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Brominated flame retardants in black plastic kitchen utensils: Concentrations and human exposure implications

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Abstract

Concerns exist that restricted brominated flame retardants (BFRs) present in waste polymers may have, as a result of recycling, inadvertently contaminated items not required to meet flame retardancy regulations (e.g. plastic kitchen utensils). To investigate the extent to which kitchen utensils are contaminated with BFRs and the potential for resultant human exposure, we collected 96 plastic kitchen utensils and screened for Br content using a hand-held X-ray fluorescence (XRF) spectrometer. Only 3 out of 27 utensils purchased after 2011 contained detectable concentrations of Br (≥ 3 μg/g). In contrast, Br was detected in 31 out of the 69 utensils purchased before 2011. Eighteen utensils with Br content higher than 100 μg/g, and 12 new utensils were selected for GC-MS analysis of BFRs. BFRs targeted were polybrominated diphenyl ethers (PBDEs) BDE-28, 47, 99, 100, 153, 154, 183 and 209, and novel BFRs (NBFRs) pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and decabromodiphenyl ethane (DBDPE). The ability of XRF to act as a surrogate metric of BFR concentration was indicated by a significant (Spearman coefficient = 0.493; p=0.006) positive relationship between Br and ΣBFR concentration. Measurements of ΣBFRs were always exceeded by those of Br. This may be due partly to the presence of BFRs not targeted in our study and also to reduced extraction efficiency of BFRs from utensils. Of our target BFRs, BDE-209

was the most abundant one in most samples, but an extremely high concentration (1,000 μg/g) of BTBPE was found in one utensil. Simulated cooking experiments were conducted to investigate BFR transfer from selected utensils (n=10) to hot cooking oil, with considerable transfer (20 % on average) observed. Estimated median exposure via cooking with BFR contaminated utensils was 60 ng/day for total BFRs. In contrast, estimated exposure via dermal contact with BFR-containing kitchen utensils was minimal.

36 **Keywords**

37 BFR, kitchen utensil, recycled plastic, human exposure, UK

38

1. Introduction

Brominated flame retardants (BFRs) are a group of organic compounds added widely to consumer goods such as electronic devices, textiles, and upholstery etc. to meet flame retardancy regulations. Over the life cycle of such items, BFRs may undergo emission to the environment and as a consequence are ubiquitous in the environment, including air (Abdallah et al., 2008; Sun et al., 2016), dust (Cristale et al., 2016; Harrad et al., 2008; Zhu et al., 2017), soil (Leung et al., 2007; Zhu et al., 2017), sediment (Barón et al., 2014; Guerra et al., 2010), as well as biota (including humans) exposed to such media (Carignan et al., 2013; Drage et al., 2017; Shi et al., 2016; Tao et al., 2017; Zhu et al., 2017). Such environmental contamination, coupled with evidence of their toxicity, means that BFRs are of great concern. As a consequence, BFRs like polybrominated diphenyl ethers (PBDEs) have been listed as persistent organic pollutants (POPs) under the Stockholm Convention and subject to bans and restrictions on their manufacture and new use in a number of jurisdictions. While to date, the majority of attention has focused on BFR exposure as a result of emissions from in-use materials, there is growing realization that the presence of BFRs in waste items also constitutes a potential problem.

Waste electrical and electronic equipment (WEEE) may be dismantled to recover precious metals and plastics, with the plastics recovered being recycled. However, use

of recycled plastics containing BFRs in new materials has led to concerns that restricted BFRs may be present in newly manufactured goods, including those which are not subject to flame retardancy regulations such as plastic food contact utensils and toys. To minimise contamination of newly manufactured goods that are not subject to flame retardancy regulations (e.g. food contact articles and children's toys) with BFRs via use of BFR-containing recycled polymers, the European Commission has under its Restriction of Hazardous Substances (RoHS) and WEEE directives, set Low POP Concentration Limits (LPCLs) for some BFRs to ensure waste plastics exceeding such limits are not recycled. These values are currently 1,000 ppm for PBDEs (not including BDE-209) and hexabromocyclododecane (HBCDD). However, reports exist that plastic goods exceeding LPCLs may still be purchased in the EU. Guzzonato et al. (2017) investigated 26 samples of toys and food-contact articles purchased from the European market, finding that ~1/3 of food-contact articles were bromine positive and around half of the toys examined exceeded LPCLs. Samsonek and Puype (2013) investigated the Br and BFR content of 30 black plastic kitchen utensils purchased from the European market, and reported a 30 % detection rate for Br. BDE-209 was the major BFR found in Br positive samples, with tetrabromobisphenol-A (TBBP-A) and decabromodiphenyl ethane (DBDPE) detected in some samples as well. Elsewhere, Chen et al. (2009) found PBDEs, DBDPE, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and polybrominated biphenyls (PBBs) in plastic toys purchased from Chinese market, while Ionas et al. (2014) found PBDEs and phosphate flame retardants (PFRs)

in toys from the European market. The Br concentrations measured by Samsonek and Puype (2013) ranged from not detected to 2,000 μg/g, while BFR concentrations measured by Chen et al. (2009) and Ionas et al. (2014) ranged from not detected to 5,000 μg/g, all of which were insufficient to impart flame retardancy, indicating these BFRs were not intentionally added into kitchen utensils or toys, and highly possibly came from recycled plastics. Considering the background above, this study seeks to augment significantly the database on the presence of BFRs in consumer goods by measuring Br (using a hand-held X-ray fluorescence (XRF) spectrometer) and a range of BFRs including PBDEs in both used and new plastic kitchen utensils from the UK. Concentrations of PBDEs and other BFRs in these utensils are compared with LPCL values, and for the first time, the potential for human exposure arising from consumer use of such utensils is assessed. This is assessed via examining BFR transfer from selected utensils to culinary oil during simulated cooking experiments and via modelling dermal uptake from handling utensils.

Given the above, the objectives of this study are to: 1) investigate the extent to which kitchen utensils from the UK market are contaminated by Br and BFRs; 2) evaluate the extent to which the XRF measurements of Br provide an accurate metric of BFR concentrations; and; 3) evaluate the potential for human exposure to BFRs as a result of using plastic kitchen utensils containing BFRs.

To achieve these objectives, we examined 96 kitchen utensils from the UK. As a first step, these were all screened for their Br content using hand-held XRF. Thirty of these utensils were then analysed for their concentrations of BFRs, including 8 polybrominated diphenyl ethers (PBDEs) (BDE-28, 47, 99, 100, 153, 154, 183 and 209), pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), BTBPE, bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and DBDPE. Ten representative utensils were then subjected to controlled experiments to study the transfer of BFRs from kitchen utensils to hot culinary oil.

2. Method and materials

2.1 Sampling

New utensils were purchased from retail outlets in Birmingham, UK between Dec 2015 and Jun 2016, while used utensils ≥ 5 years old were donated by University of Birmingham staff. All utensils were first screened for their Br content using a hand-held XRF spectrometer (Niton^{TM} XL3t GOLDD+ XRF Analyzer, Thermo Fisher Scientific). The platform on which utensils were placed for measurement was pre-cleaned with ultra-pure water and ethanol, and measured using XRF to ensure no background interference existed. Measurements of Br were taken at 3-5 randomly selected points on each utensil to minimize the impact of heterogeneity and the highest result was recorded. Utensils displaying a Br content > 100 μg/g (n=18), along with a further 12 utensils containing < 100 μg/g Br were selected for measurement of their

BFR content.

2.2 Chemicals

Native BDE-77 was used as the internal standard (IS) to quantify BDE-28, 47, 99, 100, as well as PBEB and EH-TBB; BDE-128 as internal standard for BDE-153, 154 and 183; ^{13}C-BTBPE for BTBPE; ^{13}C-BEH-TEBP for BEH-TEBP; and ^{13}C-BDE-209 for BDE-209 and DBDPE. A mixed IS solution of all the above mentioned internal standards (500 pg/μL) in iso-octane was prepared. 2,2',3,3',4,5-hexachlorobiphenyl (PCB-129) was used as a recovery determination standard (RDS) to determine the recovery of BDE-77, 128, ^{13}C-BTBPE, ^{13}C-BEH-TEBP, and ^{13}C-BDE-209. The RDS solution was prepared in iso-octane at a concentration of 250 pg/μL. All standards were purchased from Wellington Laboratories Inc. and all solvents used (acetone, hexane, iso-octane and methanol) were HPLC grade.

2.3 Pre-treatment of plastic samples

Plastic utensil samples were first cut into small pieces and then ground into a powder using a Fritsch Pulverisette 0 cryo-vibratory micro mill (Idar-Oberstein, Germany). This was achieved by adding the sample along with a 25 mm diameter stainless steel ball to the stainless steel grinding mortar (50 mL volume), cooled with liquid nitrogen. The cryogenically-cooled sample was then ground at a vibrational frequency of 30 Hz for 5 min and repeated 2-3 times. After 1 min vortexing with 10 mL hexane to achieve complete mixing, the resultant plastic powder was then extracted under 15 min

sonication and supernatant was then collected. The process of vortexing and ultrasonication were repeated for 2 more cycles and for the last extraction, the supernatant was left in contact with the sample overnight before collection to maximise recoveries. Combined extracts were reduced in volume to ~ 2 mL under a gentle stream of nitrogen gas, before mixing with 3-4 mL 98 % sulfuric acid. The hexane-acid mixture was then vortexed for 20 s followed by centrifugation at 2,000 g for 5 min. The supernatant was then collected. To ensure complete transfer, the residue was rinsed with hexane (2 mL) three times. The combined supernatant was then reduced to incipient dryness under a gentle stream of nitrogen gas. The final concentrate was re-dissolved in 200 μL PCB-129 RDS solution prior to analysis of PBDEs and NBFRs by GC-MS.

2.4 Experiments examining BFR transfer from utensil to culinary oil

Ten kitchen utensils shown to contain elevated concentrations of BFRs were subjected to experiments designed to mimic the process of cooking in oil. A small portion of kitchen utensil weighing ~0.05 g, ~ 5 mm × 4 mm × 2 mm was immersed in 0.5 mL olive oil in a test tube. The test tube was maintained at 160 ˚C for 15 min to simulate the cooking process and oil collected for analysis. After “cooking” each utensil, the experiment was repeated twice more using the same aliquot of the utensil to investigate the impact of repeated cooking in oil on BFR transfer efficiency. The collected oil samples were first diluted in 3~4 mL hexane, before added with 5~6 mL 98 % sulfuric acid. The hexane-acid mixture then underwent the same process describe in section 2.3, before dissolution in 200 μL PCB-129 RDS solution for analysis.

2.5 GC-MS Protocols

PBDEs and NBFRs were analysed by GC-MS in electron capture negative ionisation (ECNI) mode using the same method to our previous study (Kuang et al., 2016). For some plastic kitchen utensil samples with extremely high BDE-209 concentrations and the corresponding oil extracts, recoveries of ^{13}C-BDE-209 could reach 400 % ~ 1000 %, which exceeded the normal range. The reason is that when intensity is too high, the overlap between response peaks of ions on mass spectrometer could not be neglected, especially when peaks are very close. In this case, response of ^{13}C-BDE-209 (m/z 492.6, 494.6) was severely interfered by the extremely high response of BDE-209 (m/z 486.6, 488.6), so an exceptional high "apparent recovery" was observed. To address this issue, we re-injected affected samples in electron ionisation (EI) mode and satisfactory recoveries were obtained, as interference between the quantifying ions used for BDE-209 (m/z 799.4, 801.4) and ^{13}C-BDE-209 (809.4, 811.4) was weaker given the greater difference in m/z values.

2.6 QA/QC

For measurement of Br, the XRF analyzer was calibrated regularly using manufacturer-supplied solid disk standards. And for BFR measurement, three blank oil samples were analysed along with experimental samples. Satisfactory results were obtained with recoveries of internal standards ranging from 60 %~130 % (Table S1) with all native compounds not detected, except BDE-209 (Table S2). Concentrations of BDE-209 in

oil samples were corrected for blank contamination by subtracting the mean value detected in blanks. Satisfactory recoveries of 70 %~130 % were obtained for both kitchen utensil plastic (Table S3) and cooking experiment oil (Table S4) samples.

In addition, to evaluate BFR losses during cooking experiments, a matrix spike experiment was conducted 5 times by spiking known amounts of all target compounds and internal standards into blank oil samples before the cooking experiment. These matrix spike samples were then analysed and recoveries of all compounds calculated (Table S5). Recoveries of all compounds showed good performance ranging from 70 % to 170 %, and recoveries of target compound showed consistent deviation with coordinating internal standard recoveries (Table S5), ensuring a precise quantification.

3. Results and discussion

3.1 Bromine content of kitchen utensils

Table 1 reports Br concentrations in the utensil samples analysed using hand-held XRF. Of the 96 samples analysed, 69 were reported by the donors to be 5 years or older, 6 were aged 2 years, while 21 were purchased for this study between December 2015 and July 2016. It should be noted that “age” in this study refers only to the donor-reported date of purchase to the nearest year. It is important to note not only the uncertainty associated with such self-reported data, but that the date of purchase does not equate to the date of manufacture but to the date of availability on the market. Notwithstanding

this, for convenience, we use "age" as an abbreviation of "date of availability on the market" from herein. Table 1 also lists the utensil type, with the main categories being: spoons (n=33), spatulas (n=18) and ladles (n=12). Of the 27 utensils aged < 5 years, only 1 (3.7 %) contained >100 μg Br/g, 2 (7.4 %) contained ~ 5 μg Br/g, with the remaining 24 (88.9 %) containing <3 μg Br/g. In contrast, for utensils aged ≥5 years, 17 (24.6 %) contained > 100 μg Br/g, 13 (18.9 %) contained between 5 and 100 μg Br/g, and 34 (49.3 %) containing <3 μg Br/g. Given this apparent dichotomy between "older" and "newer" utensils, we evaluated the significance of this using non-parametric statistical tests as our data did not display a normal distribution. We first conducted a Mann-Whitney rank test to compare Br concentrations between the two age groups. This revealed Br concentrations to be significantly greater in utensils ≥5 years old ($p=0.016$). This was consistent with a Spearman correlation analysis which showed utensil age and Br content to be significantly and positively correlated ($r=0.237$, $p=0.020$).

Table 1 Bromine Concentrations (μg/g) in Kitchen Utensils

Sample #[a]	Utensil type	Br content, μg/g	Date of purchase[b]	Age, years
P1	Solid spoon	<3	2015	New
P2	Thermos cup lid	<3	2015	New
P3	Thermos cup lid	180	2015	New
P4	Thermos cup lid	<3	2015	New
P5	Thermos cup lid	<3	2015	New
P6	Food package	<3	2015	New
P7	Food package	<3	2015	New
P8	Food package	<3	2015	New

P9	Food package	<3	2015	New
P10	Ladle	350	2008	8
P11	slotted spatula	300	2008	8
P12	spaghetti server	<3	2013	2
P13	Solid spatula	<3	2013	2
P14	solid spatula	<3	2013	2
P15	Food clip	<3	2013	2
P16	slotted spoon	100	2009	7
P17	Solid spoon	600	2009	7
P18	Solid Spoon	6,000	2006	10
P19	solid spoon (grip)	200	Before 2011	>5
P20	Ladle	120	2001	15
P21	slotted spatula	400	2001	15
P22	solid spoon (grip)	150	2006	10
P23	Masher	90	2009	7
P24	solid spoon (grip)	170	2006	10
P25	slotted spoon (grip)	150	2006	10
P26	Ladle (grip)	140	2006	10
P27	slotted spoon	100	2009	7
P28	slotted spoon (grip)	170	2002	14
P29	Scissors	130	2002	14
P30	Scissors	4,000	2002	14
	slotted spatula	<3	2009	7
	Solid spatula	<3	2009	7
	Ladle	<3	2009	7
	slotted spatula	<3	2009	7
	slotted spoon	40	Before 2011	>5
	Solid Spoon	<3	2007	9
	slotted spoon	<3	2001	15
	Solid Spoon	<3	2016	New
	Ladle	<3	2016	New
	slotted spatula	<3	2016	New
	Solid spoon	30	2009	7
	Solid spoon	<3	2009	7
	Masher	<3	2008	8
	slotted spatula	50	2008	8
	slotted spatula	<3	2008	8
	spaghetti server	<3	2008	8
	Solid spoon	<3	2008	8
	Ladle	<3	2008	8
	slotted spoon	85	2006	10
	skimming spoon	<3	2006	10

Masher	<3	2006	10
Not recorded	<3	2006	10
Not recorded	<3	2006	10
Not recorded	<3	2006	10
Not recorded	<3	2006	10
Not recorded	<3	2006	10
Cut board	10	2009	7
Spatula	20	2009	7
Ladle	<3	2009	7
Solid spoon	<3	2006	New
slotted spatula	<3	1996	20
Solid spoon	<3	1996	20
Ladle	<3	1996	20
slotted spoon	20	1996	20
Masher	<3	1996	20
Spatula	<3	1998	18
dotted spoon	<3	1998	18
Masher	<3	1998	18
Spatula	10	2002	14
Masher	<3	2002	14
Scissors	60	2002	14
Whisk	<3	2014	2
Masher	<3	2014	2
spaghetti server	10	2001	15
slotted spatula	<3	2001	15
Ladle	<3	2001	15
slotted spoon	<3	2001	15
Masher	30	2001	15
solid spoon	<3	2016	New
slotted spatula	<3	2016	New
Masher	<3	2016	New
Ladle	5	2016	New
slotted spoon	<3	2016	New
slotted spoon	<3	2016	New
slotted spoon	7	2016	New
Scissors	<3	2016	New
solid spoon	<3	2011	5
slotted spatula	<3	2011	5
Ladle	<3	2011	5
Ladle	8	2011	5
Fork	<3	2011	5
Spatula	<3	Before 2011	>5

	Solid spoon	50	Before 2011	>5
	Solid spoon	<3	Before 2011	>5
	Slotted spoon	60	Before 2011	>5
	Skimming spoon	<3	Before 2011	>5

[a]Sample # refers to sample analysed for BFR content – see Table 2. Samples not assigned a number were not analysed for their BFR content

[b]Owner's estimate of purchase date

3.2 BFR concentrations in kitchen utensils

Based on the Br concentration data, those utensils containing >100 μg Br/g (n=18) were subjected to GC-MS determination of their BFR content, together with 12 utensils containing <100 μg Br/g to provide context. These 30 samples are numbered 1~30 in Table 1.

Table 2 shows that utensils with high Br content (>100 μg/g) display a higher BFR concentration than those indicated by XRF to contain <100 μg/g Br. We tested the statistical significance of this relationship using non-parametric tests as our data did not display a normal distribution. Specifically, a Mann-Whitney rank test showed the difference to be statistically significant ($p=0.007$), with the positive relationship between Br and BFR concentrations confirmed by Spearman correlation analysis ($r=0.493$, $p=0.006$). However, more detailed inspection of Table 2 reveals there is substantial discrepancy between our BFR and Br data for the same samples. To be explicit, our ΣBFR measurements are always lower than the corresponding Br measurements – and in some cases substantially so, for example, sample 18 contained 6,000 μg Br/g, but displayed a ΣBFR concentration of 0.6 μg/g. This is most likely due

238 to some compounds not included in our list of target BFRs for example TBBP-A, and/or
239 low extraction efficiency for BFRs using our method.
240
241 We first tested the hypothesis that the discrepancy between Br and ΣBFR was because
242 the former was due to the presence of one or more BFRs not targeted by our GC-MS
243 analyses. To do so, we studied sample 18 in more detail. Tentative support for this
244 explanation is supplied by the observation of several unidentified peaks on the m/z 79
245 and 81 traces in the GC mass chromatogram for sample 18. Hence, following solvent
246 exchange from iso-octane to methanol we re-analysed this sample on a LC-high
247 resolution MS system (UPLC-Orbitrap-MS, Thermo Fisher Scientific, Bremen,
248 Germany) in an attempt to identify BFRs not quantified via our GC-MS method such
249 as TBBP-A or HBCDD. However, this did not provide an obvious explanation for the
250 discrepancy, and thus incomplete extraction efficiency can not be ruled out as a cause
251 in this instance at least. To avoid dissolving the plastic during BFR extraction and thus
252 expedite more rapid analysis, a low polarity aliphatic solvent (hexane) was chosen for
253 extraction. We note that other studies have used different solvents (Allen et al. (2008),
254 Aldrian et al. (2015) used toluene, and Gallen et al. (2014) used dichloromethane), and
255 thus our BFR measurements may be underestimates of the true value. Also, as TBBP-
256 A is a reactive BFR which binds more firmly with polymers than additive BFRs like
257 PBDEs, hexane may be less effective at extracting it from polymers, leading it to be not
258 detected even in our LC-high resolution MS screening.

Table 2 BFR concentrations in kitchen utensils, ng/g

Sample #	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs, μg/g	Br, μg/g
P1	<0.2	0.2	6.3	7.0	42	<0.2	7.8	16	36	530	<0.2	1,100	72	1.8	<3
P2	<0.2	<0.2	37.4	6.9	26	<0.2	1.3	2.7	14	78	<0.2	620	16	0.8	<3
P3	<0.2	<0.2	110	36	150	<0.2	12	22	100	1,200	<0.2	2,500	23	4.1	180
P4	<0.2	<0.2	0.5	<0.2	1.4	<0.2	0.4	1.1	16	3.8	27	260	<9.2	0.3	<3
P5	<0.2	<0.2	1.2	0.3	2.3	<0.2	<0.4	0.5	3.9	5.4	<0.2	37	<9.2	0.1	<3
P6	<0.2	0.2	<0.2	0.5	4.6	0.5	<0.4	0.7	<1.0	<1.0	150	14	12	0.2	<3
P7	<0.2	<0.2	<0.2	<0.2	1.3	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<0.01	<3
P8	<0.2	<0.2	<0.2	<0.2	1.1	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<0.01	<3
P9	<0.2	<0.2	<0.2	<0.2	0.7	<0.2	<0.4	1.1	4.4	8.4	<0.2	340	290	0.6	<3
P10	130	<0.2	360	68	330	<0.2	48	90	330	1,400	<0.2	17,000	<9.2	20	350
P11	100	<0.2	210	82	93	<0.2	4.6	21	36	60	<0.2	2,200	<9.2	2.8	300
P12	<0.2	<0.2	7.4	1.3	7.7	<0.2	0.9	1.8	14	<1.0	<0.2	1300	<9.2	1.4	<3
P13	0.6	<0.2	25	4.8	30	<0.2	2.9	6.2	34	1.1	<0.2	2,500	<9.2	2.6	<3
P14	<0.2	<0.2	11	4.1	21	<0.2	3.6	5.6	24	<1.0	<0.2	1,200	<9.2	1.3	<3
P15	<0.2	<0.2	38	9.9	49	<0.2	5.4	9.1	46	<1.0	<0.2	2,100	<9.2	2.3	<3
P16	<0.2	<0.2	9.5	<0.2	10	<0.2	8.9	36	27	<1.0	6.8	660	58	0.8	100
P17	<0.2	<0.2	36	34	180	<0.2	1,000	1,800	1,600	<1.0	<0.2	1,000	340	6.0	600
P18	<0.2	1.1	15	82	100	<0.2	21	14	23	210	<0.2	140	<9.2	0.6	6,000
P19	<0.2	<0.2	8.8	1.8	10	<0.2	1.3	2.3	8.8	<1.0	350	260	110	0.8	200
P20	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	81	<9.2	0.1	120
P21	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	17	220	<9.2	0.2	400

P22	<0.2	4.0	57	30	240	<0.2	15	25	130	<1.0	46	110,000	5,500	120	150
P23	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	78	<9.2	0.1	90
P24	120	11	1,000	110	530	900	40	170	139	280	30,000	8,100	5,200	47	170
P25	79	14	1,000	110	370	950	23	110	66	180	25,000	1,900	3,700	34	150
P26	15	8.4	970	43	130	830	5.2	29	49	200	22,000	2,700	7,200	34	140
P27	<0.2	<0.2	<0.2	<0.2	9.0	<0.2	3.7	14	45	35	10	2,500	280	2.9	100
P28	64	8.3	82	30	260	<0.2	30	560	1,100	1,500	140	81,000	5,700	90	170
P29	<0.2	<0.2	10	0.2	12	<0.2	7.6	1,600	180	18,000	5.7	3,200	420	23	130
P30	<0.2	33	<0.2	<0.2	12	<0.2	210	120,000	13,000	1,100,000	<0.2	140,000	1,900	1,400	4,000

Given our observation that Br concentrations were significantly higher in samples ≥5 years old, than in younger utensils, we examined our data for similar age-related differences in ΣBFR concentrations, again using non-parametric tests in accordance with the distribution of our data. A Mann-Whitney rank test found significantly ($p=0.014$) higher ΣBFR concentrations in utensils ≥5 years old than in those <5 years in age. This was consistent with Spearman correlation analysis ($r=0.501$, $p=0.005$) that showed a positive relationship between BFR concentration and utensil age. These findings are likely attributable to two main factors: (1) the introduction in restrictions in use of PBDEs in the mid-2000s onwards, and (2) the more recent introduction of restrictions on the recycling of BFR-treated plastics.

In terms of the BFR distribution pattern, BDE-209 was the most abundant BFR detected and in 17 out of 30 samples (56.7 %), BDE-209 accounted for more than 70 % of ΣBFR. This is consistent with the fact that BDE-209 is mainly used in hard plastics like polyamide (Arias, 2001 cited by Alaee et al., 2003) which is used widely in kitchen utensils. Aside of this general predominance of BDE-209 however, the BFR pattern varied widely between individual utensils. For example, while P22, P23 and P24, which came from the same donor and were purchased at the same time, all contained a high percentage of BEH-TEBP (65 % ~ 75 % ΣBFR); P10 and P11 (donated by the same individual and purchased at the same time) contained substantial contributions of less brominated PBDEs like BDE-47 and -99; while P29 and P30 (which were the two handles of the same pair of scissors) were dominated (~80 % ΣBFR) by BTBPE. These

3 examples indicate that as well as age, production batch may be an important additional factor influencing the Br and BFR concentration and pattern.

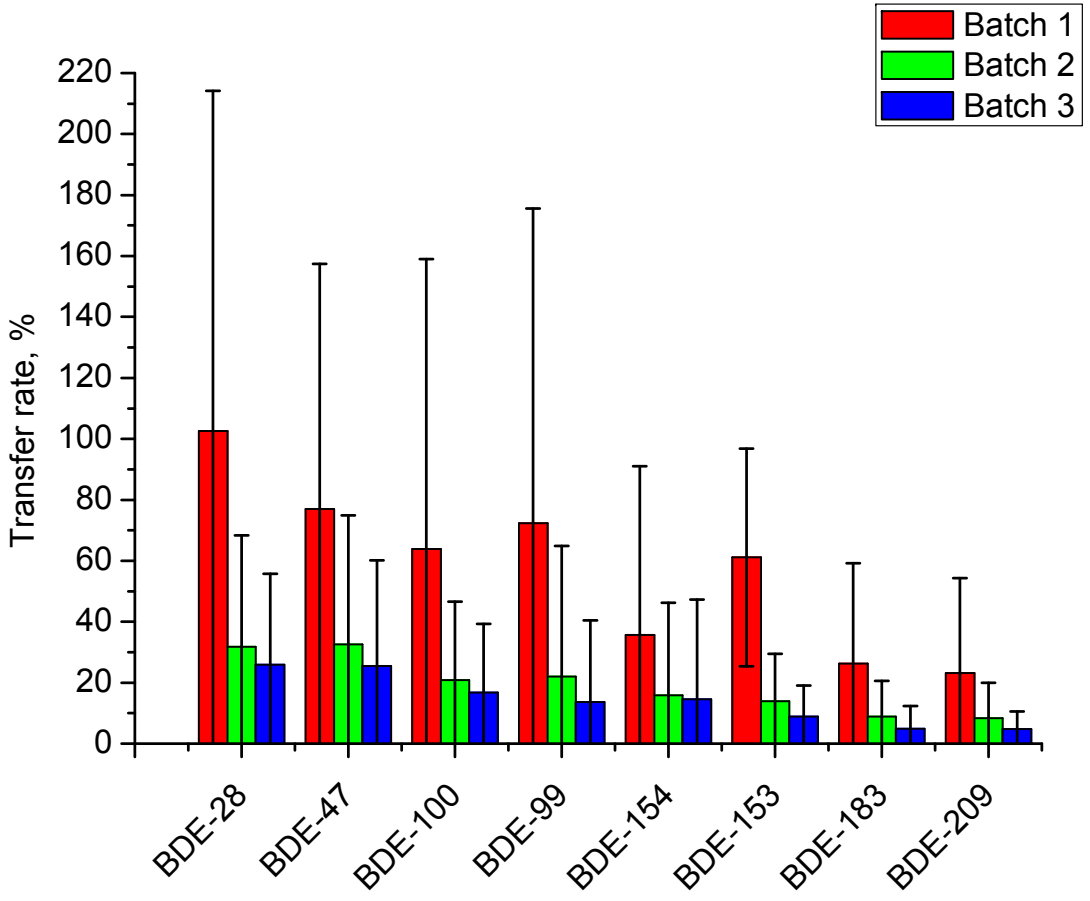
3.3 BFR transfer from utensil to oil in simulated cooking process

Table 3, as well as Figures 1 and 2 show the transfer of individual BFRs and ΣBFR from the aliquots of utensils subjected to the simulated cooking experiments. The percentage transfer in Figure 1 and 2 was calculated as $r = m_{BFR-oil} / (c_{BFR-plastic} \times m_{plastic}) \times 100\%$, where $m_{BFR-oil}$ is the mass of BFR extracted by oil, measured by GC-MS, $c_{BFR-plastic}$ is BFR concentration in plastic utensils and $m_{plastic}$ is mass of plastic used in cooking experiment. Transfer was substantial for all compounds, especially during the 1st cooking exposure (batch 1), ranging from 20 % to 100 %. The extent of transfer decreased in the order batch 1>batch 2>batch 3 and with increasing degree of bromination for PBDEs. In particular, while BDE-209 was abundant in most utensils, its transfer to oil was negligible in 6 of 10 cases. However, for samples P22, P24, P28 and P30 that contained BDE-209 concentrations in the range 10~100 μg/g, more substantial transfer was observed. The generally lower transfer efficiency of BDE-209 in our experiments is likely due to a combination of lower solubility in oil of BDE-209 compared to other BFRs, alongside greater binding of BDE-209 to plastic.

In some cases, the transfer exceeded 100 %. This may be attributable to a number of factors, namely: (a) inhomogeneous distribution of BFRs in the kitchen utensils which

could result in the BFR content of the aliquot of the utensil subjected to cooking differing from that in the aliquot used to determine BFR concentration; (b) that hot oil may be a more effective solvent for extracting BFRs from kitchen utensils than hexane; and (c) where transfers >100 % are observed for lower PBDEs, this may indicate some degree of thermal debromination of higher homologues such as BDE-209.

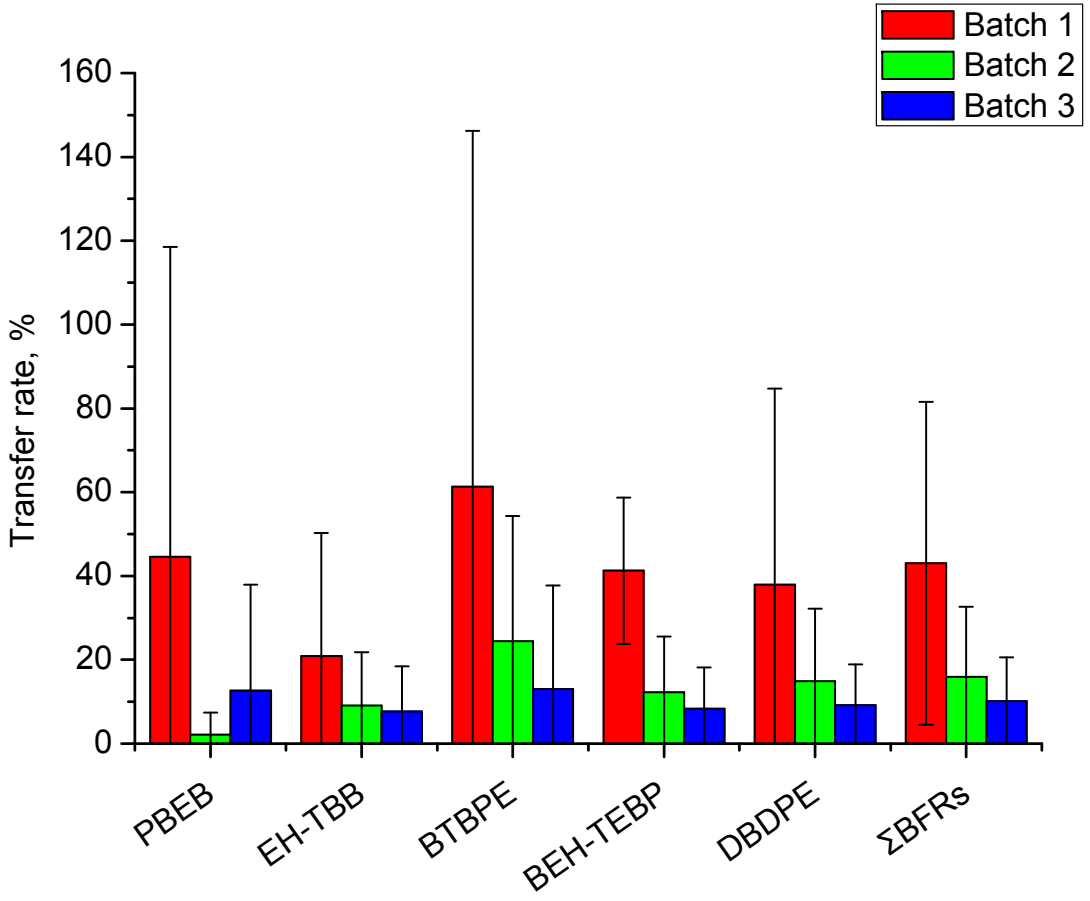
310



311

312 **Figure 1 Average percentage transfer of PBDEs from kitchen utensils in simulated cooking experiments (y-error bar represents σ_{n-1})**

313



314

315 **Figure 2 Average percentage transfer of NBFRs and ΣBFRs from kitchen utensils in simulated cooking experiments (y-error bar**

316 **represents σ_{n-1})**

317 **Table 3 BFR transfer from kitchen utensils (ng BFR/g plastic[a]) in simulated cooking experiments**

Sample	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs
P1	<0.2	0.2	6.3	7.0	42	<0.2	7.8	16	36	530	<0.2	1,100	72	1,800
Batch1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	14	<1.0	100	<0.2	62	<9.2	170
Batch2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<16
Batch3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<16
P3	<0.2	<0.2	110	35.6	150	<0.2	12	22	100	1,200	<0.2	2,500	23	4,100
Batch1	<0.2	<0.2	<0.2	<0.2	13	<0.2	<0.4	7.4	<1.0	<1.0	<0.2	<2.6	<9.2	21
Batch2	<0.2	<0.2	5.8	<0.2	0.3	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	11	<9.2	17
Batch3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	<16
P10	130	<0.2	360	68	330	<0.2	48	90	330	1,400	<0.2	17,000	<9.2	20,000
Batch1	270	2.0	410	170	170	<0.2	<0.4	21	<1.0	92	<0.2	4.8	<9.2	1,100
Batch2	86	1.2	110	41	41	<0.2	<0.4	5.2	<1.0	<1.0	<0.2	3.6	<9.2	290
Batch3	68	1.3	85	26	30	<0.2	<0.4	4.0	<1.0	20	<0.2	10	<9.2	250
P11	100	<0.2	210	81	93	<0.2	4.6	21	36	60	<0.2	2,200	<9.2	2,800
Batch1	200	2.3	320	140	160	<0.2	<0.4	21	<1.0	150	0.6	4.6	<9.2	1,000
Batch2	63	0.5	57	14	21	<0.2	<0.4	2.3	<1.0	35	<0.2	<2.6	<9.2	190
Batch3	53	0.9	33	6.1	12	<0.2	<0.4	<0.4	<1.0	<1.0	<0.2	<2.6	<9.2	100
P17	<0.2	<0.2	36	34	180	<0.2	1,000	1,800	1,600	<1.0	<0.2	990	250	6,000
Batch1	<0.2	<0.2	12	<0.2	59	<0.2	210	560	1,300	<1.0	<0.2	41	<9.2	2,200
Batch2	<0.2	<0.2	4.9	14	16	<0.2	54	140	310	I[b]	<0.2	5.0	<9.2	740

Batch3	<0.2	<0.2	3.5	21	19	<0.2	86	180	330	I[b]	<0.2	<2.6	<9.2	920
P18	<0.2	1.1	15	82	100	<0.2	21	14	23	210	<0.2	140	<9.2	600
Batch1	<0.2	2.3	36	140	340	<0.2	38	13	<1.0	100	<0.2	8.4	<9.2	670
Batch2	<0.2	<0.2	19	52	140	<0.2	20	4.8	<1.0	52	<0.2	<2.6	<9.2	290
Batch3	<0.2	<0.2	12	33	91	<0.2	22	4.3	<1.0	30	<0.2	2.7	<9.2	200
P22	<0.2	4.0	57	30	249	<0.2	15	25	130	<1.0	46	110,000	5,500	120,000
Batch1	<0.2	<0.2	11	<0.2	130	<0.2	4.1	610	59	270	17	100,000	6,400	110,000
Batch2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.4	240	21	390	<0.2	34,000	1,900	36,000
Batch3	<0.2	0.4	5.7	<0.2	<0.2	<0.2	<0.4	94	<1.0	390	<0.2	16,000	1,200	18,000
P24	120	11	1,000	110	530	900	40	170	130	280	30,000	8,100	5,200	47,000
Batch1	<0.2	4.9	990	55	230	370	15	61	43	220	7,800	3,400	3,300	17,000
Batch2	<0.2	<0.2	810	29	78	160	4.5	16	10	220	3,100	1,000	1,200	6,700
Batch3	<0.2	<0.2	920	22	53	140	2.9	7.9	5.3	200	1,800	570	820	4,600
P28	64	8.3	82	30	260	<0.2	30	560	1,100	1, 500	140	81,000	5,700	90,000
Batch1	7.7	3.3	34	<0.2	77	4.5	16	620	870	1,100	82	48,000	4,300	55,000
Batch2	<0.2	<0.2	9.8	<0.2	53	<0.2	9.4	260	380	430	36	21,000	2,200	25,000
Batch3	<0.2	5.7	<0.2	<0.2	14	<0.2	2.7	100	150	170	26	10,000	1,100	12,000
P30	<0.2	33	<0.2	<0.2	12	<0.2	210	120,000	13,000	1,100,000	<0.2	140,000	1,900	1,400,000
Batch1	<0.2	7.2	<0.2	<0.2	0.2	<0.2	66	39,000	2,900	100,000	<0.2	32,000	220	180,000
Batch2	<0.2	4.6	<0.2	<0.2	<0.2	<0.2	25	12,000	1,200	56,000	<0.2	15,000	120	85,000
Batch3	<0.2	3.0	<0.2	<0.2	<0.2	<0.2	30	13,000	1,200	51,000	<0.2	15,000	140	81,000
Batch4	<0.2	2.7	<0.2	<0.2	<0.2	<0.2	24	7,400	980	40,000	0.2	13,000	120	62,000

[a]Amount of BFRs extracted in oil (Batch 1, 2, 3) is expressed as $m_{BFR\text{-}oil}/m_{plastic}$, i.e. mass of BFR detected in each olive oil extract divided by the mass of plastic tested.

[b]Interference prevented quantification.

3.4 Preliminary exposure assessment

We considered two pathways via which human exposure to BFRs in kitchen utensils may occur: (a) transfer to food when cooking, and (b) transfer through dermal contact. The following are preliminary evaluations of the likely magnitude of human exposure via such pathways.

3.4.1 Exposure via cooking

Exposure via cooking was estimated based on the results of our simulated cooking experiments – note that as some utensils for which BFR concentrations were determined were unlikely to come into contact with hot oil during use (e.g. scissors), these utensils (P2-P5, P6-P9, plus P29 and 30) were excluded from our estimations. To estimate exposure resulting from contact between the utensil and hot oil and subsequent ingestion of the oil we made several assumptions. The first of these are that: 1) over the useful "lifetime" of every 200 mL oil (assumed 1 week) used for deep frying, the utensil is in contact with oil at 160 ^{o}C for a total period over that week of 15 min; and 2) the extent of BFR transfer is proportional to the specific surface area (i.e. surface area per unit utensil volume) of the utensil in contact with oil. We further assumed that the utensil dimensions likely to come into contact with oil during cooking are 10 cm × 8 cm × 2 mm (equivalent to that of a typical spatula), yielding a specific surface area of 10 cm^{-1}. This compares quite closely with the specific surface area of 19 cm^{-1} of the 5 mm × 4 mm × 2 mm plastic cuboids used in our cooking experiments. Based on these

assumptions, we estimated the amount of BFR transferred from kitchen utensils to hot oil during cooking via the equation below.

$$c_{BFR-oil} = \left(c_{BFR-utensil} \times m_{utensil} \times r_{real}\right) / V_{oil} \quad (1)$$

Where:

$c_{BFR-oil}$ is BFR concentration transferred to hot cooking oil (ng/mL);

$c_{BFR-utensil}$ is BFR concentration (ng/g) in kitchen utensils coming into contact with hot oil;

$m_{utensil}$ is mass of utensil contact with hot oil when cooking, whose size is 10 cm × 8 cm × 2 mm, and for density, a value of 1.4 g/cm^3 was applied based on the average measured value for several utensils on this study. So $m_{utensil} = V_{utensil} \times \rho_{utensil}$ = 10 cm × 8 cm × 2 mm ×1.4 g/cm^3 = 22.4 g;

r_{real} is BFR transfer rate (unitless) in real-life scenario and is calculated based on transfer rate obtained in cooking experiment (r_{exp}), specific surface area of utensil in experiment (A_{exp}) and in real-life scenario (A_{real}):

$$r_{real} = \frac{A_{real}}{A_{exp}} \times r_{exp} = \frac{10\ \text{cm}^{-1}}{19\ \text{cm}^{-1}} \times r_{exp} = 0.53 r_{exp};$$

V_{oil} is volume of oil involved in cooking which is assumed to be 200 mL.

Thus,

$$c_{BFR-oil} = \frac{c_{BFR-utensil} \times 22.4\ \text{g} \times 0.53 r_{exp}}{200\text{mL}} = 0.059 c_{BFR-utensil} r_{exp}\ \text{ng/mL} \quad (2)$$

According to 2015-2020 dietary guidelines for Americans (U.S. DHHS and DA, 2015), the recommended daily oil intake for an adult is 27 g. We assume that deep fried oil accounts for 15 % of daily oil intake on average, and that as noted on the food information label of the oil used, the density of olive oil was 0.9 g/mL; thus the daily BFR exposure amount is:

$$\begin{aligned} E_{BFR-oil} &= 15\% \times c_{BFR-oil} \times \frac{27 \text{ g/day}}{0.9 \text{ g/mL}} \\ &= 15\% \times 0.059 c_{BFR-utensil} r_{exp} \frac{\text{ng}}{\text{mL}} \times \frac{27 \text{ g/day}}{0.9 \text{ g/mL}} \\ &= 0.27 c_{BFR-utensil} r_{exp} \text{ ng/day} \end{aligned} \quad (3)$$

Here we use median and maximum concentration of the 20 utensils (P1, P10~P28) as the value of $c_{BFR-utensil}$ for median and high exposure scenario estimates, and the mean transfer rate of the 3 batches in the cooking experiments is used for the value of r_{exp}. The resultant exposure estimates are shown in Table 4.

Table 4 BFR exposure (ng/day) via cooking in median and high exposure scenarios[a]

	BDE-28	PBEB	BDE-47	BDE-100	BDE-99	EH-TBB	BDE-154	BDE-153	BDE-183	BTBPE	BEH-TEBP	BDE-209	DBDPE	ΣBFRs
r_{exp}	53.4%	19.8%	45.0%	37.6%	40.0%	12.5%	22.3%	27.9%	13.2%	32.9%	20.6%	11.7%	20.7%	-
Median	NA[b]	NA[b]	2.4	0.8	4.4	NA[b]	0.3	1.1	1.3	0.1	NA[b]	52.2	1.7	64.2
High	18.7	0.7	125.2	10.3	51.0	31.6	58.2	135.7	55.9	130.6	1,651.4	3,545.0	393.0	6,207.3

[a]low exposure scenario was not calculated because minimum concentrations of all BFRs but BDE-209 were not detected; median and high exposure scenarios assume transfer from a utensil containing the median and maximum values of $c_{BFR-utensil}$ respectively;

[b]not available due to a not detected concentration.

As shown in Table 4, daily exposure to total BFRs are ~60 ng and ~6,000 ng under median and high scenarios, respectively; while those for ΣBDEs are ~60 ng and 4,000 ng respectively. To place these exposure estimates into context, Besis and Samara (2012) reviewed daily intake of PBDEs via different exposure pathways in different countries, and found that dust ingestion could amount to up to 400 ng/day intake in the US and the UK. Intake in other countries was lower, ranging from 50 to 200 ng/day. Dietary intake, as another important exposure pathway, ranged from 50 to 75 ng/day according to Besis's review. Harrad et al. (2004) investigated concentrations of tetra-hexa BDEs in UK duplicate diet samples and estimated dietary exposure of 90 ng/day for ΣPBDEs (tetra-to hexa-BDEs only). D'Silva et al. (2006) investigated concentrations of 17 PBDEs in typical UK diet composite samples in 2003, and the daily dietary exposure for tri- to hepta-BDEs and BDE-209 were estimated to be 80 ng/day and 270 ng/day, respectively. For NBFRs, Tao et al. (2017) detected several NBFRs including EH-TBB, BEH-TEBP, BTBPE, DBPDE and tetrabromoethylcyclohexane (DBE-DBCH) in UK food samples, estimating the average total daily dietary exposure to the sum of these NBFRs for adults was 90 ng/day. This compares with the median and high-end estimates in this study of ~2 and ~2,000 ng/day. To place our exposure estimates into context against non-dietary exposure, Harrad et al. (2008) estimated indoor dust ingestion of PBDEs, DBDPE and BTBPE, and the median exposure for UK adult was about 200 ng/day. Ni et al. (2013) estimated PBDE exposure via indoor dust ingestion in different cities of China, the median exposure for adult ranged from 20 to 100 ng/day.

399 Compared with estimates of exposure via other pathways from by previous studies,
400 exposure via cooking using BFR-containing utensils is not negligible. Moreover,
401 although the transfer rate of BDE-209 during cooking is not high, it still accounts for
402 the largest proportion (80 %) of exposure via cooking due to its high concentration in
403 utensils.
404
405 It is important to emphasise the preliminary nature of our assessment of dietary
406 exposure arising from using BFR-containing utensils. Our simulated cooking
407 experiments involved deep frying, which is likely a worst-case scenario with respect to
408 BFR extraction. Moreover, our estimate of oil-utensil contact occurring for 15 minutes
409 over 1 week is subject to considerable uncertainty and will vary considerably between
410 households, along with the frequency with which individuals will consume deep-fried
411 food. Finally, we focused only on those utensils displaying elevated BFR concentrations,
412 with our high-end exposure estimates based on the most contaminated utensil; thus our
413 high-end estimates are likely a worst-case scenario, with our median estimates more
414 representative of exposure at the population level. Balanced against this, it is not
415 unreasonable to assume that utensils will have contained higher BFR concentrations
416 when new and thus greater BFR transfer will have occurred earlier in the life of some
417 of the older utensils studied here. On the whole therefore, we consider our estimates a
418 reasonable first-level evaluation, and that they provide evidence to suggest that further
419 investigation of the potential for human exposure arising from use of such utensils is

420 warranted.

421 **3.4.2 Dermal exposure**

422 Considering the high BFR concentration not only in the main body but also in the grip
423 of kitchen utensils, exposure via dermal contact is of concern. Dermal uptake is a
424 complex process involving two major steps. First, the transfer of BFRs from the plastic
425 polymer to the skin surface film liquid (i.e. becomes bioaccessible). Second, the
426 penetration of the skin barrier to reach the blood circulation (i.e. becomes bioavailable)
427 (Abdallah et al., 2015). With the exception of HBCDDs (Pawar et al., 2017), an
428 extensive survey of the literature revealed no available data on the dermal
429 bioaccessibility of BFRs. For the second process, Abdallah et al. (2015) reported on the
430 dermal uptake rates of mono to deca BDEs over a 24 h exposure period. Therefore, our
431 exposure model adopts a conservative approach with the assumption of 100 %
432 bioaccessibility of PBDEs (*in the absence of relevant data*), and data from Abdallah et
433 al. (2015) were applied for estimation of bioavailability. Daily exposure (ng/day) via
434 dermal contact was calculated by the equation below.

435 $$\boldsymbol{E = C \times SA \times F \times EF} \quad (4)$$

436 where E is daily dermal exposure (ng/day), C is the concentration of BFRs in the
437 utensil (ng/cm^2), SA is the skin surface area exposed (cm^2), F is the fraction absorbed
438 by the skin (unitless), EF is the fraction of time in contact with the item (day^{-1}).

439

440 To transfer BFR concentration in ng/g to concentration per surface area, a 0.5 mm

441 depth (*h*) plastic from the surface of the utensil was assumed. For utensil density
442 ($\rho_{utensil}$) a value of 1.4 g/cm^3 was applied as indicated in section 3.4.1. So
443 $C\ (area) = h \times \rho_{utensil} \times C\ (mass) = 0.05\ cm \times 1.4\ g/cm^3 \times C\ (mass) = 0.07\ C\ (mass)$.
444
445 For the exposure area, we used data from the US EPA exposure factors handbook (U.S.
446 EPA, 2011) stating the average surface area of an adult hand is 1070 cm^2 for male and
447 890 cm^2 for a female. The average area of a single palm was estimated as 1/2 × 1/2 ×
448 (1070+890)/2 cm^2 = 245 cm^2. Considering that not the whole palm will contact with
449 kitchen utensils upon handling, a 75 % coefficient was assumed resulting in an exposed
450 skin area (*SA*) of 184 cm^2. Finally, parameters F and EF were obtained from Abdallah
451 et al. (2015), who measured various absorbed fraction of PBDEs at different exposure
452 times from 15 min to 24 h.
453
454 Over a daily contact time of 15 min, no dermal uptake was observed for any PBDEs
455 which is consistent with the "lag time" reported by Abdallah et al. (2015) for the studied
456 compounds. Lag time is defined as the time required by a specific chemical from its
457 initial contact with the skin surface to reach the systemic circulation. Low dermal
458 uptake was observed when the contact time was prolonged to 0.5 h and 1 h, except for
459 higher brominated BDEs (Table 5).
460
461

462 Table 5 PBDE exposure (ng/day) via dermal contact in median and high scenarios[a]

	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣPBDEs
F (0.5 h)[b]	0.07%	0.04%	-[c]	-	-	-	-	-	
Median	NA[d]	0.05	-	-	-	-	-	-	0.05
High	1.19	5.41	-	-	-	-	-	-	6.60
F (1 h)	0.20%	0.13%	0.08%	0.08%	0.03%	0.03%	-	-	
Median	NA	0.17	0.03	0.17	0.02	0.04	-	-	0.43
High	3.40	17.58	1.18	5.51	3.85	456.43	-	-	487.95

463 [a]exposure in low scenario was not calculated because minimum concentrations of all
464 BFRs but BDE-209 were not detected; median and high exposure scenarios were
465 calculated based on median and maximum BFR concentration of P1~P30;
466 [b]data obtained from Abdallah et al. (2015);
467 [c]no transfer observed;
468 [d]not available due to a not detected concentration.

469

470 Our results indicate that human uptake of PBDEs via dermal contact with cooking
471 utensils is much lower than our intake estimates based on cooking and other pathways
472 (section 3.4.1). The exception to this is for BDE-153 in the 1 h contact high-end
473 scenario, due to the extremely high BDE-153 concentration in scissor sample P30. This
474 could be attributed to the limited daily contact time with utensils, and low penetration
475 efficiency into skin, especially for BDE-209 whose concentration was the highest.
476 Therefore, our findings suggest when using BFR-contaminated kitchen utensils,
477 exposure is dominated by utensil-oil transfer, rather than utensil-skin transfer.

478 # 4. Conclusions

479 ● 34 % of plastic kitchen utensils analysed in this study contained measurable
480 concentrations of Br.

- Under our extraction procedure, BDE-209 was predominant among our target BFRs in most utensils, but the pattern of other BFRs varied substantially between utensils. Elevated concentrations of BTBPE and BDE-153 were found in some utensils.
- BFR transfer from utensils into hot oil during simulated cooking experiments was considerable, and differed between BFRs and utensils. Transfer efficiency decreased with increasing Br substitution of PBDEs.
- Using BFR containing utensils for frying may lead to considerable dietary exposure, whilst exposure via dermal contact is negligible due to limited contact time and barrier effect of skin.

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