}$ (243000 ng/kg$_{bw}$/day) proposed by Hardy et al. (2008). The RfD values proposed by Hardy (2008) and Wang (2013), several orders of magnitude higher than our results, may not be appropriate given the shortcomings of toxicological data supporting them. In this respect, it should be noted that this RfD value was derived on the basis of old toxicological studies and little is known about chronic toxicity of brominated nFRs (Ali et al., 2012); furthermore, Hardy and coll. added to their paper a disclosure of conflicts of interest as three of them were employed by brominated FRs manufacturers (Hardy et al., 2008).

3.2.4 DPs

The estimated exposure to ∑DPs at the high dust ingestion rate was 0.182 ng/kg$_{bw}$/day at the Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table 3); this value was higher with respect to 1.4 ng/day, i.e. 0.02 ng/kg$_{bw}$/day (based on median concentrations; 100 mg/day of dust ingestion rate) in dust samples collected in 2002-2003 from 69 residential homes in Ottawa, Canada (Zhu et al., 2007). Li et al. (2015) reported median exposures to ∑DPs of 0.08 and 0.2 ng/day for the Chinese population, corresponding to 0.001 and 0.003 ng/kg$_{bw}$/day at mean and high dust ingestion rates. In a more recent work, Sun et al. (2018) estimated 0.010 (syn-DP) and 0.033 (anti-DP) ng/kg$_{bw}$/day in homes and 0.008 (syn-DP) and 0.044 (anti-DP) ng/kg$_{bw}$/day in offices from Hangzhou, East China. Higher median levels were reported by Zheng et al. (2015) in three e-waste recycling regions in Guangdong Province, South China, where indoor exposures to

∑DPs in five villages ranged 0.07-2.47 ng/kg$_{bw}$/day at the dust ingestion rate of 50 mg/day. For these chemicals Wang et al. (2013) provided a considerable RfD equal to 5 mg/kg$_{bw}$/day.

4. Conclusions

In this study PBDEs, HBCDs, and nFRs were detected in indoor dust collected in research facilities in the Antarctic Region, providing an evidence of their role as FRs local source in Antarctica. Buildings and technical cloth and gear may be ascribed as a local source for indoor environments in research stations and ships, and LRAT may be an additional source of legacy and novel FRs in the Antarctic atmosphere. The highest levels of FRs were found in common areas in all facilities, like laboratories/storage room, hall/corridor, and living room, perhaps because of the presence of electric and electronic equipment and other furniture. The concentration and relative abundance of legacy and nFRs (e.g. HBCDs, BTBPE) in indoor dust can reflect the levels and profile of dust in home and office in the country of origin, being these materials transported from the country of origin. Except DPs at Gabriel de Castilla Station, levels were low when compared to relatively populated regions, and similar or lower to concentrations reported in remote regions (Tables SM12-14).

Taking into account the toxicological relevance of our finding, no adverse effect on human health is expected from the exposure via dust ingestion to PBDEs and HBCD; HBCD isomers, and syn- and anti-DP contributed mostly to the exposure. As far as nFRs, the exposures to BTBPE on board the RRS James Clark Ross and to DPs at the Gabriel de Castilla Station were higher than the available literature data. Since these chemicals are PBTs, an exhaustive characterization of their toxicity should be performed before adopting health-based guidance values. As banned flame retardants continue to be replaced, further studies should be conducted to assess the human exposure to nFRs in Antarctic facilities, even because the use of flame retardants in Antarctic facilities is highly needed for safety reasons since the very low air humidity makes fires a major risk.

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CRediT authorship contribution statement

S. Corsolini: Conceptualization, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision; A. Metzdorff: Formal analysis, Data Curation, Writing PhD thesis (this research derives from it); D. Baroni: Formal analysis, Writing - Original Draft, Visualization; J.L. Roscales: Sampling design support, collection of samples, writing, review and editing; B. Jiménez: Acquisition of the financial support, review and editing; E. Cerro-Gálvez: collection of samples at Gabriel de Castilla; J. Dachs: Acquisition of the financial support and review; C. Galbán-Malagón: Acquisition of financial support for sampling, Review and Editing; O. Audy: Sample analysis for PBDEs, nFRs; Jiří Kohoutek: Sample analysis for HBCDs; P. Přibylová: Data management and analytical part writing; M. Poblete Morales: collection of samples; R. Avendaño-Herrera: Acquisition of financial support for sampling, review; E. Bergami: collection of samples; K. Pozo: Conceptualization, Supervision, Acquisition of the financial support for the project leading to this publication.

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Table 1: Concentrations (ng/g) of flame retardants (mean ± standard deviation, minimum - maximum, median) found in dust samples from the different research facilities in Antarctica (nd = not detected; [a] detected in three rooms at each site; [b] detected in two rooms; [c] detected in a room).

	Gabriel de Castilla			Julio Escudero			RRS James Clark Ross		
	mean ± SD	min - max	median	mean ± SD	min - max	median	mean ± SD	min - max	median
BDE-28	1.09 ± 3.03	0.04 - 9.70	0.06	0.08 ± 0.04	0.03 - 0.12	0.09	0.14 ± 0.12	<LOD-0.34	0.16
BDE-47	4.58 ± 2.96	1.22 - 10.6	3.91	5.98 ± 4.56	2.53 - 13.8	4.30	2.91±3.05	<LOD-9.12	2.75
BDE-66	0.07[a] ± 0.02	0.05-0.09	-	0.35[b] ± 0.15	-	-	0.22 ± 0.16[b]	-	-
BDE-85	0.68[c]			nd	-	-	nd	-	-
BDE-99	9.62 ± 6.55	1.80 - 16.5	10.9	8.57 ± 5.60	4.37 - 18.2	7.25	5.07 ± 3.81	2.70 - 11.8	3.84
BDE-100	1.98 ± 1.17	0.59 - 3.60	2.23	1.99 ± 1.49	0.74 - 3.64	1.59	1.07 ± 1.04	0.55 - 2.93	0.62
BDE-153	5.65 ± 5.42	0.69 - 16.5	4.27	-	-	-	10.2 ± 21.6	0.55 - 58.8	0.83
BDE-154	1.85 ± 1.76	0.33 - 4.83	1.05	0.33[c]	-	-	1.88 ± 3.04	0.24 - 8.56	0.30
BDE-183	16.3 ± 22.6	2.41 - 68.6	5.15	nd	-	-	4.74 ± 5.52	1.39 - 15.0	1.66
$\sum_{(7)}$*PBDEs*	*41.5 ± 43.5*	*7.08 - 131*	*27.6*	*18.7 ± 11.6*	*7.67 ± 35.7*	*13.2*	*27.2 ± 37.9*	*7.99 - 106*	*10.4*
α-HBCD	138 ± 197	4.76 - 648	74.6	5.78 ± 4.41	2.67 - 8.90	5.78	384 ± 501	46.3 - 1150	106
β-HBCD	76.0 ± 166	0.97 - 517	19.6	1.75 ± 0.65	1.29 - 2.21	1.75	275 ± 434	9.79 - 1020	34.2
γ-HBCD	43.1 ± 44.6	6.29 - 156	34.9	7.40 ± 9.46	<LOD-14.1	7.40	102 ± 108	24.5 - 289	50.2
δ-HBCD	nd	-	nd	nd	-	-	nd	-	-
∑*HBCDs*	*257 ± 407*	*12.0 - 1321*	*129*	*14.9 ± 14.5*	*4.66 - 25.2*	*14.9*	*761 ± 1043*	*80.6 - 2459*	*190*
HBB	2.03 ± 4.36	0.19 - 11.9	0.42	1.95 ± 2.54	0.16 - 6.07	0.52	7.67 ± 14.4	0.24 - 29.2	0.63
PBT	1.14 ± 1.78	0.08 - 4.97	0.17	0.09 ± 0.04	0.06 - 0.13	0.08	1.78 ± 2.29	0.22 - 5.81	0.81
PBBZ[a]	0.08 ± 0.21	<LOD-0.69	-	0.24 ± 0.48	<LOD-1.32	-	0.08 ± 0.17	<LOD-0.46	-
PBEB[a]	0.05 ± 0.09	<LOD-0.27	-	0.30 ± 0.70	<LOD-2.15	0.07	0.04 ± 0.05	<LOD-0.12	-
BTBPE	8.02 ± 17.2	0.42 - 56.1	2.02	0.71[c]	-	-	148 ± 336	2.97 - 905	4.52
α-TBECH	0.21 ± 0.14	0.06 - 0.49	0.19	0.51 ± 0.75	0.12 - 1.63	0.15	1.05 ± 1.04	0.22 - 2.72	0.42
β-TBECH	0.16 ± 0.11	0.05 - 0.38	0.16	0.34 ± 0.59	0.05 - 1.54	0.11	0.93 ± 0.96	0.17 - 2.52	0.34
∑*TBECHs*	*0.37 ± 0.24*	*0.11-0.87*	*0.35*	*0.45 ± 1.03*	*<LOD-3.17*	*0.10*	*1.98 ± 1.99*	*0.39-5.24*	*0.76*
syn-DP	163 ± 93.6	68.0 - 388	147	3.60 ± 2.43	2.00 - 8.14	2.40	12.2 ± 17.3	0.98 - 46.7	1.89
anti-DP	48.5 ± 61.1	3.36 - 170	22.2	6.95 ± 7.50	2.86 - 22.1	3.98	21.8 ± 20.3	4.52 - 58.3	15.60
∑*DPs*	*212 ±140*	*78-542*	*169*	*7.22 ± 9.27*	*<LOD-30.24*	*5*	*33.94 ±35.39*	*5.58-87-4*	*17.16*
$\sum_{(7)}$*NBFRs*	*224 ± 178*	*72.2 - 632*	*172*	*14.1 ± 13.8*	*5.97 ± 40.3*	*7.94*	*194 ± 392*	*9.30 - 1050*	*24.2*

Table 2: Concentration (ng/g) of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDs) and novel flame retardants (nFRs) including Dechlorane Plus (DP) from the different research facilities in Antarctica (nd = not detected; GCS: Lab 1-2 = laboratories, LR = living room, Bed 1-5 = bedrooms; JES: MRoom = meeting room, Lab = laboratory, Room 3-4 = bedrooms; RRS JCR: SS Room = sample storage room, LR A and LR B = laundry room, Lab 1B = laboratory, Cab A and Cab B = cabin; C Room = computer room; N.B.: A and B are refereed to sample replicates in the same room on board RRS JCR).

	Gabriel de Castilla										Julio Escudero						RRS James Clark Ross						
	Lab 1	Lab 2	Igloo 1	Igloo 2	LR	Bed 1	Bed 2	Bed 3	Bed 4	Bed 5	MRoom	Lab	Room 3	Room 4	Hall	Corridor	SS Room	LR A	LR B	Lab 1B	Cab A	Cab B	C Room
PBDEs																							
BDE-28	9.70	0.21	0.06	0.18	0.54	0.04	0.06	0.04	0.04	0.04	<LOD	0.12	0.09	0.09	<LOD	0.04	<LOD	0.14	0.16	<LOD	0.17	0.16	0.34
BDE-47	nd	6.46	1.22	6.13	10.6	1.97	5.75	3.92	2.35	2.80	13.8	4.30	3.27	6.03	<LOD	2.54	<LOD	2.42	2.75	<LOD	3.05	3.03	9.12
BDE-66	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.09	0.06	0.05	0.45	<LOD	<LOD	0.24	<LOD	<LOD	<LOD	0.12	0.14	<LOD	<LOD	<LOD	0.41
BDE-85	nd	0.68	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BDE-99	nd	10.9	1.80	15.0	16.5	<LOD	<LOD	<LOD	3.90	<LOD	18.2	7.25	4.92	8.10	<LOD	4.37	<LOD	2.70	2.85	<LOD	4.15	3.84	11.8
BDE-100	nd	2.23	0.59	2.37	3.60	<LOD	<LOD	<LOD	1.12	<LOD	3.64	1.59	<LOD	<LOD	<LOD	0.74	<LOD	0.55	0.62	<LOD	0.58	0.69	2.93
BDE-153	nd	16.5	6.39	<LOD	4.95	3.59	1.69	0.69	10.3	1.12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	58.8	0.65	0.55	2.66	0.58	0.83	7.27
BDE-154	nd	4.83	0.66	<LOD	2.21	4.21	0.93	0.33	1.17	0.45	<LOD	<LOD	<LOD	<LOD	<LOD	0.33	8.56	0.24	0.27	1.28	0.30	0.29	2.26
BDE-183	nd	68.6	4.51	<LOD	17.7	24.3	3.29	2.41	5.79	3.57	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.66	1.39	7.25	1.47	1.66	15.0
HBCDs																							
α-HBCD	74.4	76.5	4.76	nd	648	74.6	78.6	49.5	179	52.9	2.67	nd	8.90	nd	nd	nd	1150	76.8	46.3	1080	60.7	170	106
β-HBCD	25.6	17.9	0.97	nd	517	19.6	22.4	11.2	55.1	14.5	1.29	nd	2.21	nd	nd	nd	1020	19.2	9.79	784	10.4	45.4	34.2
γ-HBCD	34.9	35.9	6.29	nd	156	19.3	27.1	17.9	55.7	35.1	<LOD	nd	14.1	nd	nd	nd	289	45.2	30.9	224	24.5	50.2	51.5
δ-HBCD	<LOD	<LOD	<LOD	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	nd	<LOD	nd	nd	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NFRs																							
HBB	0.26	0.52	0.65	<LOD	11.9	<LOD	0.19	<LOD	0.42	0.25	0.23	0.27	6.02	0.16	4.25	0.76	<LOD	0.24	0.33	0.93	<LOD	<LOD	29.2
PBT	1.55	0.97	0.07	<LOD	4.97	<LOD	0.09	<LOD	0.16	0.17	<LOD	<LOD	0.13	0.06	<LOD	0.08	<LOD	0.64	5.81	0.81	<LOD	0.21	1.44
PBBZ	0.88	0.07	<LOD	<LOD	0.69	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	<LOD	0.55	<LOD	1.32	<LOD	<LOD	<LOD	<LOD	0.77	<LOD	<LOD	0.46
PBEB	0.14	0.09	<LOD	<LOD	0.27	<LOD	0.01	<LOD	<LOD	<LOD	0.24	0.17	0.07	<LOD	2.15	0.08	<LOD	0.02	0.07	0.88	<LOD	<LOD	0.12
BTBPE	2.86	56.1	0.42	2.03	11.4	1.14	2.25	1.14	2.01	0.87	<LOD	<LOD	<LOD	<LOD	<LOD	0.71	905	4.15	2.97	108	3.44	4.52	9.30
α-TBECH	0.06	0.07	0.11	0.27	0.32	0.23	0.49	0.16	0.08	0.29	0.14	<LOD	1.63	<LOD	0.15	0.12	2.25	0.22	0.25	1.14	0.42	0.34	2.72
β-TBECH	0.05	0.06	0.08	0.19	0.26	0.18	0.38	0.14	0.07	0.23	0.11	0.10	1.54	0.05	0.12	0.09	1.94	0.17	0.17	1.06	0.34	0.30	2.52
syn-DP	134	194	85.8	174	388	222	160	81.9	68.0	127	2.00	2.40	4.64	2.40	8.14	2.04	46.7	1.06	1.56	23.2	0.98	1.89	9.89
anti-DP	18.2	30.8	3.36	170	154	13.8	26.2	45.6	10.4	12.9	3.00	4.42	5.76	3.54	22.1	2.86	40.7	4.52	15.6	58.3	5.46	9.21	18.5

Table 3: Estimated human exposure to FRs via dust ingestion and RfD values (ng/kg_{bw}/day) ingestion at mean (20 mg/day = ing-20) and high (50 mg/day = ing-50) ingestion rate in adults ([a]USEPA, 2008; [b]NRC, 2000. Not adopted by any regulatory authority; see MOE approach by EFSA, 2011; [c]RfD - Hardy et al., 2008. Not adopted by any regulatory authority; [d]RfD - Wang et al., 2013, not adopted by any regulatory authority).

	Gabriel de Castilla		Julio Escudero		RRS James Clark Ross		RfD
	ing-20	ing-50	ing-20	ing-50	ing-20	ing-50	
BDE-47	0.002	0.004	0.001	0.003	0.001	0.003	100[a]
BDE-99	0.003	0.007	0.002	0.005	0.001	0.003	100[a]
BDE-153	0.002	0.006	<5.6E-06	<1.4E-05	0.001	0.003	200[a]
∑PBDEs	0.007	0.017	0.003	0.008	0.003	0.009	
α-HBCD	0.054	0.135	0.001	0.002	0.128	0.321	n.a.
β-HBCD	0.035	0.088	0.0003	0.001	0.085	0.213	n.a.
γ-HBCD	0.016	0.039	0.001	0.003	0.031	0.077	n.a.
∑HBCDs	0.105	0.262	0.002	0.005	0.244	0.611	200,000[b]
BTBPE	0.004	0.009	<6.9E-06	<1.7E-05	0.017	0.041	243,000[c]
syn-DP	0.056	0.140	0.001	0.003	0.003	0.009	n.a.
anti-DP	0.017	0.042	0.002	0.006	8E-06	0.020	n.a.
∑DPs	0.073	0.182	0.003	0.008	0.003	0.029	5,000,000[d]

Figure legend

Figure 1: Percentage contribution of FRs in the research stations and vessel: a) ∑PBDEs, ∑HBCDs and ∑NFRs; b) BDE congeners; c) HCBD isomers (δ-HBCD always < LOD); d) novel FRs.

Figure 2: Percentage contribution of ∑PBDEs, ∑HBCDs, other NFRs, ∑TBECHs, and ∑DPs in rooms with different use (at GCS: living room and meeting room).

Figure 3: Estimated human exposure to FRs via indoor dust ingestion at mean (20 mg/day) and high (50 mg/day) ingestion rate (percentage contribution).

GRAPHICAL ABSTRACT

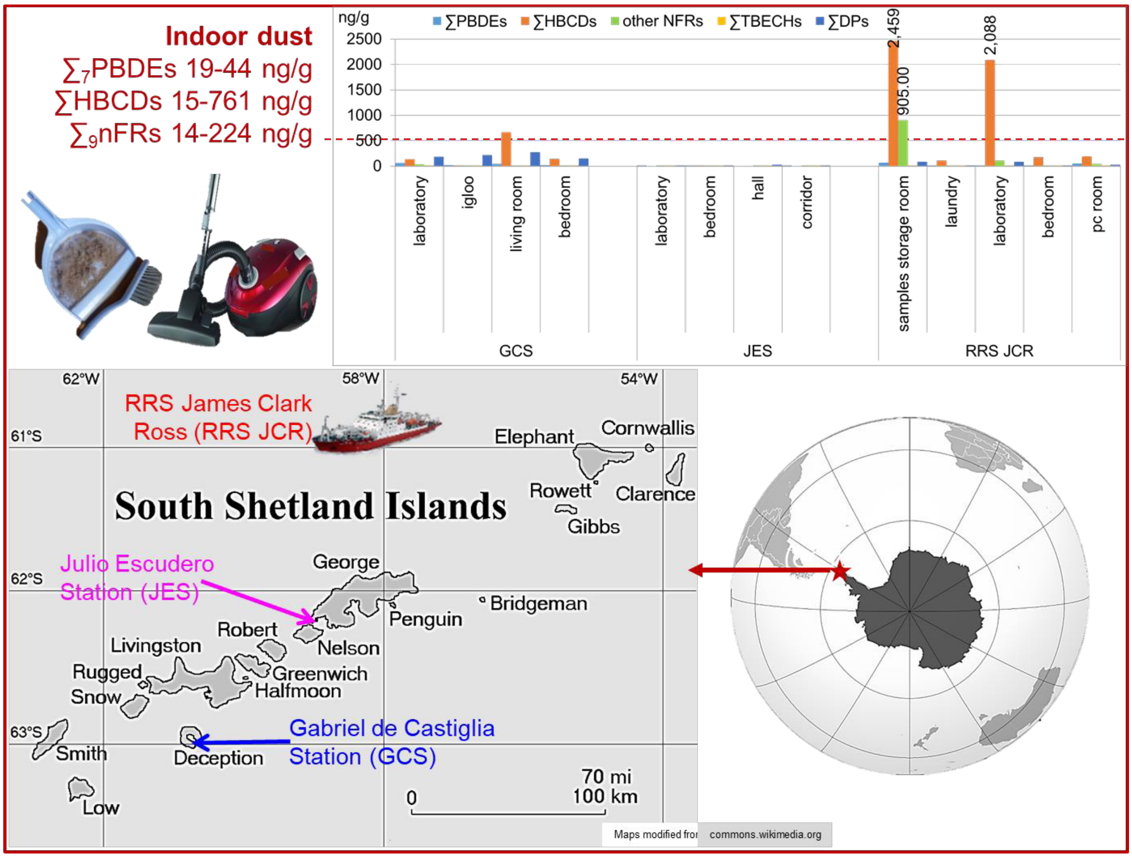


Figure 1

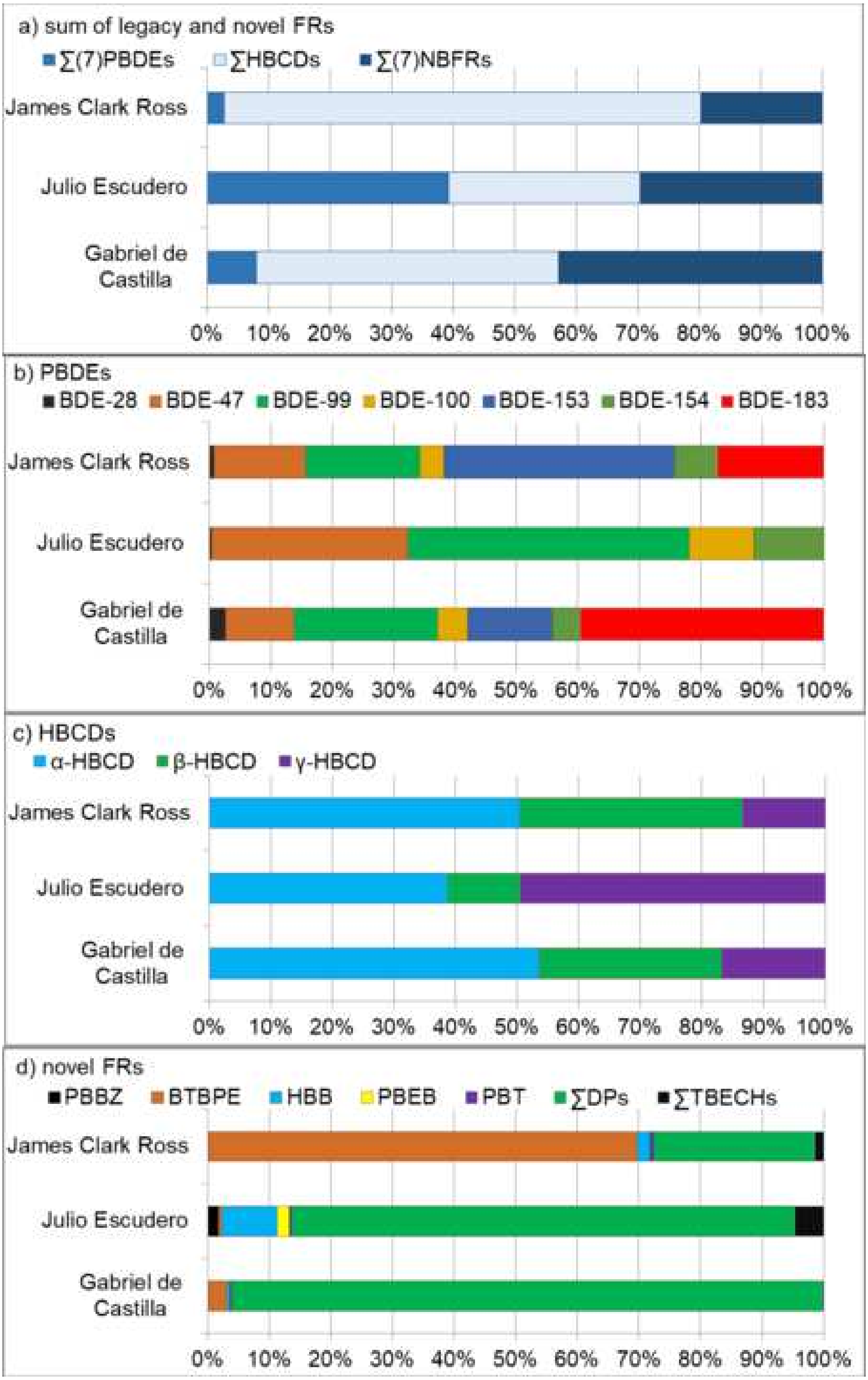
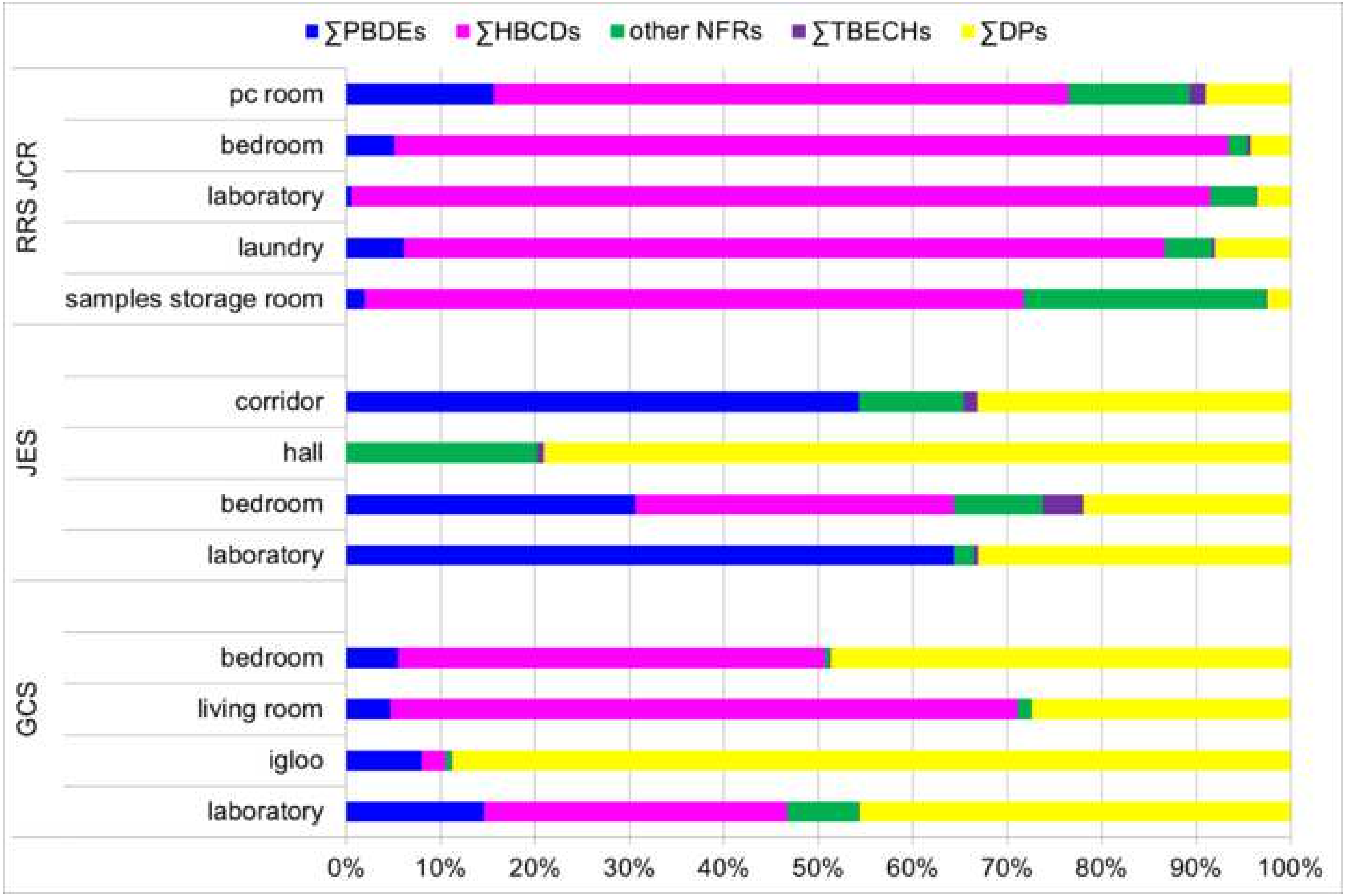

a) sum of legacy and novel FRs
∑(7)PBDEs
∑HBCDs
∑(7)NBFRs
James Clark Ross
Julio Escudero
Gabriel de Castilla
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
b) PBDEs
BDE-28
BDE-47
BDE-99
BDE-100
BDE-153
BDE-154
BDE-183
James Clark Ross
Julio Escudero
Gabriel de Castilla
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
c) HBCDs
α-HBCD
β-HBCD
γ-HBCD
James Clark Ross
Julio Escudero
Gabriel de Castilla
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
d) novel FRs
PBBZ
BTBPE
HBB
PBEB
PBT
∑DPs
∑TBECHs
James Clark Ross
Julio Escudero
Gabriel de Castilla
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%

Figure 2


∑PBDEs
∑HBCDs
other NFRs
∑TBECHs
∑DPs
RRS JCR
pc room
bedroom
laboratory
laundry
samples storage room
JES
corridor
hall
bedroom
laboratory
GCS
bedroom
living room
igloo
laboratory
0%
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30%
40%
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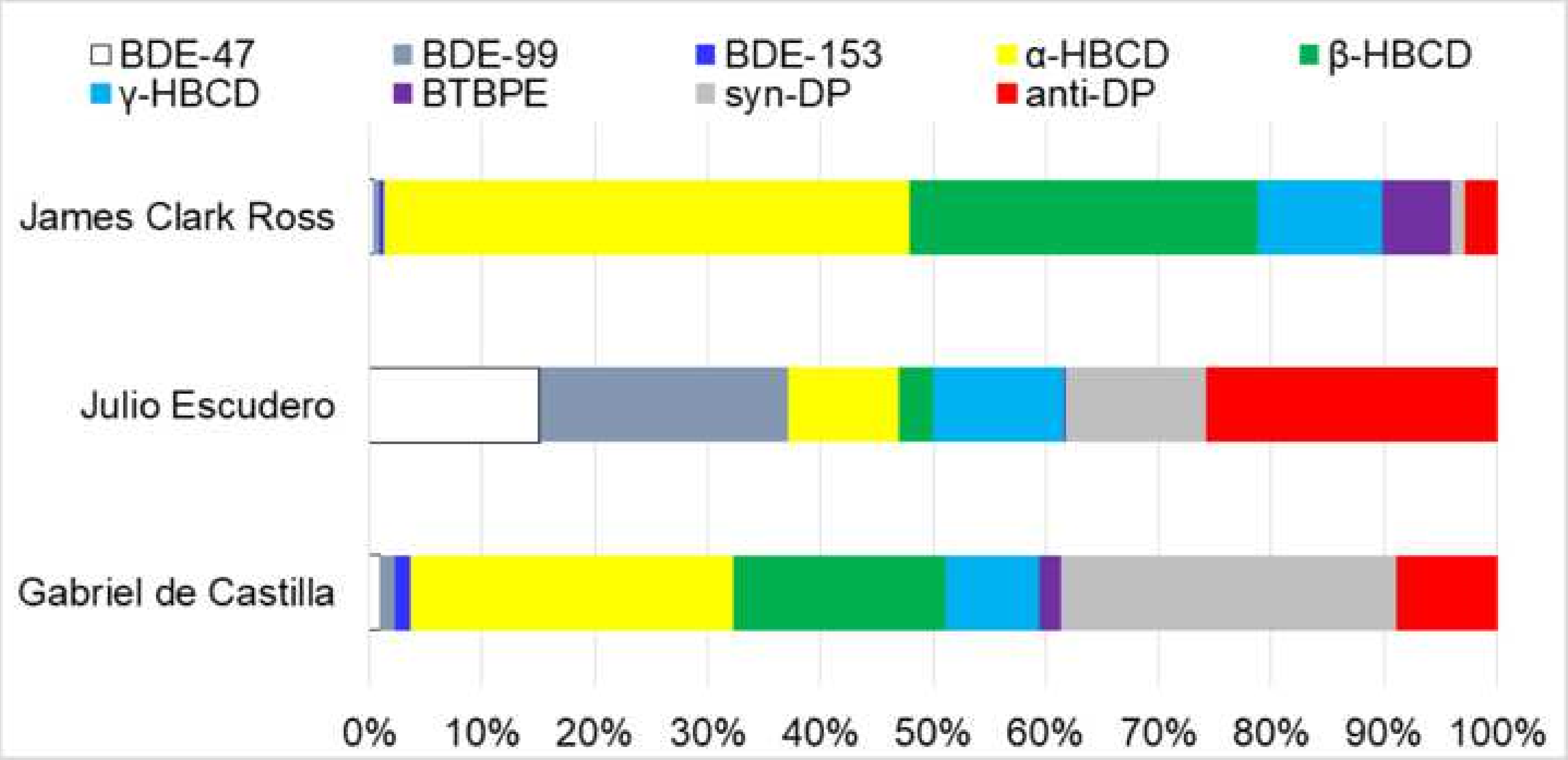
60%
70%
80%
90%
100%

Figure 3


□ BDE-47
■ BDE-99
■ BDE-153
■ α-HBCD
■ β-HBCD
■ γ-HBCD
■ BTBPE
■ syn-DP
■ anti-DP
James Clark Ross
Julio Escudero
Gabriel de Castilla
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%

Supplementary Material

Supplementary Material, pdf file

CRediT authorship contribution statement

S. Corsolini: Conceptualization, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision; A. Metzdorff: Formal analysis, Data Curation, Writing PhD thesis (this research derives from it); D. Baroni: Formal analysis, Writing - Original Draft, Visualization; J.L. Roscales: Sampling design support, collection of samples, writing, review and editing; B. Jiménez: Acquisition of the financial support, review and editing; E. Cerro-Gálvez: collection of samples at Gabriel de Castilla; J. Dachs: Acquisition of the financial support and review; C. Galbán-Malagón: Acquisition of financial support for sampling, Review and Editing; O. Audy: Sample analysis for PBDEs, nFRs; Jiří Kohoutek: Sample analysis for HBCDs; P. Přibylová: Data management and analytical part writing; M. Poblete Morales: collection of samples; R. Avendaño-Herrera: Acquisition of financial support for sampling, review; E. Bergami: collection of samples; K. Pozo: Conceptualization, Supervision, Acquisition of the financial support for the project leading to this publication.

conflict of Interest Statement

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: