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Studies into the formation of PBDEs and PBDD/Fs in the iron ore sintering process

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Abstract: Polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) were detected in stack emissions from UK sinter plants. The sum of 36 PBDE congeners was measured at a mean concentration of 295 ng/Nm³ with a standard deviation of 96 ng/Nm³. The mean PBDD/F concentrations were 0.14 ng WHO-TEQ/m³ (range = 0.03 - 0.39). PBDD/F emission concentrations were approximately ten times lower than their PCDD/F homologues. To understand the possible formation mechanisms of brominated organic species in iron ore sintering, both full-scale and laboratory experiments using an experimental sintering process were carried out. A complete PBDE mass balance was undertaken for a full scale sinter plant showing that PBDEs were already present in the raw materials such as iron ores and coke breeze and that a significant proportion of the PBDE inputs were actually destroyed during the process. A number of controlled experiments were conducted using a laboratory-scale sintering apparatus (sinter pot). These were designed to investigate: (a) mass balance of PBDEs during sintering, (b) the relationship between the availability of bromide (as KBr) and PBDE emissions, and (c) the influence of the availability of both bromide and PBDEs on PBDD/F formation. As observed in the full scale plant, the PBDEs already present in the raw materials were mostly destroyed during the process (79-96%) for all sinter pot experiments. Increasing amounts of KBr in the raw sinter mix did not result in a significant increase in PBDE formation suggesting that there was no PBDE formation in sintering via de novo synthesis. No relationship was observed between PBDE inputs and PBDD/F emissions indicating that PBDEs did not act as precursors for PBDD/Fs formation. Finally, PBDD/F formation was enhanced substantially with increasing amounts of KBr suggesting that their formation mechanism was similar to that of PCDD/Fs via de novo synthesis.

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Dear Editor-in-chief

We submit this manuscript entitled “Studies into the Formation of PBDEs and PBDD/Fs in the Iron Ore Sintering Process” by Daniel Drage, Eric Aries and Stuart Harrad to be considered for publication as a research paper for Environment International.

The manuscript describes the movement of PBDEs (and output of PBDD/Fs) through the iron ore sintering process during integrated steel manufacture – both on a commercial and laboratory scale. To the knowledge of all the authors this is the first study that has examined the raw material inputs into the sintering process for PBDEs to examine whether *de novo* formation of PBDEs and PBDD/Fs occurs, as well as the potential conversion of PBDEs to PBDD/Fs during this process. We believe the findings of this article are ideal for this journal - providing the most complete dataset on the movement of PBDEs and PBDD/Fs through the iron ore sintering process – a key anthropogenic activity conducted globally and known to be a source of direct release to the environment of persistent organic pollutants.

This is an original manuscript that has not been published before and is not currently being considered for publication elsewhere – although the initial findings were presented at BFR 2013 – the Sixth International Symposium On Flame Retardants in April 2013.

We confirm that the manuscript has been read and approved by all named authors.

We hope that you find the manuscript suitable for publication and look forward to hearing from you.

Sincerely,

Dr. Daniel Drage
Doctoral Researcher
University of Birmingham

1 Studies into the Formation of PBDEs and PBDD/Fs in the Iron 2 Ore Sintering Process

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8 ABSTRACT. Polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-
9 dioxins and furans (PBDD/Fs) were detected in stack emissions from UK sinter plants. The
10 sum of 36 PBDE congeners was measured at a mean concentration of 295 ng/Nm³ with a
11 standard deviation of 96 ng/Nm³. The mean PBDD/F concentrations were 0.14 ng WHO-
12 TEQ/m³ (range = 0.03 - 0.39). PBDD/F emission concentrations were approximately ten
13 times lower than their PCDD/F homologues. To understand the possible formation
14 mechanisms of brominated organic species in iron ore sintering, both full-scale and
15 laboratory experiments using an experimental sintering process were carried out. A complete
16 PBDE mass balance was undertaken for a full scale sinter plant showing that PBDEs were
17 already present in the raw materials such as iron ores and coke breeze and that a significant
18 proportion of the PBDE inputs were actually destroyed during the process. A number of
19 controlled experiments were conducted using a laboratory-scale sintering apparatus (sinter
20 pot). These were designed to investigate: (a) mass balance of PBDEs during sintering, (b) the
21 relationship between the availability of bromide (as KBr) and PBDE emissions, and (c) the
22 influence of the availability of both bromide and PBDEs on PBDD/F formation. As observed
23 in the full scale plant, the PBDEs already present in the raw materials were mostly destroyed
24 during the process (79-96%) for all sinter pot experiments. Increasing amounts of KBr in the
25 raw sinter mix did not result in a significant increase in PBDE formation suggesting that there
26 was no PBDE formation in sintering via *de novo* synthesis. No relationship was observed
27 between PBDE inputs and PBDD/F emissions indicating that PBDEs did not act as
28 precursors for PBDD/Fs formation. Finally, PBDD/F formation was enhanced substantially
29 with increasing amounts of KBr suggesting that their formation mechanism was similar to
30 that of PCDD/Fs via *de novo* synthesis.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been one of the most commonly used brominated flame retardants (BFRs) with a global demand of 67,000 tonnes in 2001 – the last year for which production figures were available (Bromine Science and Environmental Forum (BSEF), 2003). They have a wide range of consumer applications and uses, such as in foam-upholstered furniture, and high impact polystyrene (HIPS) casings for electrical goods, (Da'Silva et al., 2004; Bromine Science Environmental Forum, 2007). Such extensive and myriad uses have led to substantial contamination of both indoor and outdoor environments, leading to exposure of both humans and wildlife (Darnerud, 2003; Montañó et al., 2013). Such contamination, coupled with evidence of potential adverse human health effects have led to bans and restrictions on the manufacture and new use of PBDEs in various jurisdictions around the world – the most high profile of which was the listing of the Penta- and Octa-BDE commercial formulations under the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention, 2009). Although emissions of PBDEs associated with the remaining reservoir of treated products both in-use and entering the waste stream are likely to continue for the foreseeable future (Harrad and Diamond, 2006); any other sources of PBDEs are likely to assume progressively greater importance in future as the legacy of their commercial use diminishes.

An additional source of concern about PBDEs is their possible role as precursors for the formation of polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) (Buser, 1986; Wang et al., 2010b). PBDD/Fs have comparable physicochemical properties to the well-studied PCDD/Fs (Ren et al., 2009), although the comparative weakness of the C-Br bond is likely to lead to different environmental fate and behaviour to that observed for PCDD/Fs (Schecter, 2012). One of the main release pathways of PBDD/Fs is believed to be as a by-product of the use, manufacture and recycling of BFR containing goods, with PBDEs acting as precursors to PBDD/Fs in high temperature processes (Buser, 1986).

There are very few studies concerning PBDD/F emissions and exposure pathways/health effects, with a very small number of studies based on humans (Ericson Jogsten et al., 2010). The toxicity of PBDD/Fs is still relatively unknown, especially when compared to that of PCDD/Fs (Birnbaum et al., 2003). However, there is limited information on some specific congeners such as 2,3,7,8-tetrabromodibenzo-*p*-dioxin (TBDD) to which humans can be

70 exposed to through inhalation and ingestion (Birnbaum and Staskal, 2004), and it is known
71 that PBDD/Fs are metabolised extremely slowly with human half-lives of approximately 5-10
72 years (Birnbaum et al., 2003). The overall health effects of PBDD/Fs are believed to be
73 similar to those of PCDD/Fs, based on mammalian and amphibian experiments – lethality,
74 wasting, thymic atrophy, teratogenesis, reproductive disturbance, chloracne, immunotoxicity,
75 enzyme reduction, T4 vitamin A reduction, and increased hepatic porphyrins (Birnbaum et
76 al., 2003).

77 Although literature is scarce with regards to the steel industry as a source of PBDEs and
78 PBDD/Fs, there is growing evidence to suggest that it may be a source of brominated organic
79 micro-pollutants in the environment. PBDE concentrations in ambient air within a steel
80 complex in Korea were found to be twice those of background concentrations (Choi et al.,
81 2008). Ferrous scrap is believed to contain PBDEs from previous uses, such as in cars and
82 vehicles containing technical mixtures (Choi et al., 2008; Odabasi et al., 2009). The Electric
83 Arc Furnace (EAF) process which consists mainly in recycling ferrous scrap steel products
84 has therefore been identified as the main source of PBDEs from steelmaking activities
85 (Odabasi et al. 2009). However, more recently, it has also been suggested that the iron ore
86 sintering process could lead to the formation of PBDEs and PBDD/Fs (Wang et al. 2010b).
87 For use in the blast furnaces, the iron ores are first processed in large iron ore sintering plants.
88 In iron ore sintering, the objective is to agglomerate iron ore fines into a product designated
89 as sinter which is composed of permeable lumps which provide the necessary permeability
90 for blast furnace operation. The feed of the iron ore sintering process consists of a moist
91 agglomerate of fine-grained iron ores, recycled materials, coke breeze and limestone. The
92 feed is laid on a moving belt and coke particles in the top layer of the materials are ignited by
93 gas burners thus creating a combustion front. Air is drawn downwards through the sinter bed
94 into a series of wind boxes beneath the strand. The process is carried out by wet mixing the
95 ore with 3-4 % weight of coke breeze and the other additives and spreading the mixture on a
96 base moving at 2-3 m/min, typically 2-4 m wide to a depth of 0.4-0.5 m. The combustion
97 process is initiated at the top of the bed and drawn through it by an induced draught fan via a
98 series of ducts below the bed. As the coke fines burn in the bed, the heat generated sinters the
99 fine particles and the temperature of the bed reaches 1300-1480 °C. At the end of the strand,
100 the sinter product falls off into a cooling system, typically a carousel.

101 The iron ore sintering process has been studied in detail in the past with regard to the
102 formation of PCDD/Fs and PCBs, and was identified as the most significant source of these

103 compounds from steelmaking activities (Anderson and Fisher, 2002; Aries et al., 2006). In
104 sintering, the temperature of the waste gases are about 160°C, which is well below the range
105 of 250 - 450°C generally considered to be favourable for PCDD/F formation via *de novo*
106 synthesis (Vogg and Stieglitz, 1986). However, it has been proposed that PCDD/F formation
107 in iron ore sintering occurs mainly in the dry zone of the sintering bed, within the sinter bed
108 itself, ahead of the flame front. Here temperatures can reach as high as 1100 °C but areas of
109 250 to 450 °C also exist for *de novo* synthesis to take place (Anderson and Fisher, 2002;
110 Suzuki et al., 2004).

111 In comparison with PCBs and PCDD/Fs, there is little information on the potential formation
112 mechanisms of PBDD/Fs and PBDEs in iron ore sintering. Accordingly, using a combination
113 of full-scale investigations by measuring sinter stack emissions at UK sinter plants and
114 realising a series of controlled laboratory-scale experiments, this paper investigates the
115 hypothesis that the iron ore sintering process could be a source of PBDEs and PBDD/Fs to
116 the environment. In so doing, it provides novel insights into the sources and possible
117 formation pathways of these contaminants in the sintering process. In particular, we
118 investigated the possibility that: (a) PBDEs may act as precursors to the formation of
119 PBDD/Fs in the sintering process, (b) the sintering process may lead to the formation of
120 PBDEs, and (c) the bromide content of the raw mix could play a major role in the formation
121 of either PBDEs and / or PBDD/Fs during sintering. In addition, a wide range of raw material
122 inputs (iron ores, coke breeze, revert materials from iron-making and steelmaking processes)
123 and output materials (waste electrostatic precipitator (ESP) dusts, stack emission samples)
124 were analysed to carry out detailed PBDE mass balances in the sintering process.

2. Sampling methods

126 In this study, measurement of PBDEs and PBDD/Fs were realised in a wide variety of
127 samples collected at a sinter plant operated by Tata Steel in the UK. The sinter plant selected
128 for this study was typical in terms of design and operation of most sinter plants currently in
129 operation in Europe and around the world. Amongst the samples analysed, a wide range of
130 inputs (raw materials such as iron ores, coke breeze and limestone) and output samples (sinter
131 product, and waste dusts collected from the electrostatic precipitators - ESP dusts) were
132 collected. In addition, a series of stationary source emission samples were collected from the
133 sinter stack to measure waste gas emissions of PBDEs and PBDD/Fs. These samples enabled
134 the calculation of detailed mass balances for PBDEs in iron ore sintering.

135 *2.1 Sampling of solid samples*

1
2
3 136 Raw material samples were collected at various stages of the sintering process and stored in
4
5 137 glass amber jars. These samples consisted of iron ores (n = 26), revert materials (i.e. reverts)
6
7 138 – such as waste dusts from the blast furnaces or steelmaking processes (n = 20), fluxes such
8
9 139 as limestone (n = 5), and fuels such as coke breeze (n = 3). For mass balance determinations,
10
11 140 input and output samples collected during the processing of the same bed of materials were
12
13 141 analysed. These included raw sinter mix (RSM) samples (n=6), composed of a blend of iron
14
15 142 ores, reverts, fluxes and fuels and output materials including the sinter product (n = 6), and
16
17 143 ESP dusts (n = 8). All the raw materials – except for the sinter product – were collected as
18
19 144 coarse dusts and were transferred to amber jars ready for extraction and clean-up. The sinter
20
21 145 product samples were crushed into dusts using a Tema T750k laboratory disc mill prior to
22
23 146 extraction for PBDE analysis.

23
24 147 *2.2 Stack emission sampling*

25
26 148 In total, twelve sinter plant stack emission samples were analysed for PBDEs and fifteen
27
28 149 were analysed for PBDD/Fs. These were taken by MCERTs accredited sampling teams at
29
30 150 Tata Steel using the European Air Method in accordance with British and European standards
31
32 151 (BS EN 1948). Briefly, emission samples were taken isokinetically from the sinter plant stack
33
34 152 via a 3 m long heated (>120°C) titanium or quartz glass-lined sampling probe. Particulate
35
36 153 matter was collected on a glass fibre filter, contained in a heated filter box (>120°C), whilst
37
38 154 vapour phase PBDD/Fs and PBDEs were trapped on an appropriately spiked XAD-2 resin
39
40 155 contained in a water-cooled glass vessel. After sampling, the probe liner was washed
41
42 156 successively with acetone, dichloromethane, and toluene and the resulting washings were
43
44 157 collected, combined, and retained for analysis with the rest of the sampling media.

45
46 158 *2.3 Sinter Pot Sampling*

47
48 159 The sinter pot is a well-established experimental technique for studying the effects of process
49
50 160 factors on sinter quality and productivity, but in recent years the technique has been extended
51
52 161 to the study of factors governing the formation and emission of organic pollutants in the
53
54 162 sintering process (Ooi et al., 2008). Conventional sinter pots have a charge capacity of around
55
56 163 80 – 100 kg per run, but a laboratory-scale unit - shown schematically in Fig. 1 - was used in
57
58 164 the present study. The sinter pot has a capacity of 1.0 kg and the bed diameter and height are
59
60 165 100 and 150 mm, respectively. The RSM is charged as micro-pellets onto a layer of hearth
61
62
63
64
65

166 material, approximately 25 mm thick, consisting of sinter cake pieces supported on a 3 mm
167 thick stainless steel mesh. The inner walls of the sinter pot are lined with fine ores to reduce
168 adhesion of the sinter product to the inner wall of the pot and to fill fissures between the inner
169 wall and sintered material ensuring constant airflow through the bed during sintering. The SP
170 is connected to a suction fan via a windbox attached to base of the pot. Thermocouples were
171 installed at various depths through the sinter bed and in the windbox to record the progression
172 of the heat front through the sinter bed and off-gas temperature. The RSM was ignited by
173 adding a fixed amount of coke, ca. 20 g, to the top of the raw sinter material and heating it
174 with an oxy-propane burner for 30 s. A fixed sintering air velocity of 0.44 m/s, which
175 corresponds to a total gas flow of 1.0 m³ for a typical pot firing operation, was maintained
176 throughout the sintering process. Air flow measurements were made in the off gas passage
177 where the hot exhaust gas has been cooled.

178 In each experiment, approximately 1 kg of RSM was prepared for sintering in the same way
179 as in the full-scale production process. The RSM was sintered and a total emission sample
180 (both particulate and gas phase combined) collected via a PUF plug (6 cm i.d. x 7.6 cm
181 length), Supelco, UK). The outer layer of the remaining sinter product was “chiselled” with
182 samples taken from the centre and crushed using a Tema T750 k laboratory disc mill. This
183 allowed for a total mass balance of the sintering process to be calculated. In total, five
184 different SP experiments were conducted as described in Table 1. The first experiment was
185 carried out on a standard RSM designated as a base case. In experiment 2, bromide (as KBr)
186 was added to the RSM at an addition rate of 74.5 mg/kg. In experiment 3, a higher addition
187 rate of KBr was used (ca. 224 mg/kg). In experiment 4, significant amounts (ca. 50 µg/kg) of
188 two PBDE technical mixtures were added to the raw sinter mix to study the potential
189 conversion of PBDEs into PBDD/Fs during sintering. The technical mixtures used were DE-
190 71 and DE-83, Penta- and Deca-BDE formulations respectively (Cambridge Isotope
191 Laboratories (CIL), Andover, MA, USA). Finally in experiment 5, both KBr and the
192 technical mixtures were added to the RSM. Each experiment was conducted in duplicate.

193 **3. Sample preparation and analytical methods**

194 *3.1 Solid Samples (PBDEs)*

195 All the solid samples were analysed at the University of Birmingham. They were spiked with
196 known quantities of internal (or surrogate) standards (IS) (¹³C₁₂-BDEs-47, -99, -153,
197 Wellington Laboratories Inc., Ontario, Canada) prior to pressurised liquid extraction (PLE)

198 using an ASE 350 (Dionex, California, USA). The extract was concentrated to 0.5 mL under
199 a gentle stream of nitrogen using a Zymark Turbovap® II concentration workstation
200 (Hopkinton, MA, USA) reconstituted into hexane and washed with <95% concentrated
201 sulfuric acid (Sigma Aldrich, UK) in a 10 mL conical test tube. The top (hexane) layer and
202 three subsequent washings were collected and passed through a column containing florisil
203 (60-100 mesh, Sigma Aldrich, UK) and 1 g sodium sulfate (Sigma Aldric, UK). 20 mL
204 hexane was washed through the column, the complete eluate was collected in 50 mL
205 Turbovap® tubes and concentrated under nitrogen to near dryness. Known amounts of
206 recovery determination standard were added (¹³C₁₂-BDE 100, Wellington Laboratories Inc.,
207 Ontario, Canada) and the sample was made up to 50 µL in methanol.

208 3.2 Stack Emission Samples (PBDD/Fs / PCDD/Fs)

209 Stack emission samples were analysed both for their PBDD/F and PCDD/F concentrations.
210 For PCDD/Fs, samples were analysed following the CEN-1948-4 European Standard for the
211 determination of the mass concentration of PCDD/PCDF in stationary source emission
212 samples. For PBDD/Fs, emission samples were spiked with known quantities of IS (¹³C₁₂-
213 1,2,3,7,8-PeBDF, ¹³C₁₂-2,3,7,8-TeBDF, ¹³C₁₂-2,3,7,8-TBDD, ¹³C₁₂-1,2,3,7,8-PeBDD, ¹³C₁₂-
214 1,2,3,7,8,9-HxBDD) prior to PLE using an ASE 200 (Dionex, California, USA). The extracts
215 were concentrated using nitrogen and a water bath to ca. 0.5-1.0 mL before being passed
216 sequentially through a Supelco Dioxin Prep System Column of 15 mm internal diameter and
217 35 cm length containing 7 layers of treated silica gels that oxidise, reduce, and separate polar
218 interferences. The extract was subsequently cleaned up by using an activated Florisil column
219 (containing 1 g pre-extracted Florisil (Sigma Aldrich) to separate PCBs from PBDD/Fs and
220 PCDD/Fs. The eluate was then transferred along with washings into a Zymark Turbovap (II)
221 concentration workstation (Zymark, Warrington, UK) for concentration under a stream of
222 nitrogen. Nonane and a recovery determination (or syringe) standard (¹³C₁₂-2,3,4,7,8-PeBDF)
223 were added up to a volume of 50 µl prior to analysis.

224 3.2 Stack Emission Samples (PBDEs)

225 The stack emission sample analysed for PBDEs were subjected to almost identical extraction
226 and clean-up procedures as those detailed above for PBDD/Fs, except that the clean-up
227 procedure was carried out on a multi-layered silica column different from the commercially
228 available Supelco Dioxin Prep System columns. For PBDEs, a multi-layered silica column
229 containing several layers of activated silica gel (6 g), basic silica gel (6 g) and acidic silica gel

230 (30 g) was used. Prior to extraction, samples were spiked with known quantities of IS (¹³C₁₂-
231 BDE-4, ¹³C₁₂-BDE-15, ¹³C₁₂-BDE-28, ¹³C₁₂-BDE-47, ¹³C₁₂-BDE-100, ¹³C₁₂-BDE-99, ¹³C₁₂-
232 BDE-118, ¹³C₁₂-BDE-153, and ¹³C₁₂-BDE-183). After Florisil clean-up, the PBDE fraction
233 (identical to the PCB fraction) was transferred along with washings into a Zymark Turbovap
234 (II) concentration workstation for concentration under a stream of nitrogen. Nonane and
235 recovery standards (¹³C₁₂-BDE-77 and ¹³C₁₂-BDE-126) were added up to a volume of 50 µL
236 prior to analysis.

237 3.4 Sinter Pot Emission Samples

238 Sinter pot samples were extracted using toluene with an ASE 200. A 10% fraction of the
239 crude extract was retained for PBDE clean-up and analysis at the University of Birmingham
240 following the analytical procedure described in Section 1.3.1. The remainder of the crude
241 extract was analysed for PBDD/Fs at Tata Steel following the analytical procedures described
242 in Section 1.3.2.

243 3.5 PBDE analysis

244 All the PBDE analyses for the raw materials and sinter pot samples were conducted at the
245 University of Birmingham. All samples except for the RSM components (iron ores, reverts,
246 fuels and fluxes) were analysed by GC/MS. GC/MS analysis was carried out on an Agilent
247 5975 MS coupled with an Agilent 6850 GC with an Agilent DB-5ms column (30m x 0.25 i.d.
248 x 0.25 µm film thickness). 1 µL of extract was injected in splitless mode at 250 °C. The
249 initial oven temperature was 70 °C which was held for 2 minutes, then increased by 20
250 °C/min to 270 °C and held at for 53 minutes. The MS was run in EI selected ion monitoring
251 mode (ionization voltage = 70 eV; ion source temperature = 250 °C) and monitored for 6 ions
252 (BDE -47: 485.8, 483.9; BDEs -85, -99 and -100: 403.9, 405.9; BDEs -153 and -154: 483.9,
253 481.9). RSM components were analysed by LC-APPI-MS/MS for BDEs -47, -85, -99, -100, -
254 153 and -154 (Abdallah et al., 2009). Blanks of PLE pre-extracted diatomaceous earth were
255 analysed and found not to contain target PBDEs. Recoveries of internal standards ranged
256 from 37-149% with an average of 95% across all samples. Analytical precision was assessed
257 by replicate analysis (n=12) of SRM 2585 (NIST) and achieved values close to the certified
258 figures. Method detection limits were 0.36-1.4 ng/g for GC/MS and 8.8-21 ng/g for LC-
259 APPI-MS/MS.

260 With regard to the stack emission samples, analyses were carried out at Tata Steel by High
261 Resolution Gas Chromatography – High Resolution Mass Spectrometry. (HRGC – HRMS)
262 using an Agilent 5973 GC coupled to an Autospec Ultima HRMS (Waters, Manchester, UK).
263 Analysis was carried out using a DB-XLB capillary column of 30 m length, 0.25 mm i.d. and
264 0.1 µm film thickness. 1 µL of extract was injected in splitless mode with an injector
265 temperature of 280°C. The oven temperature programme started at 100°C for 1 min, then
266 ramped at 20°C/min to 310°C and held for 15 min. The HRMS was operated at 10000
267 resolution in the positive ion mode at 34eV energy with perfluorokerosene as the mass range
268 calibrant. A 7-function SIM experiment was set up to detect two isotope ion masses for each
269 of the mono- through to hepta-BDEs. A five-point calibration curve was generated using the
270 calibration solutions EO-5104 (CS2 to CS6) from Cambridge Isotope Laboratories (LGC
271 Promochem, UK). Response factors were calculated for each PBDE congener relative to
272 available ¹³C₁₂-labelled homologue standards. Recoveries for PBDEs 28, 47, 99, 100, 153,
273 154, and 183 were determined against ¹³C₁₂-labelled PBDE 77 and 126. In total, 36 PBDE
274 congeners were analysed using this method.

275 *3.6 PBDD/F analysis*

276 Analysis of PBDD/Fs was carried out at Swinden Technology Centre (Tata Steel, Moorgate,
277 Rotherham, UK) via HRGC/HRMS using an Autospec Ultima (Waters). Samples were
278 injected into a GC equipped with an Agilent DB-5MS column 30 m (length) x 0.25 mm
279 (internal diameter) x 0.1 µm (film thickness). Helium was used as the carrier gas with a
280 constant flow of 1.0 mL/min. The inlet was run in splitless mode. Initial temperature was 140
281 °C for 1 minute. The temperature was then increased to 200 °C at a rate of 20 °C/min and
282 held for 6 minutes, then increased to 280 °C at 5 °C/min and held for 4 minutes. Samples
283 were monitored for 9 PBDD/F compounds, namely: 2,3,7,8-TBDF; 1,2,3,7,8-PeBDF,
284 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 2,3,7,8-TBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD,
285 1,2,3,6,7,8-HxBDD, and 1,2,3,7,8,9-HxBDD. Using this temperature programme, 1,2,3,4,7,8-
286 HxBDD and 1,2,3,6,7,8-HxBDD co-eluted, so their concentrations are reported together in
287 this study.

291 4 Results and Discussion

292 4.1 Stack emission results for PCDD/Fs and PBDD/Fs

293 A series of fifteen stack emission samples were collected from two UK sinter plants operated
294 by Tata Steel and were analysed for their PCDD/F and PBDD/F concentrations. Table 2
295 summarises the mean and range of concentrations observed for the PBDD/F congeners
296 detected in this study. In addition, Fig. 2 compares the range of PCDD/F and PBDD/F
297 emissions at both sinter plants. For this analysis, PBDD/F emission concentrations were
298 converted to WHO-TEQ concentrations by assuming that PBDD/F and PCDD/F have
299 identical toxic equivalency factors (WHO-TEFs), as recommended by the World Health
300 Organisation (Van den Berg et al. 2013). As may be seen from Fig. 2 and Table 2, PBDD/Fs
301 were detected in the emission samples from both sinter plants within the range 0.03 - 0.39 ng
302 WHO-TEQ/m³. There were no significant differences between the range and mean PBDD/F
303 concentrations observed at the two sinter plants. When analysing the individual PBDD/F
304 congener concentrations (Table 2), PBDFs were found at significantly higher concentrations
305 than PBDDs (ca. 10-fold). For instance, the mean ΣPBDF concentration at Sinter Plant B was
306 0.66 ng/Nm³ whereas the mean ΣPBDD concentration was only 0.05 ng/Nm³. On average,
307 PBDFs contributed over 93% to the total PBDD/F concentration in all the stack emission
308 samples collected. The most abundant congeners were 2,3,7,8-TeBDF, 1,2,3,7,8 PeBDF and
309 2,3,4,7,8-PeBDF contributing on average ca. 32%, 31% and 28% of the total PBDD/F
310 concentrations, respectively. Du et al. (2010a) reported PBDD/F emission concentrations
311 from a sinter plant in China to also show a marked predominance of PBDFs over PBDDs,
312 with PBDFs contributing over 75% of the total PBDD/F concentrations. The highest PBDD/F
313 WHO-TEQ concentration reported by Du et al was 1.1 ng WHO-TEQ/Nm³, which exceeded
314 that reported in our study (ca. 0.39 ng WHO-TEQ/Nm³). In the work carried out by Du et al.
315 (2010a), emission samples from other industrial processes (including municipal waste
316 incineration, copper and lead smelting facilities) were also analysed for their PBDD/F
317 emissions. The results indicated that the highest PBDD/F emissions were found at a zinc
318 smelting plant (ca. 1.5 ng WHO-TEQ/m³), followed by a lead smelting facility (ca. 0.7 ng
319 WHO-TEQ/m³) and a copper smelting plant (ca. 0.39 ng WHO-TEQ/m³). These
320 concentrations exceeded the PBDD/F concentrations typically determined at the iron ore
321 sintering plants investigated in the current study. In Table 2 and Fig. 2, a comparison is made
322 between PBDD/F emissions and the concentrations of their chlorinated homologues
323 (PCDD/Fs). Analysis of the data showed that the magnitude of PCDD/F emissions far

324 exceeded those of PBDD/Fs. The mean PCDD/F emissions were typically 1.0 ng WHO-
325 TEQ/Nm³ at both UK sinter plants, approximately 10-fold higher than the PBDD/F
326 concentrations (Table 1). As a result, PBDD/Fs only accounted for ca. 10% of the total
327 WHO-TEQ emission concentrations (PBDD/Fs + PCDD/Fs). The contribution of PBDD/Fs
328 to the overall toxicity of sinter plant emissions was therefore very similar to the contribution
329 of the WHO-12 PCBs which have been shown to be within the range 5 – 7% in a previous
330 study at sinter plants operated by Tata Steel (Aries et al., 2006). These results clearly showed
331 that although PBDD/Fs were emitted from the iron ore sintering process, the magnitude of
332 these emissions was substantially lower than that of PCDD/Fs. It is believed that PBDD/F
333 emissions are much lower than PCDD/F emissions because the soluble bromide
334 concentrations in the raw sinter mix are substantially lower (typically below 5 mg/kg) than
335 soluble chloride concentrations (typically within the range 20 to 80 mg/kg).

336 4.2 Stack emission results for PBDEs

337 A series of twelve stack emission samples were obtained at a UK Sinter Plant operated by
338 Tata Steel and analysed for their PBDE concentrations. In total, 36 PBDE congeners were
339 analysed by HRGC – HRMS. The emission concentrations and congener profiles for the
340 compounds analysed are depicted in Fig. 3. In addition, Table 3 summarises the emissions
341 concentrations of the most predominant congeners identified in this study. The results
342 showed that the mean PBDE emission concentrations (sum of 36 PBDE congeners) was 295
343 ng/Nm³, with a standard deviation of 96 ng/Nm³. A very characteristic emission profile was
344 obtained with a clear predominance of BDE-99 (average = 109 ng/Nm³) and BDE-47
345 (average = 75 ng/Nm³), followed by BDE-71 (and/or BDE-49 since both compounds co-
346 eluted in our study) with an average concentration of 32 ng/Nm³.

347 Further analysis of the PBDE congener pattern revealed that the emission profile was very
348 similar to the percent composition of a Technical mixture of Pentabromodiphenylether as
349 shown in Fig. 4. For this analysis, the concentrations of the 10 most abundant PBDE
350 congeners found in sinter plant emissions (See Table 3) were normalised and compared with
351 the weight concentrations of these PBDEs in a commercially available Pentabromodiphenyl
352 Oxide Technical mixture for which the exact chemical composition was available (Great
353 Lakes DE-71, Technical Mixture, Wellington Laboratories). As depicted in Fig. 4, a good
354 agreement between the congener pattern observed in sinter plant emissions and the congener
355 pattern of the Pentabromodiphenyl Oxide technical mixture was observed.

356 The only previous noteworthy study describing emissions of PBDEs from the iron ore
357 sintering process was carried out by Wang et al. (2010) for several sinter plants in Taiwan. In
358 this research, the congener profiles reported showed a very clear predominance of highly
359 brominated-substituted congeners, namely BDE-209, -208, -207, -206, and -183. As a result,
360 it was difficult to directly compare the results of both studies since these PBDEs were not
361 analysed in this study. However it was noted that with regard to the low- to medium -
362 brominated congeners, BDE-47 and BDE-99 were predominant in the sinter plants
363 investigated in Taiwan which was in good agreement with the results obtained at UK sinter
364 plants. At this stage, it is difficult to explain why the congener profiles observed from UK
365 plants would exhibit a pattern similar to the composition of a Pentabromodiphenylether
366 technical mixture; however it would appear highly unlikely that if PBDEs were formed in the
367 process, such a distinctive profile would be obtained. Accordingly, work was carried out to
368 characterise further the PBDE chemical composition of input materials (raw sinter mix, iron
369 ores, fuels) entering the sinter plant to determine whether the materials used in sintering
370 could contain PBDEs prior thermal treatment.

4.3 Raw Material Input / Output Analysis – Mass Balances of PBDEs

373 In order to study in more detail the distribution of PBDEs in the iron ore sintering process,
374 representative samples of input materials (raw sinter mix) and output materials (sinter
375 product, waste dusts from the electrostatic precipitators: ESP) were collected and analysed
376 for their PBDE content for a total of four beds of materials processed at Sinter Plant A (Bed
377 #s 2258, 2259, 2265, and 2272). The analytical results were used to carry out mass balance
378 calculations of PBDE input / outputs in the iron ore sintering process. For input calculations,
379 PBDE concentrations in the raw sinter mix were multiplied by the bed tonnage and divided
380 by the sinter production. With regard to the sinter product, PBDE outputs were calculated
381 using the PBDE concentrations in the sinter product and by taking into account the sinter
382 production. The amount of ESP dust generated per bed of material is not usually measured
383 accurately; however the amounts produced were estimated assuming that the particulate
384 emission concentration at the inlet of the ESP was 850 mg/Nm^3 and that the efficiency of the
385 ESP was 94% (reducing the particulate emissions down to 50 mg/Nm^3). By multiplying the
386 amount of dust theoretically captured by the ESP with the stack flow rate and by taking into
387 consideration the bed processing time, it was possible to estimate the amounts of waste ESP
388 dusts produced per sinter bed. For Sinter Plant A, the amount of dust produced was estimated

389 to be 1.5 kg/ton sinter produced. PBDE outputs were calculated using this figure and the
390 sinter production for each bed of material investigated. Finally, stack emission outputs were
391 estimated using the mean concentrations determined in this study (Table 3) which was
392 multiplied by the stack emission flow rate and divided by the sinter production. The detailed
393 results of the calculations are provided as supplementary information (Table SI-1). However,
394 to simplify the data, Table 4 summarises the PBDE inputs and outputs expressed in mg/tonne
395 sinter for each bed of material investigated and the percent distribution of PBDE found in
396 output materials after thermal processing. This facilitated estimation the proportion of PBDEs
397 actually destroyed during sintering.

398 Analysis of the results revealed that PBDEs were already present in the raw sinter mix in
399 significant amounts before thermal treatment in the process and were originating from the
400 raw materials. This result was relatively unexpected as no previous studies highlighted the
401 presence of PBDEs in the raw materials used in the sintering process. PBDEs were also found
402 in waste ESP dusts in relatively high concentrations and in the sinter product at low
403 concentrations. The results for individual and the sum of the 9 most abundant PBDE
404 congeners are reported in Table SI-1 (Supplementary information). With regard to the raw
405 sinter mix, total PBDE concentrations ranged from 11 to 22 $\mu\text{g}/\text{kg}$, while the range of
406 concentrations observed in the sinter product was much lower (ca. 0.5 to 2.2 $\mu\text{g}/\text{kg}$). The
407 highest concentrations of PBDEs were found in the ESP dusts ranging from 22 to 81 $\mu\text{g}/\text{kg}$.
408 In terms of input, between 13 and 26 mg/ton sinter of PBDEs were found in the raw sinter
409 mix (Table 4). In contrast, very low PBDE output figures were found in the sinter product,
410 ESP dusts and stack emissions (ca. < 2 mg/ton sinter). Stack PBDE outputs represented only
411 less than 4% of PBDE inputs. Overall, the results showed that between 80% and 95% of
412 PBDEs entering the sintering process via the raw materials were destroyed during thermal
413 treatment (Table 4).

414 To understand further the source of PBDEs in input raw materials, several types of raw
415 materials were selected and analysed for their PBDE (sum of seven congeners) content.
416 These materials are typically mixed together in a bed to constitute the raw sinter mix. These
417 consisted of a series of 26 iron ores typically used at Tata Steel sinter plants, 20 revert
418 materials which included recycled materials from other processes in the integrated steelworks
419 (i.e. blast furnaces, steelmaking plant, rolling mills), 3 fuel samples (i.e. coke breeze) and
420 flux samples such as limestone and olivine. The mean PBDE and range of concentrations
421 observed are summarised in Table 5.

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422 PBDEs were mostly found in iron ores (ca. 992 ng/kg), revert materials (ca. 8286 ng/kg) and
423 fuels (ca. 4891 ng/kg). For most types of material, a relatively wide range of concentrations
424 was observed showing a high variability in the PBDE content of the materials used in the iron
425 ore sintering process. When comparing the iron ore Σ PBDE concentrations (5 - 1623 ng/kg)
426 to those reported for soil samples at several locations such as Spain (Eljarrat et al., 2008),
427 China (Chen et al., 2012), USA (Yun et al., 2008) and Sweden (Sellstrom et al., 2005), it was
428 found that the iron ores used in sintering fell within the range of concentrations reported
429 previously for soils (140 - 260000 ng/kg). The same was observed for the fuels used in
430 sintering. These results suggested that PBDEs were already present in some input materials to
431 the sintering process and were thus perhaps not formed during thermal treatment. The
432 resemblance between the congener pattern in some input materials and that in the Penta-BDE
433 commercial formulation suggests that exposure of input materials to a Penta-BDE source is
434 occurring at some point. This source in the raw materials is currently unknown, although it is
435 assumed that their presence may occur between the mining of iron ore and coals, storage,
436 transportation and preparation for the commercial sintering process. However, with over
437 thirty different sources of iron ores from across the world and a similar situation for coals, it
438 was not feasible to investigate this further in the current study. The revert materials did
439 exhibit higher PBDE concentrations than other types of materials; this result was also
440 difficult to explain. It may be due to the fact that the PBDEs which are transferred to the
441 blast furnaces and downstream processes via the sinter product are volatilised and
442 concentrated further in waste dusts emitted from the blast furnace / steelmaking operations,
443 however further work would be needed to confirm this. The contribution of each type of input
444 materials to the sinter plant was studied in more detail for five different sinter beds, and the
445 results depicted in Fig. 5. As may be seen from Fig. 5, for some beds, the main PBDE inputs
446 were mostly associated with the revert materials (ca. 60 – 80%), but for some other beds
447 PBDEs originated equally from the iron ores, revert and fuels materials (ca. 20 to 40% each).
448 For all beds, PBDE inputs from fluxes (i.e. limestone / olivine) were negligible. These results
449 highlighted the fact that there were multiple raw material sources of PBDEs in the sintering
450 process with significant variability.

451 The mean PBDE congener profiles for each type of input material was studied and the results
452 depicted in Fig. 6. The congener profiles for each type of the raw materials (iron ores, fuels,
453 reverts and fluxes) were almost identical with BDE-47 and BDE-99 representing the majority
454 of Σ PBDE content. The congener profiles in all components appeared to be similar to that of

1 455 the PentaBDE commercial formulations (La Guardia et al. 2006), in good agreement with the
2 456 data described earlier for sinter plant stack emissions.
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4 457 4.4 Results from the sinter pot study (PBDEs and PBDD/Fs) 5

6 458 A series of sinter pot experiments were carried out to investigate whether PBDEs and
7 459 PBDD/Fs could be formed in the sintering process following similar pathways to those
8 460 identified for their chlorinated homologues (PCDD/Fs and PCBs) such as *de novo* synthesis.
9 461 Experiments were also carried out to investigate whether PBDEs could be potential PBDD/F
10 462 precursors in the sintering process *via* thermal conversion of PBDEs into PBDD/Fs as shown
11 463 in laboratory experiments by Buser (1986). To this end, KBr was added at two addition rates
12 464 (74.5 mg/kg and 225 mg/kg RSM: experiments 2 and 3) to the raw sinter mix, while PBDE
13 465 technical commercial mixtures of Penta- and Deca-BDE were added at 50 µg/kg RSM in
14 466 experiment 4. In experiment 5, both KBr (high addition rate) and the two technical PBDE
15 467 formulations at 50 µg/kg were added. The results obtained in experiments 2 to 5 were
16 468 compared with a base case for which no KBr or PBDE technical mixture was added to the
17 469 raw sinter mix (experiment 1). Experiment 1 can be associated with typical operations at a
18 470 commercial sinter plant. Fig. 7 depicts the PBDE inputs (raw sinter mix) and outputs (sinter
19 471 product + emissions) expressed as ng/kg raw sinter mix for each experiment. Fig. 8 shows the
20 472 PBDD/F emissions expressed in ng WHO-TEQ PBDD/F/kg raw sinter mix.
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35 473 Analysis of the PBDE data showed that in experiments 1 to 3, for which no PBDEs were
36 474 added, there was a mean overall \sum PBDE input of 1400 ng/kg raw sinter mix (range: 1400-
37 475 2100 ng/kg raw sinter mix respectively). In experiments 4 and 5, where PBDE technical
38 476 formulations were added, PBDE concentrations were 18000 and 19000 ng/kg raw sinter mix
39 477 respectively highlighting the additional PBDE inputs (Fig. 7). However, examination of
40 478 PBDE outputs showed that in all experiments there was net destruction of \sum PBDEs with an
41 479 average of 88% (range: 79-96%). This result was consistent with the mass balance data
42 480 previously described in Section 1.4.3. The addition of KBr in experiments 2 and 3 did not
43 481 result in any significant increase in \sum PBDE outputs with net PBDE reductions of 90% and
44 482 79%, respectively. This result suggested that *de novo* synthesis of PBDEs did not occur in the
45 483 sintering process, rather destruction of PBDEs that were already present in the raw materials
46 484 prior to thermal treatment.
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58 485 Examination of the PBDD/F results (Fig. 8) showed that very low PBDD/F emissions were
59 486 observed in experiment 1 where no KBr was added to the raw sinter mix. However, the
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487 results obtained for experiments 2 and 3 showed a marked increase in PBDD/F emissions
488 with increasing availability of bromide. These results suggest that PBDD/F formation in iron
489 ore sintering could follow a similar pathway to that of their chlorinated homologues (i.e. *de*
490 *novo* formation). It must be noted however that the relatively high addition rates of bromide
491 used in this study were not representative of standard operating conditions for a commercial
492 sinter plant for which bromide concentrations are typically below 5 mg/kg. These high
493 addition rates of bromide were only used for research purposes to study a possible link
494 between bromide concentrations in the raw sinter mix and PBDD/F sinter plant emissions.
495 Interestingly, no significant increase in PBDD/F emissions was observed in experiment 4
496 where significant additions of Penta-BDE and Deca-BDE technical mixtures were used. This
497 result suggests that PBDD/Fs were not formed *via* the conversion of PBDEs used as
498 precursors in iron ore sintering. In all sinter pot experiments, PBDFs constituted the majority
499 of PBDD/F emissions. On average, 89 % (range: 55-98%) of Σ PBDD/Fs were PBDFs with
500 2,3,7,8-TBDF the dominant congener in 7 out of 10 sinter pot runs as previously observed in
501 the emissions of the full scale sinter plant (Table 2).

5. Conclusions

503 This study showed that both PBDEs and PBDD/Fs were emitted from the iron ore sintering
504 process. With regard to PBDD/Fs, the mean emission concentrations were 0.14 ng WHO-
505 TEQ/m³ assuming that PBDD/F and PCDD/F have identical toxic equivalency factors
506 (WHO-TEFs). This study showed that PBDD/F emissions were significantly lower than those
507 of PCDD/Fs in the same samples, accounting for only ca. 10% of the total WHO-TEQ
508 emission concentrations (PBDD/Fs + PCDD/Fs). The average concentration in sinter plant
509 emissions of the sum of 36 PBDE congeners was 295 ng/Nm³ with a standard deviation of 96
510 ng/Nm³. The PBDE congener pattern was very similar to that of a Penta-BDE formulation.
511 PBDE mass balances were carried out at a full scale sinter plant showing that PBDEs were
512 already present in the raw materials such as iron ores and coke breeze and that a significant
513 proportion of the PBDE inputs were actually destroyed during the process (ca. 80 to 95%).
514 While detailed source attribution of the PBDEs in the raw materials was outside the scope of
515 this study, the similarity of the congener pattern in some raw materials to the Penta-BDE
516 formulation, suggests that contamination of such raw materials occurred prior to sintering.
517 Laboratory tests using an experimental sinter pot were carried out to study the formation
518 mechanisms of PBDD/Fs and PBDEs. Results showed that PBDD/F formation increased with
519 increasing amounts of bromide in the raw sinter mix indicating a possible *de novo* formation

520 pathway. However, this was not the case for PBDEs for which the bromide content of the raw
521 mix exerted no influence. In fact, the results suggested that PBDEs are not formed in iron ore
522 sintering, but instead the PBDEs present in the raw materials are destroyed. Finally, the sinter
523 pot tests showed that PBDD/F formation was not influenced by the presence of PBDEs in the
524 raw sinter mix. This suggests that PBDEs do not act as PBDD/F precursors during sintering.

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List of Figures and Tables

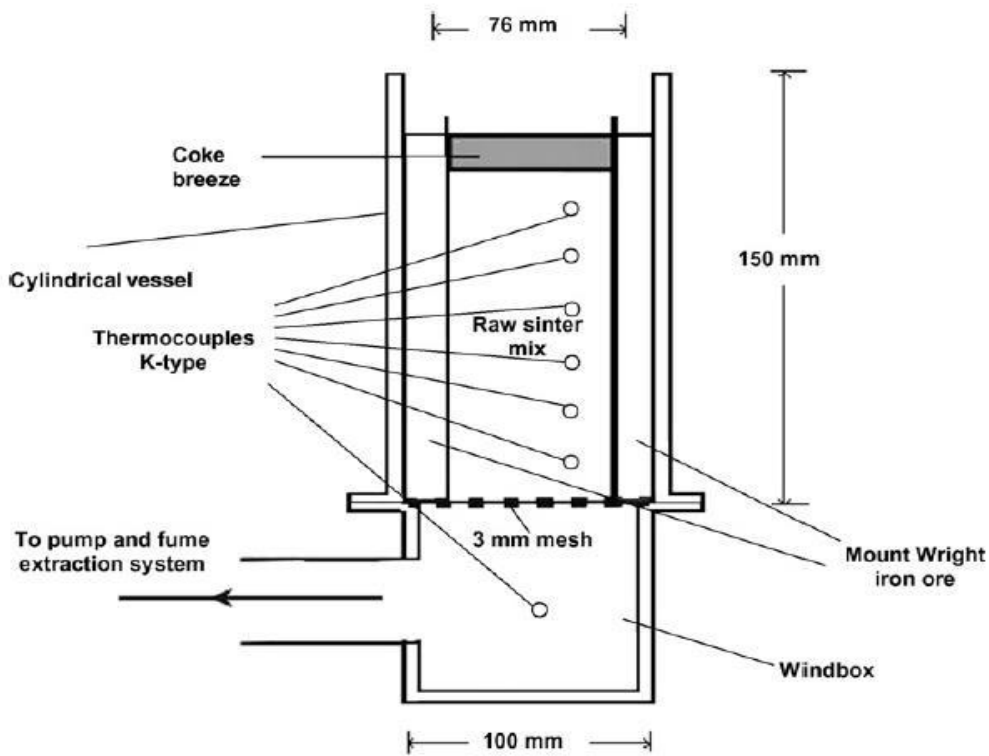


Figure 1 – A schematic diagram of the laboratory sinter pot apparatus used to investigate the potential formation of PBDEs and PBDD/Fs in iron ore sintering (Ooi et al., 2008)

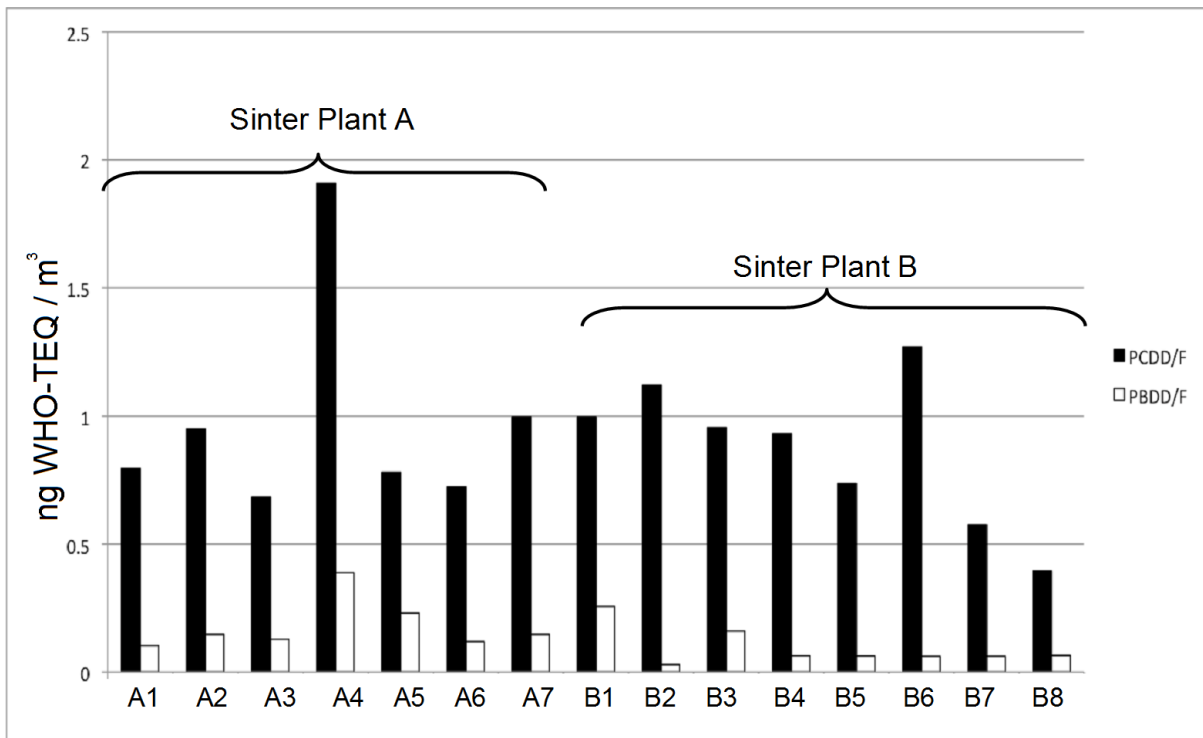
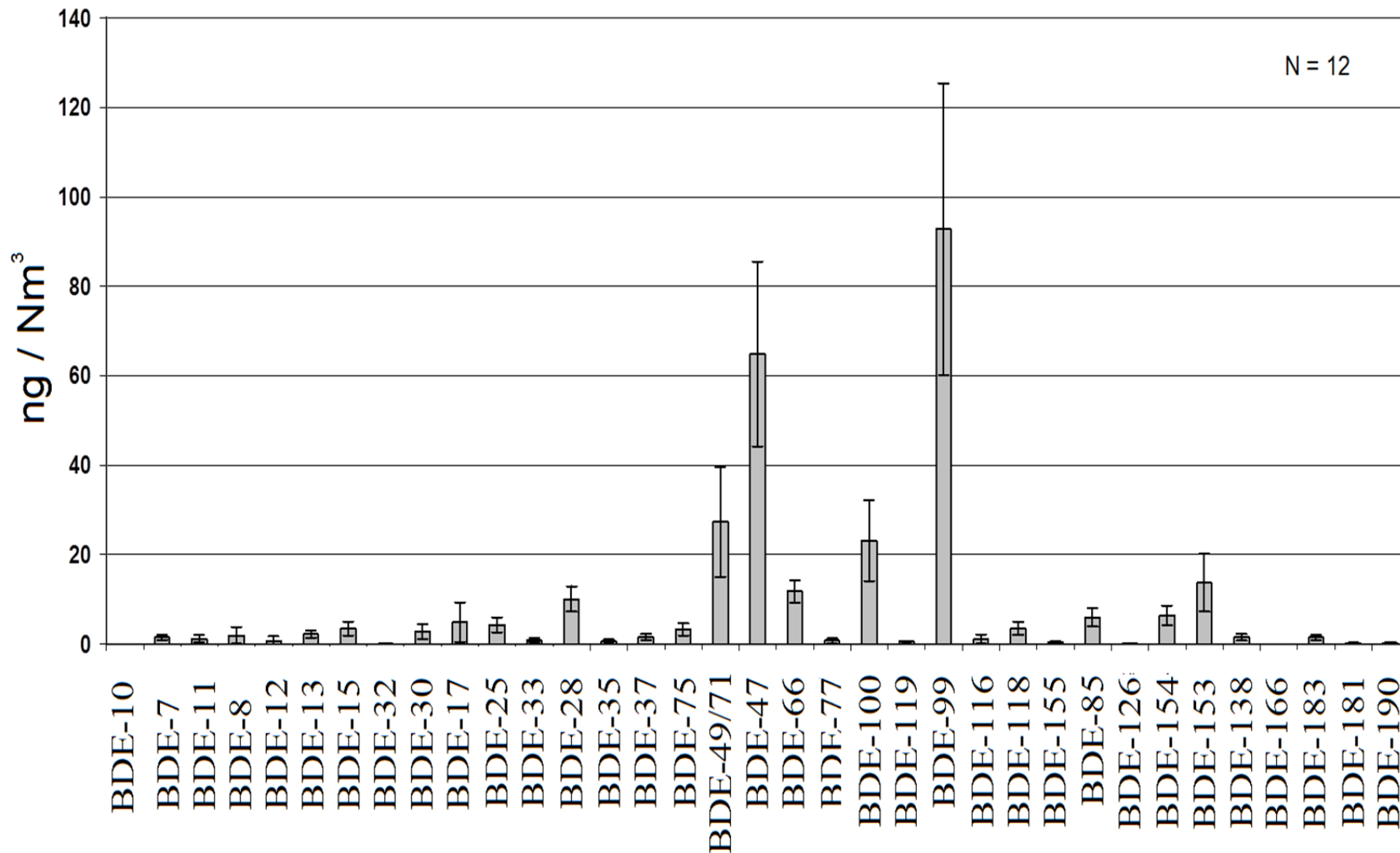


Figure 2 - PCDD/F and PBDD/F WHO-TEQ concentrations at two UK sinter plants operated by Tata Steel.

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674 *Fig. 3 – PBDE emission concentrations and congener profile at a UK sinter plant operated by Tata Steel*

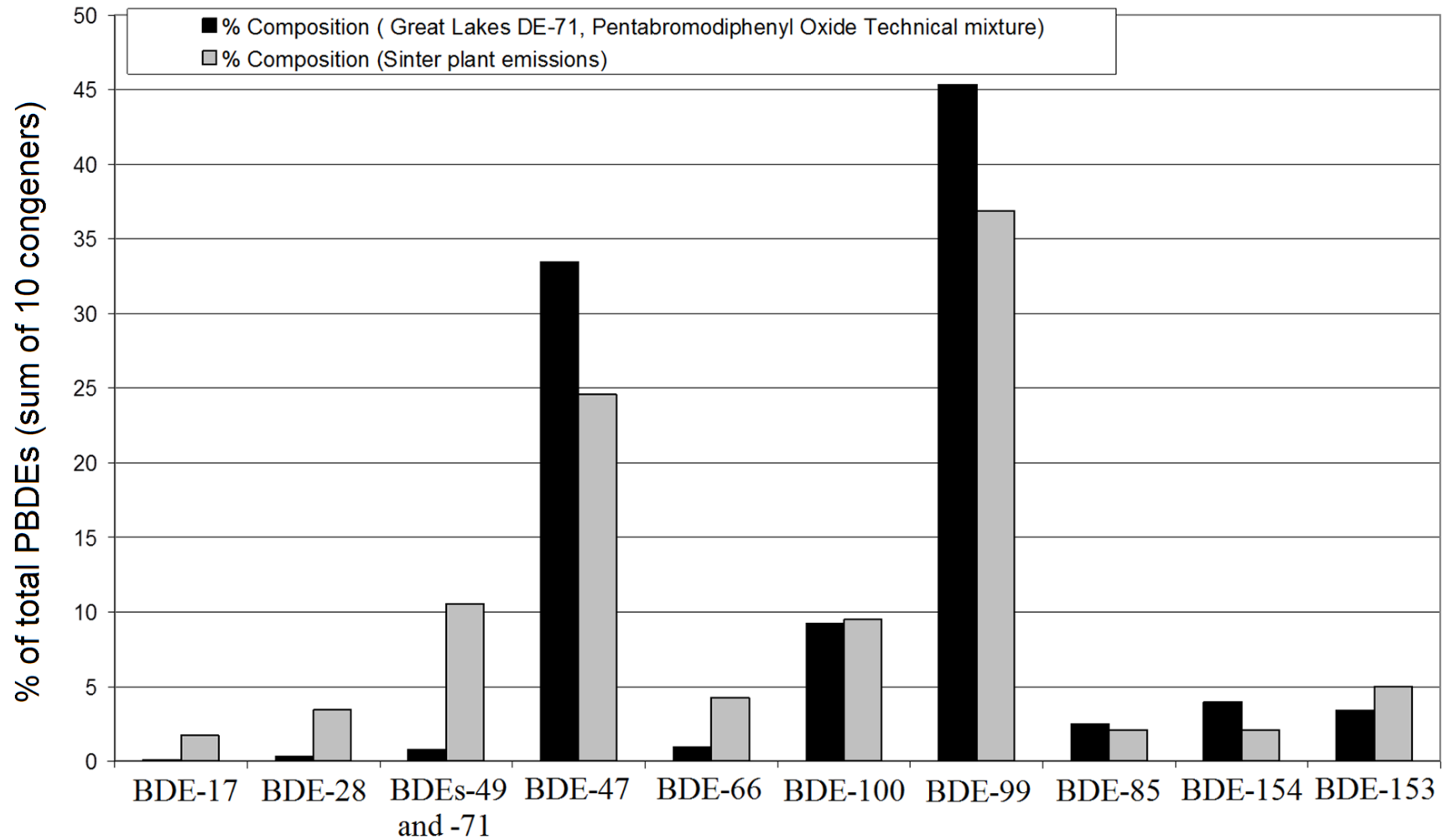


Fig. 4. Comparison between the percent composition of PBDEs in a Pentabromodiphenyl Oxide mixture and the percent composition of PBDEs in sinter plant emissions.

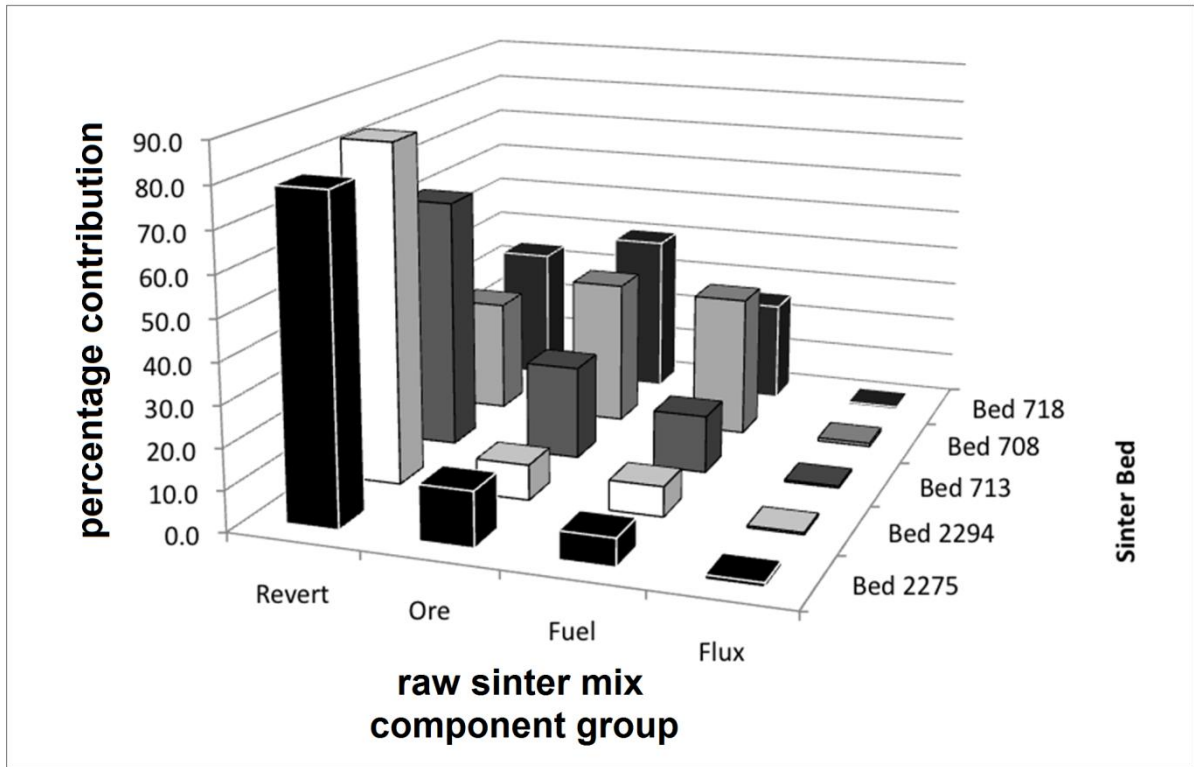


Fig. 5 – Contribution of each component of the raw sinter mix to total PBDE inputs.

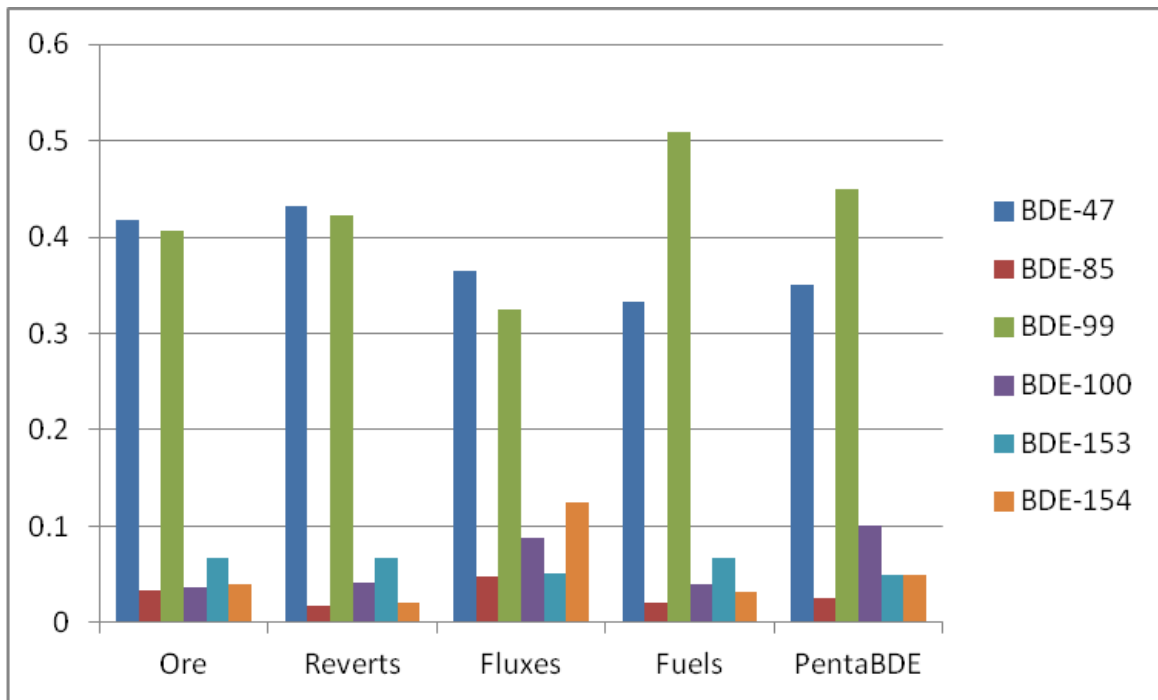


Fig. 6 – Average congener profiles for RSM component groups and the PentaBDE mixture DE-71 (La Guardia et al. 2006).

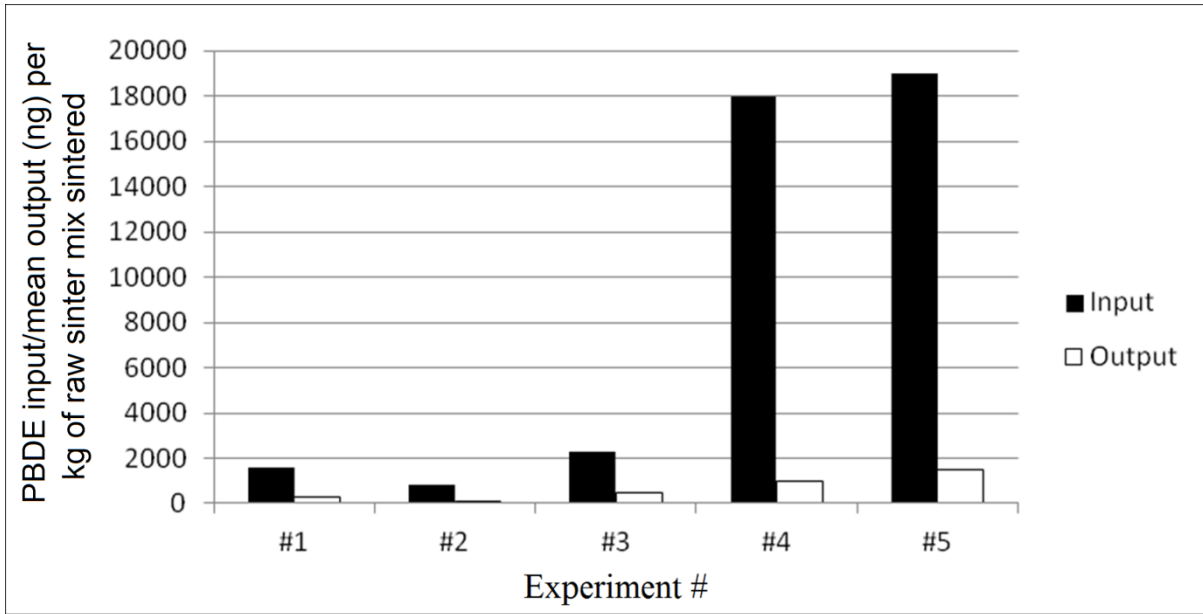


Fig. 7: Input and outputs of Σ PBDEs (ng) per kg of raw sinter mix for each laboratory sinter pot experiment carried out to investigate the possible formation of PBDEs in iron ore sintering

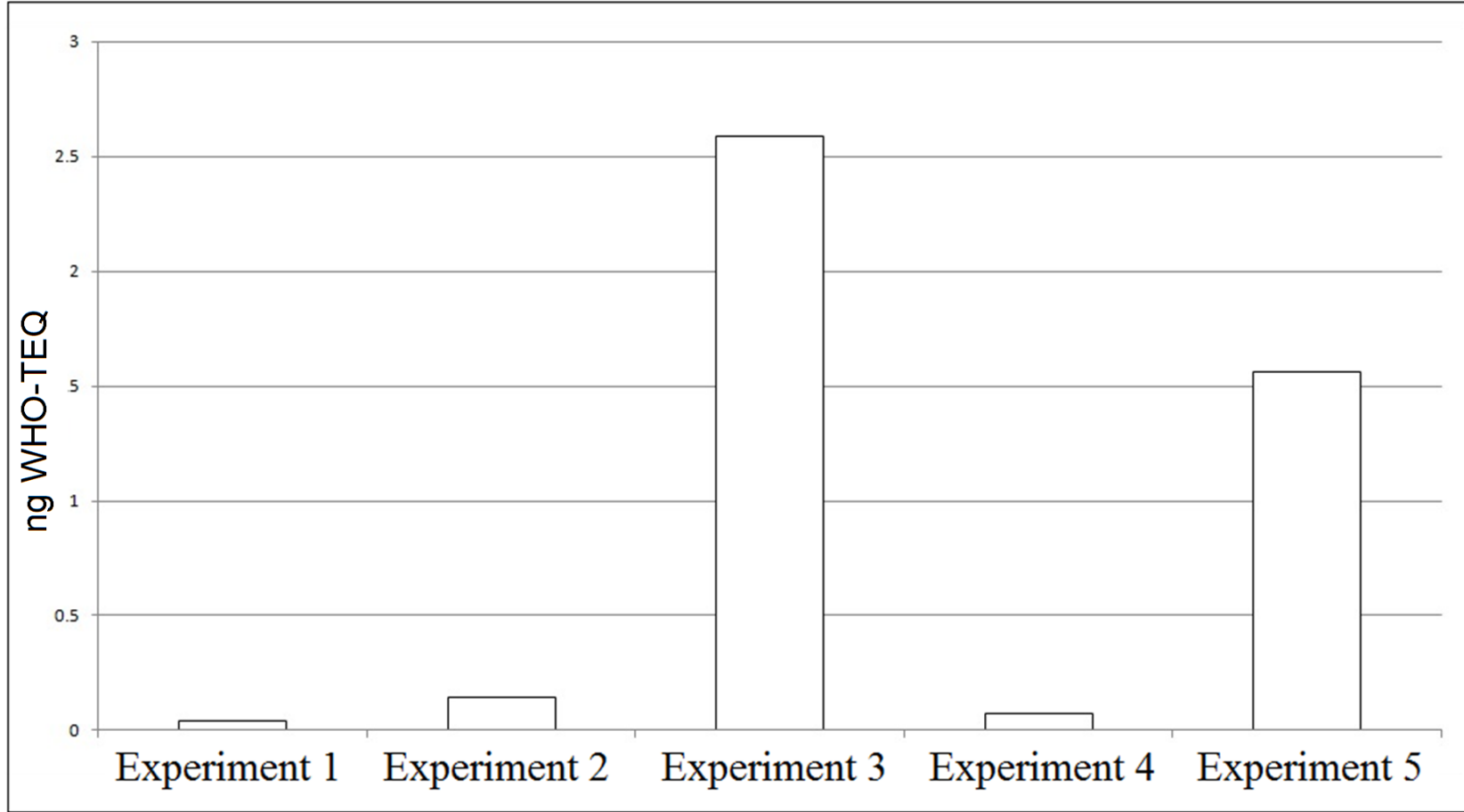


Fig. 8: Emissions of PBDD/Fs expressed as ng-WHO-TEQ formed per kg of raw sinter mix for each laboratory sinter pot experiment carried out to investigate the possible formation of PBDD/Fs in iron ore sintering

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Table 1 – Laboratory Sinter Pot Experimental Conditions to study PBDE and PBDD/F formation in the iron ore sintering process

Experiment N.	Condition
1	“Base Case” (Standard Raw Sinter Mix : RSM)
2	“Base Case”+ 74.5 mg/kg KBr (50 mg/kg Br ⁻)
3	“Base Case” + 224 mg/kg KBr (150 mg/kg Br ⁻)
4	“Base Case” + PBDE Penta- and Octa- technical mixtures ^a
5	“Base Case” + 224 mg/kg KBr (150 mg/kg Br ⁻) + PBDE Penta- and Octa- technical mixtures ^a

^a 50 µg / kg PentaBDE (DE-71) and 50 µg/kg DecaBDE (DE-83) (Cambridge Isotope Laboratories (CIL), Andover, MA, USA)

694 **Table 2. PBDD/F and PCDD/F emission concentrations at two UK sinter plants**
 695 **operated by Tata Steel.**

Compound	Sinter Plant B (N = 8) Emission concentrations (ng/Nm³)		Sinter Plant A (N = 7) Emission concentrations (ng/Nm³)	
	Mean	Range	Mean	Range
<u>PBDD/Fs</u>				
2378-TBDF	0.12	0.04 - 0.28	0.26	0.14 - 0.57
12378-PeBDF	0.12	0.05 - 0.38	0.21	0.14 - 0.39
23478-PeBDF	0.11	0.04 - 0.31	0.19	0.12 - 0.34
123478-HxBDF	< 0.003 ^a	< 0.003 ^a	< 0.003 ^a	< 0.003
∑ PBDFs	0.35	0.12 - 0.97	0.66	0.42 - 1.30
2378-TBDD	0.02	0.01 - 0.04	0.05	0.01 - 0.12
12378-PeBDD	0.01	< 0.003 - 0.005	0.01	0.007 - 0.02
123478/123678- HxBDD	< 0.003 ^a	< 0.003 ^a	0.01	< 0.002 - 0.02
123789-HxBDD	< 0.003 ^a	< 0.003 ^a	0.006	< 0.003 - 0.006
∑ PBDDs	0.02	0.005 - 0.06	0.05	0.02 - 0.13
WHO-TEQ (PBDD/Fs)	0.10	0.03 - 0.26	0.18	0.10 - 0.39
<u>PCDD/Fs</u>				
WHO-TEQ (PCDD/Fs)	1.01	0.46 – 1.50	1.17	0.80 – 2.40

^a Compound was not detected. The value indicated is the limit of detection.

703 **Table 3. PBDE concentrations (ng/Nm³) of the 10 most abundant PBDEs and the sum of**
 704 **36 PBDE congeners in emissions from a sinter plant in the UK operated by Tata Steel.**

Compound	Emission concentrations N = 12 measurements	
	Mean	Standard deviation
BDE-17 (2,2',4-TrBDE)	4.9	4.4
BDE-28 (2,4,4'-TrBDE)	10.1	2.8
BDE-49 and BDE-71 ^a (2,2',4,5' & 2,3',4',6-TeBDE)	27.3	12.2
BDE-47 (2,2',4,4'-TeBDE)	64.9	20.6
BDE-66 (2,3',4,4'-TeBDE)	11.8	2.5
BDE-100 (2,2',4,4',6-PeBDE)	23.1	9.0
BDE-99 (2,2',4,4',5-PeBDE)	92.8	32.6
BDE-85 (2,2',3,4,4'-PeBDE)	6.0	2.1
BDE-154 (2,2',4,4',5,6'-HxBDE)	6.5	2.2
BDE-153 (2,2',4,4',5,5'-HxBDE)	13.7	6.5
Σ PBDEs (36 congeners)	295	96

^a Compounds co-eluted.

707 **Table 4. PBDE inputs / outputs and distribution at an iron ore sintering plant operated**
 708 **by Tata Steel. The results are expressed in mg / ton sinter produced for four beds of**
 709 **materials.**

	PBDE inputs / outputs expressed in mg / ton sinter				PBDE distribution in the iron ore sintering process (%)			
	Raw mix	Sinter produc t	ESP dusts	Stack emission s	ESP dusts	Sinter product	Stack emission s	Destroyed during sintering
Bed 2258	26.0	0.5	0.06	0.7	0.2	1.9	2.7	95.2
Bed 2259	13.5	2.2	0.06	0.5	0.4	16.0	3.7	79.9
Bed 2265	15.1	0.6	0.05	0.6	0.3	4.0	4.0	91.7
Bed 2272	14.5	1.2	0.20	0.6	1.4	8.3	4.1	86.2

712 **Table 5. Average and range of concentrations (ng/kg) for PBDEs^a in the components of**
 713 **raw sinter mix used in the iron ore sintering process.**

Component	n	Mean	Range
Iron Ores	26	992	5 – 1623
Reverts	20	8286	30 – 11263
Fuels	3	4891	2092 – 8133
Fluxes	5	240	9 – 940

714 ^aSum of seven PBDE congeners (BDE-47; BDE-85; BDE-99; BDE-100; BDE-153; BDE154 ; BDE-183).

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717 **Supplementary information**718 **Table SI-1. Detailed PBDE mass balances at an iron ore sintering plant operated by**
719 **Tata Steel in the UK for four beds of materials**

Sinter Bed Conditions	Bed 2258	Bed 2259	Bed 2265	Bed 2272
Raw Sinter Mix (Tonnes)	60378	60097	60867	60776
Sinter production (Tonnes)	50440	49316	52608	52324
Estimated waste ESP dust produced (Tonnes)	126	123	132	131
Bed duration (h)	111.5	86	96.5	105.3
Stack flow rate (Nm ³ /s)	348	348	348	348
Material PBDE input concentrations (µg/kg)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.15	0.07	0.08	0.021
BDE-28	0.39	0.19	0.23	0.18
BDE-49	2.0	0.9	1.1	0.9
BDE-47	3.8	1.9	2.3	2.3
BDE-85	1.0	0.6	0.5	0.7
BDE-100	1.4	0.8	0.2	0.7
BDE-99	10.0	5.1	6.5	5.6
BDE-153	2.6	1.3	1.7	1.4
BDE-154	0.5	0.3	0.4	0.6
Σ PBDEs (9 congeners)	21.8	11.1	13.0	12.5
Inputs to Sinter Plant (expressed in g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	9.1	4.1	5.1	1.3
BDE-28	23.5	11.4	14.0	10.9
BDE-49	120.8	56.5	67.0	57.1
BDE-47	229.4	114.2	140.0	139.8
BDE-85	60.4	34.3	32.9	43.2
BDE-100	84.5	45.7	12.2	43.2

BDE-99	603.8	306.5	395.6	340.3
BDE-153	157.0	78.1	103.5	85.1
BDE-154	30.2	16.2	23.7	37.7
Σ PBDEs (9 congeners)	1318.7	667.0	793.9	758.5
Output to sinter product (µg / kg)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.002	0.020	0.006	<0.002
BDE-28	0.004	0.027	0.008	0.024
BDE-49	0.014	0.054	0.016	0.260
BDE-47	0.078	0.760	0.190	0.270
BDE-85	0.160	0.160	0.013	0.250
BDE-100	0.130	0.260	0.130	<0.005
BDE-99	0.130	0.310	0.080	0.086
BDE-153	<0.01	0.270	0.083	0.240
BDE-154	<0.01	0.300	0.053	0.093
Σ PBDEs (9 congeners)	0.520	2.200	0.580	1.200
Output to sinter product (g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.08	0.99	0.32	n/a
BDE-28	0.19	1.33	0.41	1.26
BDE-49	0.71	2.66	0.84	13.60
BDE-47	3.93	37.48	10.00	14.13
BDE-85	8.07	7.89	0.68	13.08
BDE-100	6.55	12.8	6.8	n/a
BDE-99	6.55	15.3	4.2	4.5
BDE-153	n/a	13.3	4.4	12.6
BDE-154	n/a	14.8	2.8	4.9
Σ PBDEs (9 congeners)	26.0	108.5	30.5	62.8

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Output to waste ESP dust ($\mu\text{g} / \text{kg}$)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.089	0.078	0.12	0.16
BDE-28	0.25	0.25	0.3	0.57
BDE-49	1.3	1.4	1.5	3.6
BDE-47	2.4	2.5	2.7	7.9
BDE-85	0.8	1.0	0.82	4.1
BDE-100	1.6	1.7	1.3	4.1
BDE-99	9.3	11.0	7.7	39.0
BDE-153	5.3	4.9	4.3	17.5
BDE-154	1.1	1.2	1.0	3.8
Σ PBDEs (9 congeners)	22.2	24.0	19.8	80.8
Output to waste ESP dust (g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.01	0.01	0.02	0.02
BDE-28	0.03	0.03	0.04	0.08
BDE-49	0.16	0.17	0.20	0.47
BDE-47	0.3	0.31	0.36	1.04
BDE-85	0.11	0.12	0.11	0.54
BDE-100	0.2	0.21	0.17	0.53
BDE-99	1.17	1.36	1.01	5.10
BDE-153	0.67	0.60	0.57	2.29
BDE-154	0.14	0.15	0.13	0.50
Σ PBDEs (9 congeners)	2.8	3.0	2.6	10.6
Output to sinter plant stack (ng/Nm^3)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	4.9	4.9	4.9	4.9
BDE-28	10.1	10.1	10.1	10.1
BDE-49	27.3	27.3	27.3	27.3

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BDE-47	64.9	64.9	64.9	64.9
BDE-85	6.0	6.0	6.0	6.0
BDE-100	23.2	23.2	23.2	23.2
BDE-99	92.8	92.8	92.8	92.8
BDE-153	13.7	13.7	13.7	13.7
BDE-154	6.5	6.5	6.5	6.5
Σ PBDEs (9 congeners)	249.4	249.4	249.4	249.4
Output to sinter plant stack (g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.7	0.5	0.6	0.6
BDE-28	1.4	1.1	1.2	1.3
BDE-49	3.8	2.9	3.3	3.6
BDE-47	9.1	7.0	7.8	8.6
BDE-85	0.8	0.6	0.7	0.8
BDE-100	3.2	2.5	2.8	3.1
BDE-99	13.0	10.0	11.2	12.2
BDE-153	1.9	1.5	1.7	1.8
BDE-154	0.9	0.7	0.8	0.9
Σ PBDEs (9 congeners)	34.8	26.9	30.2	32.9

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