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

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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.

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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~~ ~~†~~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 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.~~ 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~~ 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~~ 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),

130 commercialized in a technical mixture of α - and β - diastereoisomers that can be thermally
131 isomerized to γ -TBECH and δ -TBECH (de Wit et al., 2010; Covaci et al., 2011). These compounds
132 are mainly applied in polyurethane products and expandable polystyrene beads used in thermal
133 insulation for housing (Tomy et al., 2008). Dechlorane plus (DP) is an important chlorinated FR
134 developed to replace the banned Mirex (Xian et al., 2011) and proposed as possible alternative to
135 the now restricted DecaBDE (Sverko et al., 2011). Commercial products contain a mixture of syn-
136 and anti-DP stereoisomers (UNEP, 2019) and are used in many applications such as cable coatings,
137 electrical wires, plastic roofing materials, and computer and television connectors (Kim et al.,
138 2014). In 2019, DP was proposed to be included in the SC-POP list (UNEP, 2019).

139 ~~Indoor dust has been identified as an important source of flame retardants in home and public~~
140 ~~buildings are released from many household products and building materials and are adsorbed on~~
141 ~~indoor dust that has been identified as an important FR source~~ (e.g. Jones-Otazo et al., 2005, Wu et
142 al., 2010; Kim et al., 2019) ~~because they are released from many household products and building~~
143 ~~materials~~. Previous studies ~~on the presence~~ of flame retardants in indoor dust have indicated that a
144 variety of factors, including the number of household appliances, building age and cleaning rate can
145 influence the concentration of PBDEs and other contaminants in indoor environment (Harrad et al.,
146 2009; Wu et al., 2010). Due to the remoteness of ~~the~~ Antarctica continent and Southern Ocean and
147 to the fact that all materials used in the scientific stations are transported there from other continents
148 (no local production exists), the indoor presence of FRs in research stations should be ascribed
149 mainly to those sources. Moreover, FRs can also be transported by LRAT (Möller et al., 2012; Kim
150 et al., 2018) and fell by wet and dry depositions, which amplify their concentrations by snow
151 scavenging of contaminants in air (Casal et al. 2019, Khairy et al. 2016). However, such LRAT has
152 a limited potential to affect directly indoor air contamination, since outdoor atmospheric
153 concentrations of FR are low (Khairi et al. 2016) ~~and then contributing to indoor contamination~~.

154 Legacy and novel FRs have already been ~~already~~ detected in abiotic and biotic environmental

155 compartments (e.g. ~~Chen et al., 2012; Wolschke~~Loganathan et al., 201520), and their ~~distribution~~
156 presence in ecosystems from Antarctica and Southern Ocean has been ~~largely~~ reported in the
157 scientific literature (e.g.: Corsolini et al., 2006; Borghesi et al., 2009; Wolschke et al., 2015;
158 AMAP, 2017; Roscales et al., 2016; Mello et al., 2016; Corsolini et al., 2017; Kim et al., 2018; Gao
159 et al., 2018; Corsolini et al., 2019).

160 The main aims of the present study were: to evaluate the levels of legacy FRs (PBDE IUPAC nos.
161 28, 47, 66, 85, 99, 100, 153, 154, 183, and α -, β -, γ - and δ -isomers of HBCD) and nFRs (HBB,
162 PBT, PBBZ, PBEB, BTBPE, α - and β -TBECH, syn- and anti-DP) in indoor dust from different
163 rooms in two Antarctic research stations (Gabriel de Castilla and Julio Escudero), and on board of
164 the RRS James Clark Ross sailing from Punta Arenas, Chile, to the Drake Passage and Bransfield
165 Strait; to estimate the human exposure to FRs via dust ingestion during a research expedition in
166 Antarctica.

169 2. Materials and Methods

171 2.1 Collection of samples

172 Dust samples (n = 23) were collected in two Antarctic research stations, Julio Escudero Station,
173 Chile (JES, 62°12'57"S 58°57'35"W) and Gabriel de Castilla Station, Spain (GCS,
174 62°58'38"S; 60°40'33"W), and on board the Royal Research Ship James Clark Ross (RRS JCR) of
175 the British Antarctic Survey, UK, (Figure SM1) using a commercial ARIETE Model 2735 vacuum
176 cleaner; control samples and field blanks were conducted at each sampling site using the sampling
177 vacuum and carefully stored and transported in individual sealed bags to avoid cross
178 contaminations.

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

194 2.2 Sample preparation and analysis

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

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

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

206 The samples were extracted ~~ibyn~~ ultrasonic assisted extraction (UAE, Banderlin Sonorex) three
207 times (3 x 15 minutes) with 10 mL hexane, in order to increase the diffusion and desorption rate of
208 analytes from the sample matrix. After the extraction, the sample volume was reduced under a
209 gentle stream of nitrogen at ambient temperature. Sample clean-up was achieved by mixing 3 mL of
210 sulphuric acid with the sample (Covaci et al., 2007). Then samples were eluted with 40 mL
211 hexane/dichloromethane (DCM 1/1, v/v) in a chromatographic column packed with 1 g active silica
212 gel, 8 g of 44% sulphuric acid-impregnated silica gel, and 1 g active silica gel on the top, then
213 micro-concentrated by a stream of nitrogen in a TurboVap II concentrator unit (Caliper Life
214 Sciences, USA) and finally transferred into a mini vial and filled with nonane to the final volume of
215 50 µL.

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

220 2.3 Instrumental analysis

221 *nFRs and PBDEs* -

222 In this study FRs were identified and quantified using ~~a~~ gas chromatography - high resolution mass
223 spectrometry (GC-HRMS); the 7890A GC (Agilent, USA) was equipped with a 15 m x 0.25 mm x
224 0.10 µm RTX-1614 column (Restek, USA) coupled with an AutoSpec Premier MS (Waters,
225 Micromass, UK). The MS was operated in EI+ mode at > 10000 resolution (10% valley definition).
226 The injection volume was 2 µL and injection was splitless at 280°C, with He as carrier gas at 1
227 mL/min. The GC temperature program was 80°C (1 min hold), then 20°C/min to 250°C, followed

228 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-
229 MS analysis are reported in Venier et al. (2016).

230 HBCDs

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

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

242 *2.4 Quality Assurance and Quality Control (QA/QC)*

243 The method for quality control (QC) (Harrad et al., 2008) —was performed by analyzing laboratory
244 (n=2), trip and several—field blanks—blank evaluation. To track cross contamination, one blank was
245 taken per room category at each station (n=4).: i) —Sodium sulfate (Na₂SO₄) was extracted before
246 sampling with DCM for 18 hours and then used in the trip and field blanks—prepared—during
247 sampling, and ii) —procedural blanks (Na₂SO₄ prepared before sample extraction prepared before
248 sample extraction). —Na₂SO₄ was deposited inside the bags to keep a record of the potential
249 contamination of the zip bag itself. Thus the field blanks consisted in vacuum bags with Na₂SO₄;
250 these plastic bags were transported to the research station with the rest of materials and, once there,
251 they were placed into de vacuum system (deactivated). The trip blanks were analysed and quantified

252 and levels were 5 times lower in magnitude. The recoveries of ¹³C-labeled compounds were within
253 an acceptable range according to EPA method 1614 (25-150%).

254 The limit of detection (LOD) was calculated from the lowest calibration point as an amount
255 producing a signal to noise 3; the LODs of the analyzed chemicals were: 2.07-36.4 pg/g for PBDEs,
256 0.6-1.8 ng/g for HBCDs, 0.02-23.0 pg/g for nFRs (Table SM1). The limits of quantification (LOQs)
257 were set as the mean value of target compounds detected in procedural blanks plus ten times of
258 standard deviations. For the undetectable compounds in blanks, the LOQs were set as a signal to
259 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
260 and 0.07 to 69.2 pg/g for nFRs (Table SM1). Three solvent blanks were used to evaluate
261 contamination from the laboratory procedures. The FR peaks-concentrations in all procedural and
262 field blank samples were low (maximum value: <11.2 pg/g for PBDEs; 1350 pg/g for nFRs) and no
263 correction was necessary.

265 *2.5 Calculation of estimated daily exposure to FRs*

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

$$269 \text{EsEx-EDE} = \sum(C \times \text{EFT} \times \text{DI})/\text{BW} \quad [1]$$

270 where: EsEx-EDE is the estimated exposure; *C* is the concentration (ng/g) of FRs in dust samples
271 from different rooms (average concentration was taken into account for two or more rooms with
272 same use); EFT is the estimated fraction of time spent in each room during the day (see Table
273 SM2); *DI* is the daily dust ingestion rate, which was assumed to be 20 mg/day and 50 mg/day for
274 adults to take into account a mean and high dust ingestion scenarios, respectively (Jones-Otazo et
275 al., 2005; Abdallah et al., 2008); *BW* is the body weight assumed for adults (70 kg) (EFSA, 2012).

276 Given the uncertainties about the bioavailability of these substances, a conservative approach has

277 been chosen in exposure assessment considering 100% absorption after their oral ingestion
278 (McGrath et al., 2018).

279 280 2.6 Statistical analysis

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

284 The Shapiro-Wilk (S-W) and the Kolmogorov-Smirnov (K-S) tests were used to test if data were
285 normally distributed (Tables SM3-5). As some data sets were not normally distributed,
286 concentrations were log₁₀-transformed. Data were then analyzed again by S-W and K-S and ~~were~~
287 normally ~~distribution was ed~~confirmed (p>0.05). A one-way ANOVA (software SPSS version 22)
288 was applied (Tables SM6-8) to evaluate concentration differences among the three facilities for all
289 studied contaminants. After ANOVA, the post-hoc Tukey test was run in order to assess pairwise
290 comparisons~~verify differences between sampling sites~~ (Tables SM9-11). All comparisons were
291 based on a confidence interval of ~~All contaminants were considered using 95% and a confidence~~
292 ~~interval with statistical~~ significance level of p<0.05. ~~The concentrations below LOD were assigned~~
293 ~~a value equal to LOD/2.~~

294 295 296 3. Results and Discussion

297
298 The following FRs were detected in the dust samples collected indoor of the research facilities in
299 Antarctica: BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, α -, β -, and γ -
300 HBCD, HBB, PBT, BTBPE, α -TBECH, β -TBECHs, syn- and anti-DPs. The BDEs 66 and 85,
301 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 SM12. 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-JCRRRS 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, oOnly 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-JCRRRS 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-JCRRRS James Clark Ross~~ (15.0 ng/g) (Table SM12). 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. acrylonitrile-butadiene-styrene 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 $\Sigma_{(3)}$ BDEs (BDEs 47, 99, 100) made up >40% of the BDE residue in rooms at ~~GCS~~Gabriel de Castilla Station and on ~~RRS-JCRRS~~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 $\Sigma_{(4)}$ 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 SM2) in agreement with the Σ_9 PBDE 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 found in Σ_8 PBDE 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. $\Sigma_{(10)}$ PBDEs = 179 \pm 3.2 ng/g in U.K., (Harrad et al., 2008), $\Sigma_{(27)}$ PBDE = 400 ng/g in Guangzhou, China (Wang et al., 2014), and $\Sigma_{(10)}$ PBDE = 1600 ng/g in TexasCanada, USA (Harrad et al., 2008).) (Table SM12).

350 ~~Except for the igloo 2, the HBCDs were detected in all dust samples at GCS with 257 ± 407 ng/g~~
351 ~~($12 - 1321$ 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),~~
352 ~~and in all rooms on board the RRS JCR with 761 ± 1043 ng/g ($80.6 - 2459$ ng/g) (Tables 1, SM12).~~

353 3.1.2 HBCDs

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

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

364
365 The HBCD isomer abundance varied between Stations (~~δ -HBCDs $< LOD$ in all samples~~) and was:
366 γ -HBCD $>$ α -HBCD $>$ β -HBCD at ~~JES~~ Julio Escudero Station; α -HBCD $>$ β -HBCD $>$ γ -HBCD at
367 ~~GCS~~ Gabriel de Castilla Station and onboard the ~~RRS JCR~~ RRS James Clark Ross (Figure 1c). ~~The~~
368 ~~α - and γ -HBCD were both higher at RRS James Clark Ross $>$ Gabriel de Castilla Station $>$ Julio~~
369 ~~Escudero Station and differed between the sampling sites ($F > 3.39$, $p < 0.05$; β -HBCD: $p > 0.05$),~~
370 ~~namely between Julio Escudero Station and Gabriel de Castilla Station, and between Julio Escudero~~
371 ~~Station and RRS James Clark Ross (Tables SM4, SM7, SM10). The α -HBCD isomer was reported~~
372 ~~to be~~ the most abundant also in house dust of UK (Abdallah et al., 2013), suggesting the indoor dust
373 reflects the levels and profile of home and office dust in the country of origin, being them likely
374 built and furnished with the same materials. The highest Σ HBCD concentrations found in indoor

375 dust from Antarctic Stations were of the same order of magnitude than values reported for urban
376 areas in Belgium (~~160 ± 170 ng/g, 33-770 ng/g~~) (Roosens et al., 2009) and USA (~~810 ± 1100~~
377 ~~ng/g, 79-2000 ng/g~~) (Abdallah et al., 2008) (Table SM13).

379 3.1.3 novel FRs

380 Among the nFRs, β -TBECH, syn-DP, anti-DP were detected in all samples (Tables 1, SM3). HBB,
381 PBT, and DPs were higher at RRS James Clark Ross > 2.03 ± 4.36 ng/g in rooms at GCS Gabriel
382 de Castilla Station > , 1.95 ± 2.54 ng/ at JES Julio Escudero Station, and 7.67 ± 14.4 ng/g on RRS
383 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
384 JCR; BTBPE BTBPE was higher onboard the 8.02 ± 17.2 ng/g in rooms at GCS, 148 ± 336 ng/g
385 on RRS JCR RRS James Clark Ross > Gabriel de Castilla Station, and it was <LOD in all rooms at
386 JES Julio Escudero Station except the corridor (~~0.71 ng/g, Table SM12~~); The the TBECHs highest
387 concentrations were found in dust samples of lower at RRS James Clark Ross > Julio Escudero
388 Station > Gabriel de Castilla Station GCS (α -TBECH: 0.21 ± 0.14 ng/g; β -TBECH: 0.16 ± 0.11
389 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 -
390 TBECH: 1.05 ± 1.04 ng/g; β -TBECH: 0.93 ± 0.96 ng/g). The sum of DP isomers was 212 ± 140
391 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
392 DPs made up most of the total nFR residue being together >95% ca. of the nFR burden (Figure 1d);
393 t. The levels of BTBPE, anti-DP, syn-DP, α -TBECH, β -TBECH significantly differed between
394 research facilities ($p < 0.05$; HBB, PBT: $p > 0.05$; Tables SM5, SM8, SM11).

396 3.1.3.1 BTBPE

397 ~~BTBPE and DPs made up most of the total nFR residue being together >95% ca. of the nFR burden~~
398 ~~(Figure 1d)~~. The physical-chemical properties of several nFRs allow them to remain mostly in the
399 gaseous phase (Li et al., 2015), but in the case of BTBPE, 50% ca. was reported to be trapped in the

400 particle respect to the gaseous phase (Zhao et al., 2020). In the case of DP and other nFRs with
401 relative low volatility, it is thought that they are mainly associated with atmospheric particulate
402 which allow their transport and deposition (ECHA, 2017), hence from surface media they can be
403 dispersed with dust, being the reason why they were detected in indoor dust.

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

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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, Σ DPs represented at least 50% of the concentrations of all studied flame retardants in the bedrooms, igloos, and laboratories (Figure SM2); 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-, SM12; Figure SM32). T-, and the Σ DP concentration was sum was highest in the hall ($\approx 80\%$, Figure SM2). 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 Σ DPs was detected in the Southern Ocean atmosphere at concentration of 0.31 pg/m³ (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; Basis and Samara, 2012; Kim et al., 2016; McGrath et al., 2018; Bu et al., 2019). For these 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

450 also considered for assessing the human exposure via dust ingestion in view of their high levels
451 measured in the dust samples. The ~~formula 1 (section 2.6) was applied and the values and~~
452 percentage contribution of estimated daily exposure are showed in the Table ~~2-3~~ and Figure 3,
453 respectively. ~~The higher exposure scenario with an ingestion of 50 mg/day to selected PBDEs~~
454 returned Overall, the highest exposure was ascribed to α - > β - > γ -HBCDs isomer values of 0.007
455 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
456 RRS JCR. These estimated values for each chemical were far below their corresponding RfD (Table
457 2)(RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station), and to syn- and
458 anti-DP (Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station) (Figure 3).

460 3.2.1 Σ_3 BPDEs

461 In the Antarctic facilities, the higher exposure scenario for each congener with an ingestion of 50
462 mg/day to selected PBDEs returned exposure values far below their corresponding RfD: the
463 exposure to BDE-47, -99, -153 was < 0.017 ng/kg_{bw}/day and highest values were calculated in
464 samples from Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table
465 3). Exposure to Σ_3 BPDEs in Antarctic research facilities was generally much lower than the
466 expected intake via dust ingestion to tri- to hexa-BDEs in indoor environments, reported in
467 different countries across Europe, North America, Asia and Australia (Besis and Samara, 2012).
468 Besis and Samara (2012) reported that for human exposure both in house and office, the intake
469 through diet likely prevails in countries where the use of PBDEs is high.

471 3.2.2 HBCDs

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

475 ~~al., 2016; Sun et al., 2018).~~ Over the past years, some guidance values had been derived to assess
476 the health implication of human exposure to Σ HBCDs ~~(NRC, 2000, RfD = 0.2~~
477 ~~mg/kg_{bw}/day; UBA, 2001, TDI = 139 μ g/kg_{bw}/day), but no protective reference value as RfD,~~
478 ~~tolerable daily intake (TDI) or minimal risk level (MRL) is currently adopted by the competent~~
479 ~~institutions.~~ For instance, the US National Research Council Subcommittee on Flame-Retardant
480 Chemicals reported a HBCD Reference Dose (RfD) of 0.2 mg/kg_{bw}/day for rats (NRC, 2000). The
481 Panel on Contaminants in the Food Chain (CONTAM) of the European Food Safety Authority
482 (EFSA) recognized that neurodevelopmental effects on behavior are the “critical endpoint” and
483 then proposed a method based Starting by on a benchmark dose (lower confidence limit) limit for a
484 benchmark response of 10% (BMDL₁₀) of 0.79 mg/kg body weight; the database showed
485 limitations and uncertainties, thus the CONTAM Panel concluded that this BMDL is inadequate to
486 establish a health-based guidance value (EFSA, 2011). Moreover, the Panel observed that HBCD
487 elimination in humans and animals are different and alternatively used a margin of exposure (MOE)
488 method based on body burden (EFSA, 2011); ~~the CONTAM Panel derived a chronic Σ HBCD~~
489 ~~human dietary intake for Σ HBCDs of 0.003 mg/kg_{bw}/day is associated with the body burden at the~~
490 ~~BMDL₁₀ to use for the a MOE calculation of a MOE of = 0.003 mg/kg_{bw}/day/estimated dietary~~
491 ~~intake; a MOE higher than 8 indicates that there is no health concern due to the dietary intake of~~
492 ~~these chemicals (EFSA, 2011).~~

493 The Σ HBCD exposure values at the high dust ingestion rate (50 mg/day) showed the following
494 order: RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero Station (Table 3), and
495 they were consistent with the literature data, ranging from 0.03-1.3 ng/kg_{bw}/day (Ali et al., 2012;
496 Fromme et al., 2016; Sun et al., 2018). According to Barghi et al. (2016), we alternatively used the
497 ~~margin of exposure (MOE) approach introduced by the Panel on Contaminants in the Food Chain~~
498 ~~EFSA (CONTAM Panel) of the European Food Safety Authority (EFSA).~~ Starting by a benchmark
499 ~~dose (lower confidence limit) for a benchmark response of 10% (BMDL₁₀), the CONTAM Panel~~

500 ~~derived a chronic human dietary intake for Σ HBCDs of 0.003 mg/kg_{bw}/day associated with the~~
501 ~~body burden at the BMDL₁₀ to use for the calculation of a MOE = 0.003 mg/kg_{bw}/day/estimated~~
502 ~~dietary intake; a MOE higher than 8 indicates that there is no health concern due to the dietary~~
503 ~~intake of these chemicals (EFSA, 2011).~~ Applying this model approach to our exposure assessments
504 from to dust estimated ingestion, estimated on RRS JCR and at the GCS, we obtained a MOE of
505 4900 units on RRS James Clark Ross and 11500 ca., at the Gabriel de Castilla Station, respectively,
506 showing that the exposure to HBCDs is below levels of health concern.

508 3.2.3 BTBPE

509 Although BTBPE is commonly detected in indoor dust, ~~international studies~~ the scientific literature
510 have generally reported lower levels than other nFRs, probably due to low production volumes in
511 the USA and EU (McGrath et al., 2018). Mean or median concentrations (ng/g) reach double-digit
512 levels in North America, while in the other continents they are generally lower (Stapleton et al.,
513 2008; Ali et al., 2012; Fromme et al., 2016; Venier et al., 2016; McGrath et al., 2018; Bu et al.,
514 2019; De la Torre et al., 2020); the corresponding median exposure values, when calculated, were
515 always <0.01 ng/kg_{bw}/day (Ali et al., 2012; Bu et al., 2019; De la Torre et al., 2020). On board the
516 RRS James Clark Ross, a high concentration was measured in dust collected in the sample storage
517 room (Table 2) and the exposure values at the high dust ingestion rate in the Antarctic facilities
518 were lower than the RfD_{BTBPE} (243000 ng/kg_{bw}/day) proposed by Hardy et al. (2008). ~~On board the~~
519 ~~RRS JCR, a mean value of 148 ng/g of BTBPE was obtained, due to the particularly high level~~
520 ~~measured in dust collected in the sample storage room (905 ng/g). The exposures at the high dust~~
521 ~~ingestion rate were: 0.041 ng/kg_{bw}/day for RRS JCR > 0.009 ng/kg_{bw}/day for GCS > 1.7E-05~~
522 ~~ng/kg_{bw}/day for JES, thus significantly lower than the RfD_{BTBPE} proposed by Hardy et al. (2008) of~~
523 243000 ng/kg_{bw}/day. The RfD values proposed by Hardy (2008) and Wang (2013), several orders of
524 magnitude higher than our results, may not be appropriate given the shortcomings of toxicological

525 data supporting them. In this respect, it should be noted that this RfD value was derived on the basis
526 of old toxicological studies and little is known about chronic toxicity of brominated nFRs (Ali et al.,
527 2012); furthermore, Hardy and coll. ~~the authors~~ added to their paper (~~Hardy et al., 2008~~) a
528 disclosure of conflicts of interest as three of them were employed by brominated FRs manufacturers
529 (Hardy et al., 2008).

530

531 3.2.4 DPs

532 The estimated exposure ~~to Σ DPs at the high dust ingestion rate to DP~~ was 0.182 ng/kg_{bw}/day at the
533 GCS Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table 3); this
534 value was higher with respect to 1.4 ng/day, i.e. 0.02 ng/kg_{bw}/day (based on median concentrations;
535 100 mg/day of dust ingestion rate) in dust samples collected in 2002-2003 from 69 residential
536 homes in Ottawa, Canada (Zhu et al., 2007). Li et al. (2015) reported median exposures to Σ DPs of
537 0.08 and 0.2 ng/day for the Chinese population, corresponding to 0.001 and 0.003 ng/kg_{bw}/day at
538 mean and high dust ingestion rates. In a more recent work, Sun et al. (2018) estimated 0.010 (syn-
539 DP) and 0.033 (anti-DP) ng/kg_{bw}/day in homes and 0.008 (syn-DP) and 0.044 (anti-DP)
540 ng/kg_{bw}/day in offices from Hangzhou, East China. Higher median levels were reported by Zheng et
541 al. (2015) in three e-waste recycling regions in Guangdong Province, South China, where indoor
542 exposures to Σ DPs in five villages ranged 0.07---2.47 ng/kg_{bw}/day at the dust ingestion rate of 50
543 mg/day. For these chemicals Wang et al. (2013) provided a considerable RfD equal to 5
544 mg/kg_{bw}/day.

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547 **54. Conclusions**

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549 In this study PBDEs, HBCDs, and nFRs were detected in indoor dust collected in research facilities
550 in the Antarctic Region, providing an evidence of their role as nFRs local source in Antarctica.
551 Buildings and technical cloth and gear may be ascribed as a local source for indoor environments in
552 research stations and ships, and LRAT may be an additional source of legacy and novel FRs in the
553 Antarctic atmosphere, ~~while buildings and technical cloth and gear may be ascribed as an additional~~
554 ~~local source for indoor environments in research stations and ships.~~ The highest levels of FRs were
555 found in common areas in all facilities, like laboratories/storage room, hall/corridor, and living
556 room, perhaps because of the presence of electric and electronic equipment and other furniture. The
557 concentration and relative abundance of legacy and ~~novel flame retardants~~nFRs (e.g. HBCDs,
558 BTBPE) in indoor dust can reflect the levels and profile of dust in home and office in the country of
559 origin, being these materials transported from the country of origin. Except DPs at ~~GCS~~Gabriel de
560 Castilla Station, levels ~~we~~are low when compared to relatively populated regions~~when compared to~~
561 ~~anthropized regions~~, and similar or lower to concentrations reported in remote regions (Tables
562 ~~SM13~~SM12-1514).

563
564 Taking into account the toxicological relevance of our finding, no adverse effect on human health is
565 expected from the exposure via dust ingestion to PBDEs and HBCD; HBCD isomers, and syn- and
566 anti-DP contributed mostly to the exposure. As far as ~~novel~~nFRs, the exposures to BTBPE on
567 board the RRS James Clark Ross and to DPs at the Gabriel de Castilla Station were higher than the
568 available literature data; ~~in the latter case exposure reached a value comparable to the levels~~
569 ~~estimated for residents in one of the most DP polluted areas in the world (Wang et al., 2013).~~ Since
570 these chemicals are PBTs, an exhaustive characterization of their toxicity should be performed
571 before adopting health-based guidance values. As banned flame retardants continue to be replaced,
572 further studies should be conducted to assess the human exposure to nFRs in Antarctic facilities,

573 even because the use of flame retardants in Antarctic facilities ~~can be considered~~is highly needed
574 for safety reasons ~~as~~since the very low air humidity makes fires a major risk.

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594 Group).

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603

604 **CRedit authorship contribution statement**

605 S. Corsolini: Conceptualization, Writing - Original Draft, Writing - Review & Editing,
606 Visualization, Supervision; A. Metzdorff: Formal analysis, Data Curation, Writing PhD thesis (this
607 research derives from it); D. Baroni: Formal analysis, Writing - Original Draft, Visualization; J.L.
608 Roscales: Sampling design support, collection of samples, writing, review and editing; B. Jiménez:
609 Acquisition of the financial support, review and editing; E. Cerro-Gálvez: collection of samples at
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612 PBDEs, nFRs; Jiří Kohoutek: Sample analysis for HBCDs; P. Příbylová: Data management and
613 analytical part writing; M. Poblete Morales: collection of samples; R. Avendaño-Herrera:
614 Acquisition of financial support for sampling, review; E. Bergami: collection of samples; K. Pozo:
615 Conceptualization, Supervision, Acquisition of the financial support for the project leading to this
616 publication.

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619 **References**

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- 877 and organochlorines in indoor dust from several e-waste recycling sites in South China:
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882 Table 1: Concentrations (ng/g) of flame retardants (mean \pm standard deviation, minimum -
883 maximum, median) found in dust samples from the different research facilities in Antarctica (nd =
884 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		
	<u>M</u> mean \pm SD	<u>M</u> min - <u>M</u> max	<u>M</u> median	<u>M</u> mean \pm SD	<u>M</u> min - <u>M</u> max	<u>M</u> median	<u>M</u> mean \pm SD	<u>M</u> min - <u>M</u> max	<u>M</u> median
BDE-28	1.09 \pm 3.03	0.04 - 9.70	0.06	0.08 \pm 0.04	0.03 - 0.12	0.09	0.14 \pm 0.12	<LOD-0.34	0.16
BDE-47	4.58 \pm 2.96	1.22 - 10.6	3.91	5.98 \pm 4.56	2.53 - 13.8	4.30	2.91 \pm 3.05	<LOD-9.12	2.75
BDE-66	0.07 ^a \pm 0.02	0.05-0.09	-	0.35 ^b \pm 0.15	-	-	0.22 \pm 0.16 ^b	-	-
BDE-85	0.68 ^c			nd	-	-	nd	-	-
BDE-99	9.62 \pm 6.55	1.80 - 16.5	10.9	8.57 \pm 5.60	4.37 - 18.2	7.25	5.07 \pm 3.81	2.70 - 11.8	3.84
BDE-100	1.98 \pm 1.17	0.59 - 3.60	2.23	1.99 \pm 1.49	0.74 - 3.64	1.59	1.07 \pm 1.04	0.55 - 2.93	0.62
BDE-153	5.65 \pm 5.42	0.69 - 16.5	4.27	-	-	-	10.2 \pm 21.6	0.55 - 58.8	0.83
BDE-154	1.85 \pm 1.76	0.33 - 4.83	1.05	0.33 ^c	-	-	1.88 \pm 3.04	0.24 - 8.56	0.30
BDE-183	16.3 \pm 22.6	2.41 - 68.6	5.15	nd	-	-	4.74 \pm 5.52	1.39 - 15.0	1.66
Σ (7)BDEs	41.5 \pm 43.5	7.08 - 131	27.6	18.7 \pm 11.6	7.67 \pm 35.7	13.2	27.2 \pm 37.9	7.99 - 106	10.4
α -HBCD	138 \pm 197	4.76 - 648	74.6	5.78 \pm 4.41	2.67 - 8.90	5.78	384 \pm 501	46.3 - 1150	106
β -HBCD	76.0 \pm 166	0.97 - 517	19.6	1.75 \pm 0.65	1.29 - 2.21	1.75	275 \pm 434	9.79 - 1020	34.2
γ -HBCD	43.1 \pm 44.6	6.29 - 156	34.9	7.40 \pm 9.46	<LOD-14.1	7.40	102 \pm 108	24.5 - 289	50.2
δ -HBCD	nd	-	nd	nd	-	-	nd	-	-
Σ HBCDs	257 \pm 407	12.0 - 1321	129	14.9 \pm 14.5	4.66 - 25.2	14.9	761 \pm 1043	80.6 - 2459	190
HBB	2.03 \pm 4.36	0.19 - 11.9	0.42	1.95 \pm 2.54	0.16 - 6.07	0.52	7.67 \pm 14.4	0.24 - 29.2	0.63
BBT	1.14 \pm 1.78	0.08 - 4.97	0.17	0.09 \pm 0.04	0.06 - 0.13	0.08	1.78 \pm 2.29	0.22 - 5.81	0.81
PBBZ ^a	0.08 \pm 0.21	<LOD-0.69	-	0.24 \pm 0.48	<LOD-1.32	-	0.08 \pm 0.17	<LOD-0.46	-
PBEB ^a	0.05 \pm 0.09	<LOD-0.27	-	0.30 \pm 0.70	<LOD-2.15	0.07	0.04 \pm 0.05	<LOD-0.12	-
BTBPE	8.02 \pm 17.2	0.42 - 56.1	2.02	0.71 ^c	-	-	148 \pm 336	2.97 - 905	4.52
α -TECH	0.21 \pm 0.14	0.06 - 0.49	0.19	0.51 \pm 0.75	0.12 - 1.63	0.15	1.05 \pm 1.04	0.22 - 2.72	0.42
β -TECH	0.16 \pm 0.11	0.05 - 0.38	0.16	0.34 \pm 0.59	0.05 - 1.54	0.11	0.93 \pm 0.96	0.17 - 2.52	0.34
Σ TECHs	0.37 \pm 0.24	0.11-0.87	0.35	0.45 \pm 1.03	<LOD-3.17	0.10	1.98 \pm 1.99	0.39-5.24	0.76
syn-DP	163 \pm 93.6	68.0 - 388	147	3.60 \pm 2.43	2.00 - 8.14	2.40	12.2 \pm 17.3	0.98 - 46.7	1.89
anti-DP	48.5 \pm 61.1	3.36 - 170	22.2	6.95 \pm 7.50	2.86 - 22.1	3.98	21.8 \pm 20.3	4.52 - 58.3	15.60
Σ DPs	212 \pm 140	78-542	169	7.22 \pm 9.27	<LOD-30.24	5	33.94 \pm 35.39	5.58-87-4	17.16
Σ (7)BFRs	224 \pm 178	72.2 - 632	172	14.1 \pm 13.8	5.97 \pm 40.3	7.94	194 \pm 392	9.30 - 1050	24.2

Table 2: Concentration (ng/g) of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDs) and novel flame retardants (NFRsnFRs) 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: MRRoom = 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	MRRoom	Lab	Room 3	Room 4	Hall	Corridor	SS Room	LR A	LR B	Lab 1B	Cab A	Cab B	C Room
27	PBDEs																						
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
29	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
30	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
31	nd	0.68	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
32	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
33	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
34	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
35	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
36	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
43	HBCDs																						
44	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
45	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
46	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
47	<LOD	<LOD	<LOD	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	nd	<LOD	nd	nd	nd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
49	NFRs																						
50	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
51	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
52	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	<LOD	0.77	<LOD	0.46
53	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
54	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
55	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
56	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
57	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
58	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

1 Table 3: Estimated human exposure to FRs via dust ingestion and RfD values
 2 (ng/kg_{bw}/day) ingestion at mean (20 mg/day = ing-20) and high (50 mg/day = ing-50)
 3 ingestion rate in adults (^a-USEPA, 2008; ^b-NRC, 2000. Not adopted by any regulatory
 4 authority; see MOE approach by EFSA, 2011; ^c-RfD - Hardy et al., 2008. Not adopted
 5 by any regulatory authority; ^d-RfD - Wang et al., 2013, not adopted by any regulatory
 6 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
ΣPBDEs	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.
ΣHBCDs	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.
ΣDPs	0.073	0.182	0.003	0.008	0.003	0.029	5,000,000 ^d

11 **Figure legend**

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13 Figure 1: Percentage contribution of FRs in the research stations and vessel: a)
14 \sum PBDEs, \sum HBCDs and \sum NFRs; b) BDE congeners; c) HCBd isomers (δ -HCBd
15 always < LOD); d) novel FRs.

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

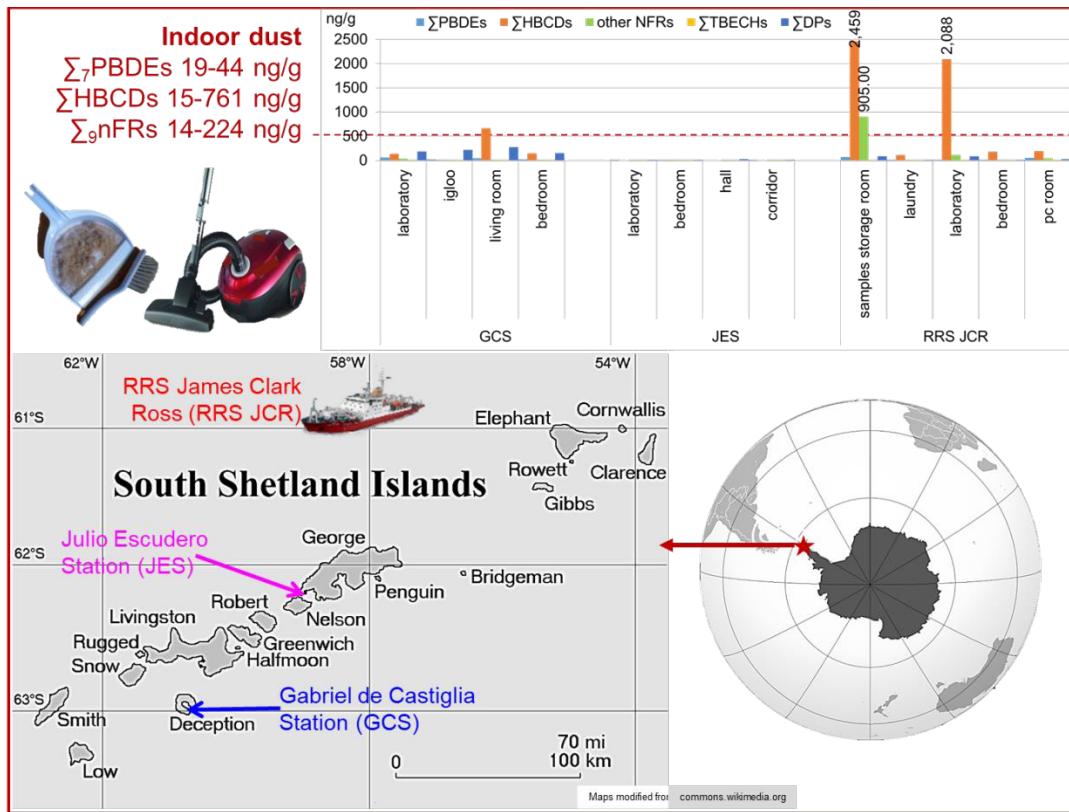
18 Figure 3: Estimated human exposure to FRs via indoor dust ingestion at mean (20
19 mg/day) and high (50 mg/day) ingestion rate (percentage contribution).

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GRAPHICAL ABSTRACT

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

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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.

58 **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 uninhabited. 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

99 hexabromocyclododecanes (HBCDs), among others (Alaee et al., 2003). PBDEs have been used
100 since 1970s and their production has continued until recently. During the last decade, PBDEs have
101 been progressively regulated: in 2009 their commercial formulations known as PentaBDE
102 (containing tetra- and penta-BDE congeners) and OctaBDE (containing hexa- and hepta-BDE) were
103 included in the Annex A (eliminate production and use) to the Stockholm Convention; DecaBDE
104 (containing deca-BDE 97-98%, nona-BDE 2.5%, octa-BDE 0.04%) was added in May 2017 and
105 implemented by the European Commission (EU Regulation, 2017). PBDE regulation has led to an
106 increase in the manufacture and use of replacement products such as novel flame retardants (nFRs)
107 (SC-POPs, 2017; McGrath et al., 2017). Hexabromocyclododecanes (HBCDs) are brominated
108 aliphatic cyclic hydrocarbons used as flame retardants in thermal insulation building materials,
109 upholstery textiles, and electronics devices (Loganathan et al., 2020); they are replaced by nFRs
110 since 2011 (Kajiwara et al., 2011) and since May 2013 are listed in the Annex A to the SC-POPs
111 (SC-POPs, 2017), with specific exemptions for production and use in expanded and extruded
112 polystyrene used in building material (UNEP, 2013). To date, as many as 75 nFRs have been
113 manufactured (McGrath et al., 2017); these chemicals are considered priority contaminants with
114 respect to their production volume, distribution in the environment, bioaccumulation and toxic
115 potential (de Wit et al., 2010; Covaci et al., 2011). Among nFRs: hexabromobenzene (HBB),
116 mainly produced in China and historically used in polymers, plastics, textiles, wood, and paper
117 (Covaci et al., 2011); pentabromotoluene (PBT), mostly used in textiles, polyester resins, paint
118 emulsions, plastics, and rubbers (De Wit et al., 2011); 2-bis(2,4,6-tribromophenoxy)ethane
119 (BTBPE), recently detected in the environment, has been produced since the mid-1970s and is now
120 being used as a replacement for Octa-BDE (Ali et al., 2012); 1,2-dibromo-4-(1,2-
121 dibromoethyl)cyclohexane (TBECH), commercialized in a technical mixture of α - and β -
122 diastereoisomers that can be thermally isomerized to γ -TBECH and δ -TBECH (de Wit et al., 2010;
123 Covaci et al., 2011). These compounds are mainly applied in polyurethane products and expandable

124 polystyrene beads used in thermal insulation for housing (Tomy et al., 2008). Dechlorane plus (DP)
125 is an important chlorinated FR developed to replace the banned Mirex (Xian et al., 2011) and
126 proposed as possible alternative to the now restricted DecaBDE (Sverko et al., 2011). Commercial
127 products contain a mixture of syn- and anti-DP stereoisomers (UNEP, 2019) and are used in many
128 applications such as cable coatings, electrical wires, plastic roofing materials, and computer and
129 television connectors (Kim et al., 2014). In 2019, DP was proposed to be included in the SC-POP
130 list (UNEP, 2019).

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

149 The main aims of the present study were: to evaluate the levels of legacy FRs (PBDE IUPAC nos.
150 28, 47, 66, 85, 99, 100, 153, 154, 183, and α -, β -, γ - and δ -isomers of HBCD) and nFRs (HBB,
151 PBT, PBBZ, PBEB, BTBPE, α - and β -TBECH, syn- and anti-DP) in indoor dust from different
152 rooms in two Antarctic research stations (Gabriel de Castilla and Julio Escudero), and on board of
153 the RRS James Clark Ross sailing from Punta Arenas, Chile, to the Drake Passage and Bransfield
154 Strait; to estimate the human exposure to FRs via dust ingestion during a research expedition in
155 Antarctica.

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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,

174 one cabin (n =2), one computer room. The collection of samples was carried out according to a
175 strict standard protocol: in each room, one squared meter of carpet was vacuumed for 2 minutes
176 and, in case of bare floor, four squared meters were vacuumed for four minutes (Harrad et al.,
177 2008). The dust samples were collected using specially designed sampling socks (313 x 175 x 254
178 mm) made by craft paper which were closed, sealed in a plastic bag and stored at -20 °C; they were
179 mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed
180 with a twist tie.

182 2.2 Sample preparation and analysis

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

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

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

194 The samples were extracted by ultrasonic assisted extraction (UAE, Banderlin Sonorex) three times
195 (3 x 15 minutes) with 10 mL hexane, in order to increase the diffusion and desorption rate of
196 analytes from the sample matrix. After the extraction, the sample volume was reduced under a
197 gentle stream of nitrogen at ambient temperature. Sample clean-up was achieved by mixing 3 mL of
198 sulphuric acid with the sample (Covaci et al., 2007). Then samples were eluted with 40 mL

199 hexane/dichloromethane (DCM 1/1, v/v) in a chromatographic column packed with 1 g active silica
200 gel, 8 g of 44% sulphuric acid-impregnated silica gel, and 1 g active silica gel on the top, then
201 micro-concentrated by a stream of nitrogen in a TurboVap II concentrator unit (Caliper Life
202 Sciences, USA) and finally transferred into a mini vial and filled with nonane to the final volume of
203 50 μ L.

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

207 *2.3 Instrumental analysis*

208 *nFRs and PBDEs* - In this study FRs were identified and quantified using gas chromatography -
209 high resolution mass spectrometry (GC-HRMS); the 7890A GC (Agilent, USA) was equipped with
210 a 15 m x 0.25 mm x 0.10 μ m RTX-1614 column (Restek, USA) coupled with an AutoSpec Premier
211 MS (Waters, Micromass, UK). The MS was operated in EI+ mode at > 10000 resolution (10%
212 valley definition). The injection volume was 2 μ L and injection was splitless at 280°C, with He as
213 carrier gas at 1 mL/min. The GC temperature program was 80°C (1 min hold), then 20°C/min to
214 250°C, followed by 1.5°C/min to 260°C (2 min hold) and 25°C/min to 320°C (4.5 min hold).
215 Further details on GC-MS analysis are reported in Venier et al. (2016).

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

224 Concentrations of chemical residue in dust samples are given in ng/g dry weight throughout the
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227 *2.4 Quality Assurance and Quality Control (QA/QC)*

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

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237 The limit of detection (LOD) was calculated from the lowest calibration point as an amount
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238 producing a signal to noise 3; the LODs of the analyzed chemicals were: 2.07-36.4 pg/g for PBDEs,
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239 0.6-1.8 ng/g for HBCDs, 0.02-23.0 pg/g for nFRs (Table SM1). The limits of quantification (LOQs)
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240 were set as the mean value of target compounds detected in procedural blanks plus ten times of
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241 standard deviations. For the undetectable compounds in blanks, the LOQs were set as a signal to
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242 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
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243 and 0.07 to 69.2 pg/g for nFRs (Table SM1). Three solvent blanks were used to evaluate
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244 contamination from the laboratory procedures. The FR concentrations in all procedural and field
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245 blank samples were low (maximum value: <11.2 pg/g for PBDEs; 1350 pg/g for nFRs) and no
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246 correction was necessary.

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248 *2.5 Calculation of estimated daily exposure to FRs*

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249 Three PBDEs (BDE-47, BDE-99 and BDE-153), HBCDs (stereoisomers α -, β -, and γ -HBCD), and
250 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:

$$252 \text{ EDE} = \sum(C \times \text{EFT} \times \text{DI})/\text{BW} \quad [1]$$

253 where: *EDE* is the estimated exposure; *C* is the concentration (ng/g) of FRs in dust samples from
254 different rooms (average concentration was taken into account for two or more rooms with same
255 use); *EFT* is the estimated fraction of time spent in each room during the day (see Table SM2); *DI*
256 is the daily dust ingestion rate, which was assumed to be 20 mg/day and 50 mg/day for adults to
257 take into account a mean and high dust ingestion scenarios, respectively (Jones-Otazo et al., 2005;
258 Abdallah et al., 2008); *BW* is the body weight assumed for adults (70 kg) (EFSA, 2012). Given the
259 uncertainties about the bioavailability of these substances, a conservative approach has been chosen
260 in exposure assessment considering 100% absorption after their oral ingestion (McGrath et al.,
261 2018).

263 2.6 Statistical analysis

264 The software Microsoft Office Excel 2010 (Microsoft, Redmond, WA) and SPSS (V17, Statistical
265 Product and Service Solutions, Chicago, USA) were used to perform the statistical analysis of the
266 data. The concentrations below LOD were assigned a value equal to LOD/2. The Shapiro-Wilk (S-
267 W) and the Kolmogorov-Smirnov (K-S) tests were used to test if data were normally distributed
268 (Tables SM3-5). As some data sets were not normally distributed, concentrations were log₁₀-
269 transformed. Data were then analyzed again by S-W and K-S and normal distribution was confirmed
270 ($p > 0.05$). A one-way ANOVA (software SPSS version 22) was applied (Tables SM6-8) to evaluate
271 concentration differences among the three facilities for all studied contaminants. After ANOVA, the
272 post-hoc Tukey test was run in order to assess pairwise comparisons (Tables SM9-11). All
273 comparisons were based on a confidence interval of 95% and a significance level of $p < 0.05$.

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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 $\sum_{(7)}\text{PBDEs}$ and $\sum_{(4)}\text{HBCDs}$, 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 $\sum_{(7)}\text{PBDEs}$ 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

299 (40%) > BDE-99 (23%) > BDE-153 (14%) at Gabriel de Castilla Station; BDE-99 (50%) > BDE-47
300 (35%) at Julio Escudero Station; BDE-153 (37%) > BDE-99 (22%) > BDE-183 (21%) on RRS
301 James Clark Ross (Figure 1b). The BDE-183 showed the highest concentrations in the laboratory of
302 Gabriel de Castilla Station (68.6 ng/g) and in the computer room of the RRS James Clark Ross
303 (15.0 ng/g) (Table 2). This congener made up 13–42% of the Octa-BDE and it is considered a
304 marker of its use (Alaee et al., 2003). This formulation has been mainly used in hard plastic (e.g.
305 acrylonitrile-butadiene-styrene and high impact polystyrene) which in turn are used for EEE (Yogui
306 and Sericano, 2009). It was reported that DecaBDE transfer to indoor dust is linked to polymer
307 weathering and abrasion (Webster et al., 2009): the same process might be the reason why
308 OctaBDE is abundant in rooms where EEE are in use.

309 The $\sum_{(3)}$ BDEs (BDEs 47, 99, 100) made up >40% of the BDE residue in rooms at Gabriel de
310 Castilla Station and on RRS James Clark Ross, and 90% at Julio Escudero Station (Figure 1b);
311 these congeners are the main components of the PentaBDE mixture used in polyurethane foam. As
312 PentaBDE was banned in 2009 (SC-POPs, 2017), its presence in indoor dust of remote research
313 facilities may suggest old furniture, carpets or upholstery are still in use in these rooms.

314 Nonetheless, higher BDE concentrations have been reported in other Antarctic sites, e.g. the
315 $\sum_{(4)}$ PBDEs (BDE-47, BDE-99, BDE-183, BDE-209) was 9560 ng/g and 2240 ng/g at McMurdo
316 Station and Scott Base (Ross Sea), respectively (Hale et al., 2008).

317 Our results showed that PBDEs were higher in laboratory, sample storage room and living rooms
318 respect to bedrooms (Figure 2) in agreement with the \sum_9 PBDE concentration detected in home and
319 office dust samples in an urban area of South Africa (Kefeni & Okonkwo, 2014). Overall, PBDE
320 concentrations found in our samples were lower than the lowest average concentrations found in
321 dust samples from rural regions (e.g. Pakistan and Kuwait) (Table SM12). One or more order of
322 magnitude higher levels were reported in urban areas compared to those measured here (e.g. U.K.,
323 China, Canada, USA) (Table SM12).

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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 Σ 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

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

357 3.1.3.1 BTBPE

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

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

374 (2020) also reported BTBPE low detection frequency and preferential distribution through LRAT in
375 air samples collected at the Great Wall Station, China, 2 km South of Julio Escudero Station
376 (detection frequencies = 30% ca., concentrations: n.d. - 0.021 ng/g) (Zhao et al., 2020).
377 Interestingly, in the Arctic BTBPE was detected in 0% of air samples and in 45% of organisms
378 from Station Nord (81°N, 16°E, NE Greenland) and E and W Greenland, respectively (Vorkamp et
379 al. 2015), suggesting a different transport and/or use of BTBPE-containing products in the Arctic
380 and Antarctic regions.

381 382 3.1.3.2 DPs

383 The syn-DP anti-DP made up 73% and 22% of nFR residue at Gabriel de Castilla Station.
384 Accordingly, Σ DPs represented at least 50% of the concentrations of all studied flame retardants in
385 the bedrooms, igloos, and laboratories (Figure 2); at Julio Escudero Station, anti-DP was higher
386 than syn-DP and they represented 45% and 24% of nFRs (Tables 1-2; Figure SM2). The Σ DP
387 concentration was highest in the hall (\approx 80%, Figure 2). The DP is used in a range of products, e.g.
388 electronic wiring and cables, automobiles, plastic roofing materials, and hard plastic connectors in
389 televisions and computer monitors, wire coatings, and also in furniture (Zhang et al., 2015) and
390 building material (Hou et al., 2018). Moreover, as Σ DPs was detected in the Southern Ocean
391 atmosphere at concentration of 0.31 pg/m³ (Möller et al., 2012), future work will need to elucidate
392 the relative contributions of LRAT and local sources to this atmospheric occurrence.

393 394 3.2 Assessment of human exposure to FRs via dust ingestion

395 Inadvertent indoor dust ingestion is considered a major human exposure pathway to FRs, alongside
396 dietary intake (Jones-Otazo et al. 2005; Basis and Samara, 2012; Kim et al., 2016; McGrath et al.,
397 2018; Bu et al., 2019). For the PBDEs, the USEPA provided a reference dose value (RfD), defined
398 as “an estimate of a daily oral exposure of the human population that is likely to be without an

399 appreciable risk of deleterious effects during a lifetime” (USEPA, 2008). To our knowledge, no
400 health-based guidance value has currently been adopted by USEPA or other regulatory authorities
401 for the remaining compounds investigated in this study. However, HBCDs, BTBPE and DPs were
402 also considered for assessing the human exposure via dust ingestion in view of their high levels
403 measured in the dust samples. The values and percentage contribution of estimated daily exposure
404 are showed in the Table 3 and Figure 3, respectively. Overall, the highest exposure was ascribed to
405 α - > β - > γ -HBCDs isomer (RRS James Clark Ross > Gabriel de Castilla Station > Julio Escudero
406 Station), and to syn- and anti-DP (Gabriel de Castilla Station > RRS James Clark Ross > Julio
407 Escudero Station) (Figure 3).

408 409 3.2.1 \sum_3 BPDEs

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

419 420 3.2.2 HBCDs

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

424 (NRC, 2000). The Panel on Contaminants in the Food Chain (CONTAM) of the European Food
425 Safety Authority (EFSA) recognized that neurodevelopmental effects on behavior are the “critical
426 endpoint” and then proposed a method based on a benchmark dose (lower confidence) limit for a
427 benchmark response of 10% (BMDL₁₀) of 0.79 mg/kg body weight; the database showed
428 limitations and uncertainties, thus the CONTAM Panel concluded that this BMDL is inadequate to
429 establish a health-based guidance value (EFSA, 2011). Moreover, the Panel observed that HBCD
430 elimination in humans and animals are different and alternatively used a margin of exposure (MOE)
431 method based on body burden (EFSA, 2011): a chronic Σ HBCD human dietary intake is associated
432 with the body burden at the BMDL₁₀ to use for a MOE calculation of 0.003 mg/kg_{bw}/day/estimated
433 dietary intake; a MOE higher than 8 indicates that there is no health concern due to the dietary
434 intake of these chemicals (EFSA, 2011).

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

444 3.2.3 BTBPE

445 Although BTBPE is commonly detected in indoor dust, the scientific literature have generally
446 reported lower levels than other nFRs, probably due to low production volumes in the USA and EU
447 (McGrath et al., 2018). Mean or median concentrations (ng/g) reach double-digit levels in North
448 America, while in the other continents they are generally lower (Stapleton et al., 2008; Ali et al.,

449 2012; Fromme et al., 2016; Venier et al., 2016; McGrath et al., 2018; Bu et al., 2019; De la Torre et
450 al., 2020); the corresponding median exposure values, when calculated, were always <0.01
451 ng/kg_{bw}/day (Ali et al., 2012; Bu et al., 2019; De la Torre et al., 2020). On board the RRS James
452 Clark Ross, a high concentration was measured in dust collected in the sample storage room (Table
453 2) and the exposure values at the high dust ingestion rate in the Antarctic facilities were lower than
454 the RfD_{BTBPE} (243000 ng/kg_{bw}/day) proposed by Hardy et al. (2008). The RfD values proposed by
455 Hardy (2008) and Wang (2013), several orders of magnitude higher than our results, may not be
456 appropriate given the shortcomings of toxicological data supporting them. In this respect, it should
457 be noted that this RfD value was derived on the basis of old toxicological studies and little is known
458 about chronic toxicity of brominated nFRs (Ali et al., 2012); furthermore, Hardy and coll. added to
459 their paper a disclosure of conflicts of interest as three of them were employed by brominated FRs
460 manufacturers (Hardy et al., 2008).

462 3.2.4 DPs

463 The estimated exposure to Σ DPs at the high dust ingestion rate was 0.182 ng/kg_{bw}/day at the
464 Gabriel de Castilla Station > RRS James Clark Ross > Julio Escudero Station (Table 3); this value
465 was higher with respect to 1.4 ng/day, i.e. 0.02 ng/kg_{bw}/day (based on median concentrations; 100
466 mg/day of dust ingestion rate) in dust samples collected in 2002-2003 from 69 residential homes in
467 Ottawa, Canada (Zhu et al., 2007). Li et al. (2015) reported median exposures to Σ DPs of 0.08 and
468 0.2 ng/day for the Chinese population, corresponding to 0.001 and 0.003 ng/kg_{bw}/day at mean and
469 high dust ingestion rates. In a more recent work, Sun et al. (2018) estimated 0.010 (syn-DP) and
470 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
471 offices from Hangzhou, East China. Higher median levels were reported by Zheng et al. (2015) in
472 three e-waste recycling regions in Guangdong Province, South China, where indoor exposures to

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

475
476

477 **4. Conclusions**

478

479 In this study PBDEs, HBCDs, and nFRs were detected in indoor dust collected in research facilities
480 in the Antarctic Region, providing an evidence of their role as FRs local source in Antarctica.
481 Buildings and technical cloth and gear may be ascribed as a local source for indoor environments in
482 research stations and ships, and LRAT may be an additional source of legacy and novel FRs in the
483 Antarctic atmosphere. The highest levels of FRs were found in common areas in all facilities, like
484 laboratories/storage room, hall/corridor, and living room, perhaps because of the presence of
485 electric and electronic equipment and other furniture. The concentration and relative abundance of
486 legacy and nFRs (e.g. HBCDs, BTBPE) in indoor dust can reflect the levels and profile of dust in
487 home and office in the country of origin, being these materials transported from the country of
488 origin. Except DPs at Gabriel de Castilla Station, levels were low when compared to relatively
489 populated regions, and similar or lower to concentrations reported in remote regions (Tables SM12-
490 14).

491 Taking into account the toxicological relevance of our finding, no adverse effect on human health is
492 expected from the exposure via dust ingestion to PBDEs and HBCD; HBCD isomers, and syn- and
493 anti-DP contributed mostly to the exposure. As far as nFRs, the exposures to BTBPE on board the
494 RRS James Clark Ross and to DPs at the Gabriel de Castilla Station were higher than the available
495 literature data. Since these chemicals are PBTs, an exhaustive characterization of their toxicity
496 should be performed before adopting health-based guidance values. As banned flame retardants
497 continue to be replaced, further studies should be conducted to assess the human exposure to nFRs

498 in Antarctic facilities, even because the use of flame retardants in Antarctic facilities is highly
499 needed for safety reasons since the very low air humidity makes fires a major risk.

500

501

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527 Islands Map, colors and details of sampling by the Authors,
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530 **CRedit authorship contribution statement**

531 S. Corsolini: Conceptualization, Writing - Original Draft, Writing - Review & Editing,
532 Visualization, Supervision; A. Metzdrorf: Formal analysis, Data Curation, Writing PhD thesis (this
533 research derives from it); D. Baroni: Formal analysis, Writing - Original Draft, Visualization; J.L.
534 Roscales: Sampling design support, collection of samples, writing, review and editing; B. Jiménez:
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795 Zhu J., Feng Y.L., Shoeib M., 2007. Detection of Dechlorane Plus in Residential Indoor Dust in the
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799 Table 1: Concentrations (ng/g) of flame retardants (mean \pm standard deviation, minimum -
800 maximum, median) found in dust samples from the different research facilities in Antarctica (nd =
801 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 \pm SD	min - max	median	mean \pm SD	min - max	median	mean \pm SD	min - max	median
BDE-28	1.09 \pm 3.03	0.04 - 9.70	0.06	0.08 \pm 0.04	0.03 - 0.12	0.09	0.14 \pm 0.12	<LOD-0.34	0.16
BDE-47	4.58 \pm 2.96	1.22 - 10.6	3.91	5.98 \pm 4.56	2.53 - 13.8	4.30	2.91 \pm 3.05	<LOD-9.12	2.75
BDE-66	0.07 ^a \pm 0.02	0.05-0.09	-	0.35 ^b \pm 0.15	-	-	0.22 \pm 0.16 ^b	-	-
BDE-85	0.68 ^c			nd	-	-	nd	-	-
BDE-99	9.62 \pm 6.55	1.80 - 16.5	10.9	8.57 \pm 5.60	4.37 - 18.2	7.25	5.07 \pm 3.81	2.70 - 11.8	3.84
BDE-100	1.98 \pm 1.17	0.59 - 3.60	2.23	1.99 \pm 1.49	0.74 - 3.64	1.59	1.07 \pm 1.04	0.55 - 2.93	0.62
BDE-153	5.65 \pm 5.42	0.69 - 16.5	4.27	-	-	-	10.2 \pm 21.6	0.55 - 58.8	0.83
BDE-154	1.85 \pm 1.76	0.33 - 4.83	1.05	0.33 ^c	-	-	1.88 \pm 3.04	0.24 - 8.56	0.30
BDE-183	16.3 \pm 22.6	2.41 - 68.6	5.15	nd	-	-	4.74 \pm 5.52	1.39 - 15.0	1.66
Σ PBDEs	41.5 \pm 43.5	7.08 - 131	27.6	18.7 \pm 11.6	7.67 \pm 35.7	13.2	27.2 \pm 37.9	7.99 - 106	10.4
α -HBCD	138 \pm 197	4.76 - 648	74.6	5.78 \pm 4.41	2.67 - 8.90	5.78	384 \pm 501	46.3 - 1150	106
β -HBCD	76.0 \pm 166	0.97 - 517	19.6	1.75 \pm 0.65	1.29 - 2.21	1.75	275 \pm 434	9.79 - 1020	34.2
γ -HBCD	43.1 \pm 44.6	6.29 - 156	34.9	7.40 \pm 9.46	<LOD-14.1	7.40	102 \pm 108	24.5 - 289	50.2
δ -HBCD	nd	-	nd	nd	-	-	nd	-	-
Σ HBCDs	257 \pm 407	12.0 - 1321	129	14.9 \pm 14.5	4.66 - 25.2	14.9	761 \pm 1043	80.6 - 2459	190
HBB	2.03 \pm 4.36	0.19 - 11.9	0.42	1.95 \pm 2.54	0.16 - 6.07	0.52	7.67 \pm 14.4	0.24 - 29.2	0.63
PBT	1.14 \pm 1.78	0.08 - 4.97	0.17	0.09 \pm 0.04	0.06 - 0.13	0.08	1.78 \pm 2.29	0.22 - 5.81	0.81
PBBZ ^a	0.08 \pm 0.21	<LOD-0.69	-	0.24 \pm 0.48	<LOD-1.32	-	0.08 \pm 0.17	<LOD-0.46	-
PBEB ^a	0.05 \pm 0.09	<LOD-0.27	-	0.30 \pm 0.70	<LOD-2.15	0.07	0.04 \pm 0.05	<LOD-0.12	-
PBPE	8.02 \pm 17.2	0.42 - 56.1	2.02	0.71 ^c	-	-	148 \pm 336	2.97 - 905	4.52
α -TBECHECH	0.21 \pm 0.14	0.06 - 0.49	0.19	0.51 \pm 0.75	0.12 - 1.63	0.15	1.05 \pm 1.04	0.22 - 2.72	0.42
β -TBECHECH	0.16 \pm 0.11	0.05 - 0.38	0.16	0.34 \pm 0.59	0.05 - 1.54	0.11	0.93 \pm 0.96	0.17 - 2.52	0.34
Σ TBECHECHs	0.37 \pm 0.24	0.11-0.87	0.35	0.45 \pm 1.03	<LOD-3.17	0.10	1.98 \pm 1.99	0.39-5.24	0.76
syn-DP	163 \pm 93.6	68.0 - 388	147	3.60 \pm 2.43	2.00 - 8.14	2.40	12.2 \pm 17.3	0.98 - 46.7	1.89
anti-DP	48.5 \pm 61.1	3.36 - 170	22.2	6.95 \pm 7.50	2.86 - 22.1	3.98	21.8 \pm 20.3	4.52 - 58.3	15.60
Σ DPs	212 \pm 140	78-542	169	7.22 \pm 9.27	<LOD-30.24	5	33.94 \pm 35.39	5.58-87-4	17.16
Σ NBFRs	224 \pm 178	72.2 - 632	172	14.1 \pm 13.8	5.97 \pm 40.3	7.94	194 \pm 392	9.30 - 1050	24.2

Table 2: Concentration (ng/g) of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDs) and novel flame retardants (nFRs) including Decchlorane 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 referred 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							
27																														
28																														
29	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							
30																														
31																														
	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							
43																														
	HBCDs																													
α -HBCD	74.4	76.5	4.76	4.76	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							
49																														
	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							
PBE	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	<LOD	0.77	<LOD	0.46							
PBBB	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							
BTPE	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							
synDP	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							
an60DP	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							
61																														
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1 Table 3: Estimated human exposure to FRs via dust ingestion and RfD values
 2 (ng/kg_{bw}/day) ingestion at mean (20 mg/day = ing-20) and high (50 mg/day = ing-50)
 3 ingestion rate in adults (^aUSEPA, 2008; ^bNRC, 2000. Not adopted by any regulatory
 4 authority; see MOE approach by EFSA, 2011; ^cRfD - Hardy et al., 2008. Not adopted
 5 by any regulatory authority; ^dRfD - Wang et al., 2013, not adopted by any regulatory
 6 authority).
 7

	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
ΣPBDEs	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.
ΣHBCDs	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.
ΣDPs	0.073	0.182	0.003	0.008	0.003	0.029	5,000,000 ^d

8

9

10 **Figure legend**

11

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

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

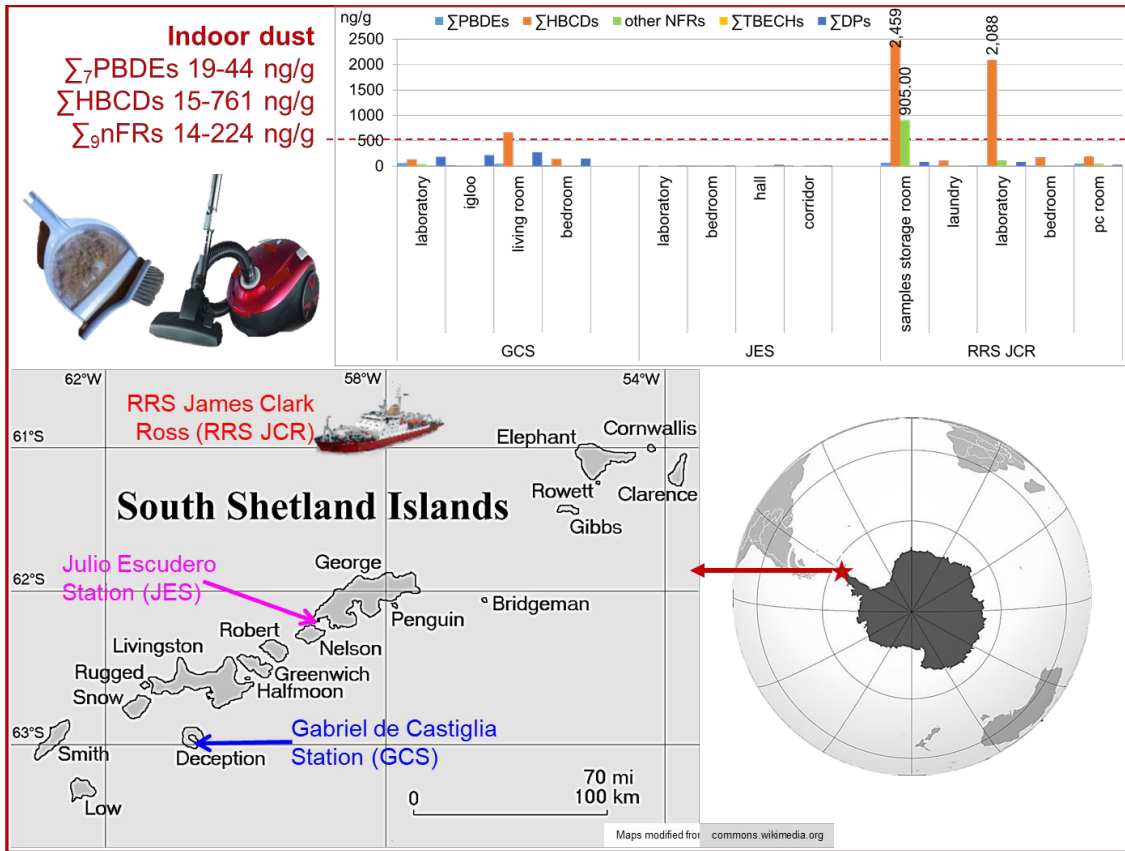
17 Figure 3: Estimated human exposure to FRs via indoor dust ingestion at mean (20
18 mg/day) and high (50 mg/day) ingestion rate (percentage contribution).

19

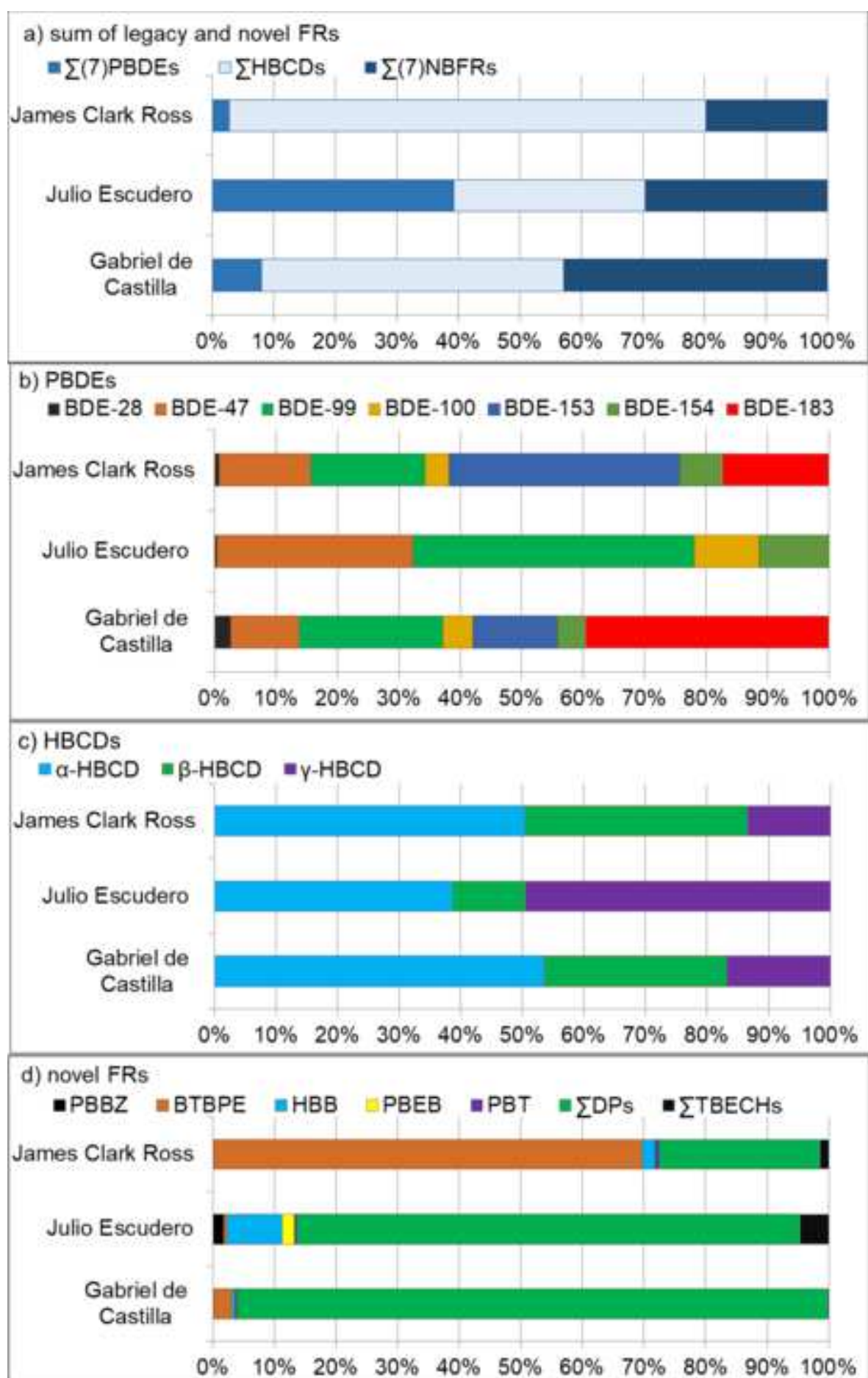
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GRAPHICAL ABSTRACT

21



22



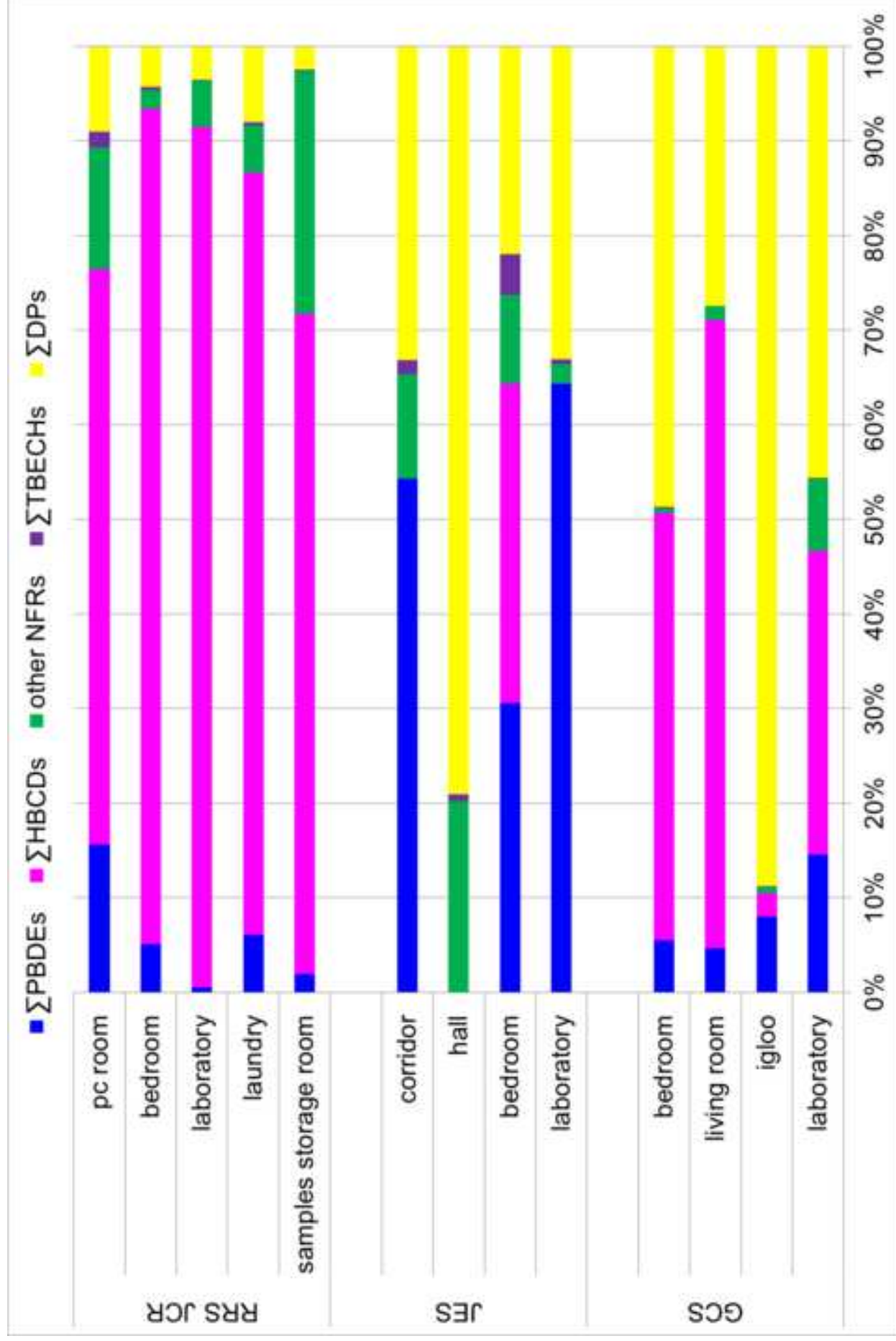
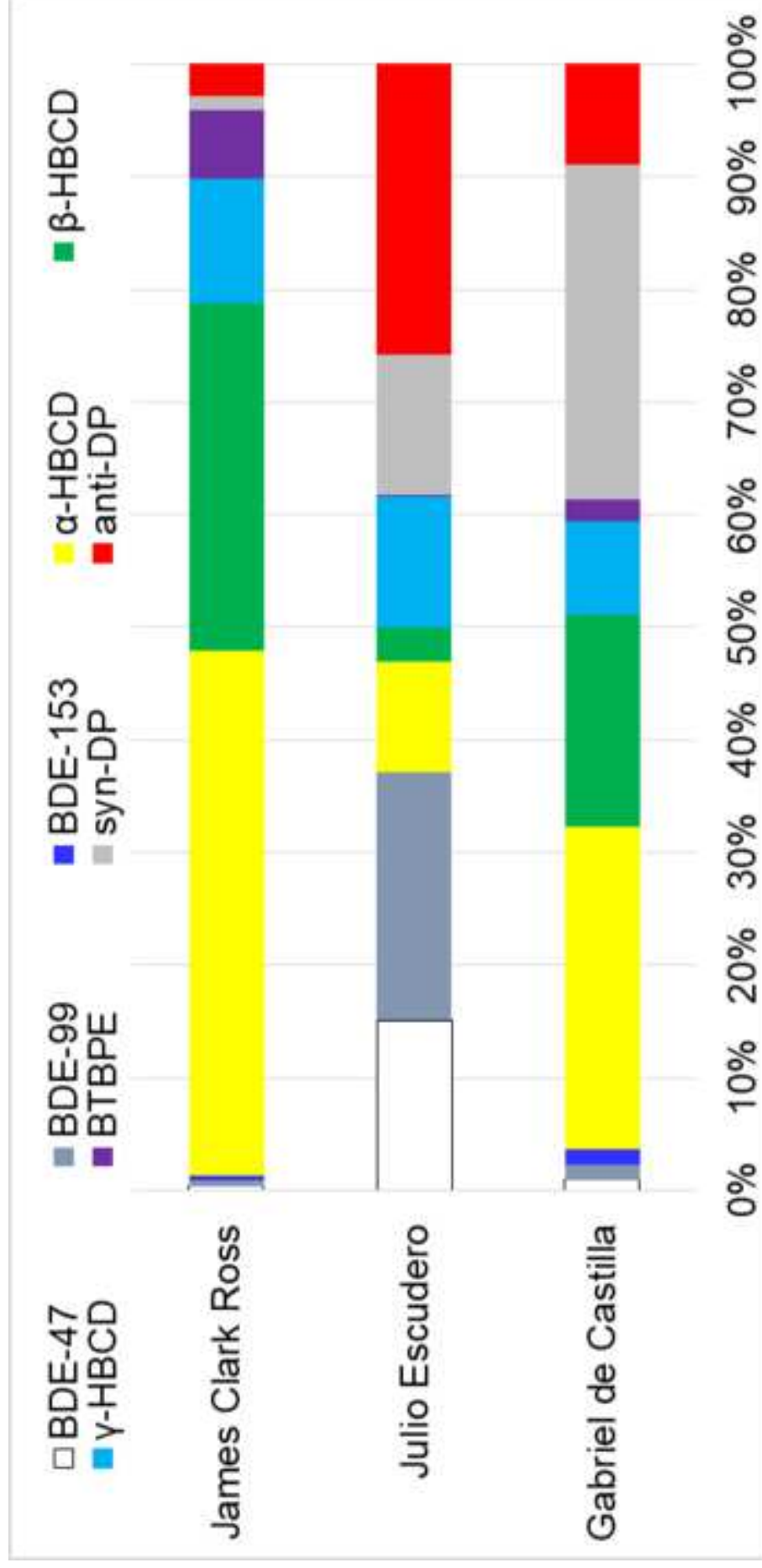


Figure 2







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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. Příbylová: 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.

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: