Hydrodebromination of Decabromodiphenyl Ether (BDE-209) in Cooking Experiments with Salmon Fillet

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Ⓢ *Supporting Information*

ABSTRACT: Polybrominated diphenyl ethers (PBDEs) are environmental contaminants regularly detected in biota and food. Seafood has been identified as the major dietary source for human uptake. Fish is predominantly consumed after cooking, and this process may alter the actual human intake of contaminants. This study thus aimed to investigate the fate of PBDEs in this cooking process. Heating of fish fortified with 2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether (BDE-209) at typical cooking conditions (200 °C, in plant oil) resulted in a decrease of its concentration in favor of the formation of lower brominated congeners. After 15 min, ~25% of BDE-209 was transformed into nona- to octabrominated congeners. The major transformation route was BDE-209 → BDE-206 → BDE-196 and BDE-199. Low amounts of heptabrominated congeners as well as one hexabromodibenzofuran and a heptabromodibenzofuran isomer were also detected. However, penta- and tetrabrominated diphenyl ethers were not observed, and heating of BDE-47 did not produce new transformation products.

KEYWORDS: *heated food, fish, brominated flame retardants, polybrominated diphenyl ethers, BDE-209, transformation*

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) have been heavily used as additive flame retardants, for example, in polyurethane foam, textiles, and furniture foam as well as in plastics used in electrical and electronic equipment.[1] PBDEs were synthesized by bromination of diphenyl ether to three different degrees, that is, technical pentaBDE, technical octaBDE, and technical decaBDE.[1] Each product contains only a maximum of about 10 relevant congeners, whereas all of the theoretically possible 209 PBDEs are currently available as individual reference standards. The bioaccumulative potential of different PBDE congeners led to their detection in various environmental compartments and foods.[1] Major toxic effects emerged from endocrine disruption of the thyroid function by constituents of the technical pentaBDE and octaBDE products.[2] Therefore, both products were classified as persistent organic pollutants (POPs) under the Stockholm Convention on POPs.[3] Hence, the only product still in use is technical decaBDE.[3]

DecaBDE is being discussed as a potential source of the lower brominated congeners such as BDE-47, which are usually dominant in biota.[4−6] The highest environmental residues of BDE-209 were reported in abiotic matrices such as dust and sediment.[7] However, recent research also reported residues of BDE-209 in seafood.[8] Major transformation routes of decaBDE were identified to be induced by UV light[4,6,9] or zerovalent metals[10,11] and after exposure to chemical reduction agents such as sodium borohydride.[12] In addition, biotic transformation was reported to occur in sediment bacteria[5,13,14] and in fish.[15−17]

Market basket studies showed that fish contributed significantly to the human PBDE uptake.[8,18,19] There are also hints that cooking of food could change both the concentrations and residue patterns of organohalogen compounds.[20−24] For instance, heating of contaminated food was accompanied by a reduction of the polychlorinated biphenyl

(PCB) load, mainly by leaching out together with fat and/or by volatilization[25] as observed during desodoration of edible oils.[26] Similar effects were expected for PBDEs.[19] Perelló et al. showed that cooking of contaminated food could decrease the concentration of some PBDE congeners while others were enriched.[21] However, knowledge of the fate of BDE-209 and other PBDEs in fish during cooking processes is rather limited.

The aim of the study was to investigate the fate of PBDE congeners when heated in fish. Initially, two model congeners, BDE-47 (i.e., the most prominent congener in fish) and BDE-209 (still in use and increasingly detected in environmental samples, including seafood), were selected as reference compounds. Both compounds were spiked into small portions of fish that were tested to be virtually free of PBDEs. The samples were heated for different times at 200 °C in plant oil. The simple small-scale fish−plant oil−PBDE system was chosen to exclude variations in the results originating from inhomogeneous subsamples and effects caused by water loss during cooking and for the presentation of a quantitative balance of the PBDE residues after heating.

MATERIALS AND METHODS

Chemicals, Standards, and Samples. Sodium sulfate (water-free, p.a., ≥99%) and silica gel 60 (for column chromatography) were from Sigma-Aldrich (Taufkirchen, Germany), Supelclean ENVI-Carb, 120−400 mesh, and Celite 545-AW were from Supelco (Deisenhofen, Germany), sulfuric acid (>98%) was from BASF (Ludwigshafen, Germany), and sodium chloride (p.a., >99.8%) was from Carl Roth (Karlsruhe, Germany). Cyclohexane (>99.5%) and ethyl acetate (>99.5%), both from Sigma-Aldrich, were combined and purified by azeotropic distillation (46:54, w/w). *n*-Hexane (for residue analysis,

>99%) was from Th. Geyer (Renningen, Germany), whereas toluene (Pestanal, >99%) and *iso*-octane (Pestanal, >99%) were from Fluka (Steinheim, Germany). Technical pentaBDE (DE-71), octaBDE (DE-79), and decaBDE (DE-83R; BDE-209 with purity ~ 97%) were produced by Great Lakes Chemical (Indianapolis, IN, USA). 2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47; purity ~ 98%) and the internal standards 2′-MeO-BDE-68 and 6′-MeO-BDE-66 were synthesized in our laboratory according to published protocols.[27−30] Standards of BDE-197/183 (ratio 7:8, w/w), BDE-196, BDE-183, BDE-154, and BDE-153 were isolated by HPLC from octaBDE.[31] A standard mixture of 40 PBDE congeners (EO-4980) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA), and an individual standard of BDE-199 was from Wellington (Guelph, ON, Canada). Refined sunflower oil and farmed salmon fillet (*Salmo salar*) from Chile (water content ~ 70%, lipid content ~ 5%), which was virtually free of PBDEs,[32] were purchased in a German retail store. The fish was stored frozen and thawed directly before the experiment started.

Cooking Experiments. Portions of salmon fillet (1 g) were spiked with 200 ng of decaBDE and BDE-47 (20 ng/μL in toluene). Sunflower oil (180 mg) and occasionally sodium chloride (80 mg) were placed in 10 mL glass test tubes (12 mm internal diameter, 80 mm height), to which the spiked fish was added. The test tube with the sample was placed in a preheated heating block (Labtherm, Liebisch Labortechnik, Bielefeld, Germany) at 200 °C for 0 (reference value), 15, 30, 45, 60, and 90 min, respectively. Alternatively, the heating tubes were sealed with screw lids equipped with Teflon septa and heated for 0 (reference value), 15, 30, 45, 60, 90, 120, and 180 min. An additional sample was used to measure the temperature in the heating tubes every minute by means of a thermometer. Within the first 2−3 min, water released from the fish was visible in the tube. During this time, the temperature in the tube reached 130 °C. After 5 min, the temperature in the tubes increased to 150 °C, and after 10 min the target temperature of 200 °C was obtained. Before and immediately after heating, the test tubes were covered with aluminum foil. Additional experiments were performed in which the spikes of BDE-209 and BDE-47 were substituted with 10 μL of a methanolic solution containing BDE-197 (14 ng), BDE-183 (400 ng), BDE-196 (75 ng), BDE-154 (19 ng), and BDE-153 (125 ng). These samples were heated for 30, 60, and 90 min, respectively ($n = 3$) in open tubes. Blank experiments (heating of BDE-209 in sunflower oil with or without salt) resulted in uncorrected recovery rates of >80%, which were comparable with nonheated samples. No degradation products of BDE-209 were observed under these conditions.[24]

Sample Extraction. The heated samples were spiked with 200 ng of either 2′-MeO-BDE-68 or 6′-MeO-BDE-66 (with 20 ng/μL toluene) as internal standard (IS) and transferred with 80 mL of cyclohexane/ethyl acetate (46:54, w/w) into 250 mL microwave vessels (borosilicate glass). Open-vessel microwave-assisted extraction was performed with a modified Star-System microwave (CEM, Kamp-Lintfort, Germany) similarly to the method of Batista et al.[33] During the extraction the temperature was increased within 10 min to 88 °C (10 min hold) and then within 5 min to 95 °C (30 min hold). This program was adapted from Weichbrodt et al.[34]

Sample Preparation. Extracts were passed through a fluted filter into pear-shaped flasks (100 mL) and rinsed with 5 × 2 mL of cyclohexane/ethyl acetate (46:54, w/w). Then the solvent was changed to *iso*-octane by rotary evaporation. The sample was transferred with 5 × 2 mL of *n*-hexane into a 20 mL test tube (Pyrex, 16 mm internal diameter, 160 mm height), and 5 mL of concentrated sulfuric acid was added for lipid decomposition. After vigorous shaking and phase separation, the organic layer was transferred into a pear-shaped flask (100 mL), and the remaining acid phase was re-extracted twice with 5 mL of *n*-hexane.[24] Remaining lipids and other polar substances were removed by adsorption chromatography with 3 g of 30% deactivated silica gel topped with 1 g of sodium sulfate. The PBDEs were eluted with 60 mL of *n*-hexane.[34] Samples were then brought to 1 mL and subjected to gas chromatography coupled to electron capture negative ion mass spectrometry (GC/ECNI-MS) or electron capture detection (GC/

ECD) analysis. All glassware was made of amber glass or covered with aluminum foil.

Activated Carbon Column Chromatography. A mixture of 0.5 g of Celite and 0.5 g of ENVI-Carb was filled in a 1 cm internal diameter glass column according to Natzeck et al. with modifications.[35] One-fourth (250 μL) of a purified heated sample extract (heated for 120 min with a closed lid) was placed on the column and eluted with (i) 50 mL of *n*-hexane, (ii) 50 mL of *n*-hexane/toluene (95:5, v/v), and (iii) 50 mL of toluene. Each fraction was concentrated to 250 μL and then subjected to GC/ECNI-MS analysis (5 μL injected), and the resulting chromatograms were compared with the unfractionated sample (5 μL injected).

Quality Control. Procedural blanks did not show traces of PBDEs. All experiments were performed at least in duplicates or more replications. Recoveries of the spikes in unheated samples and neat sunflower oil (heated and unheated) were ~80% for BDE-209 and BDE-47, which compared well with the recoveries of the IS 2′-MeO-BDE-68 or 6′-MeO-BDE-66 (~80%). Therefore, we corrected all compounds by the recoveries of the IS. Repeated spiking of decaBDE (200 ng) into sample extract after heating for 120 min gave identical results for BDE-209 after subtraction of the added amount. This demonstrated that BDE-209 was neither retarded by matrix compounds nor decomposed in the injection port. No difference was observed in the samples with and without NaCl addition, and therefore all samples are discussed together in the following. Duplicate analyses varied by <10%, or the experiment was repeated (see Table S1, Supporting Information).

Gas Chromatography Coupled to Electron Capture Negative Ion Mass Spectrometry. An Agilent (Waldbronn, Germany) 7890/5975c system, equipped with a 7693A autosampler, was used for GC/ECNI-MS analyses. If not stated differently, 1 μL of sample solution was injected into a programmed temperature vaporizer (PTV) injector (CIS-4, Gerstel, Mülheim, Germany) operated in pulsed splitless mode (25 psi until 1 min). The injector temperature was held at 80 °C for 0.01 min, then ramped at 700 °C/min to 300 °C (hold 2 min), and finally cooled at 10 °C/min to 260 °C until the end of the run. A DB-5HT (15 m × 0.25 mm internal diameter, 0.1 μm film thickness) capillary column (J&W Scientific, Folsom, CA, USA) was used in combination with the following GC oven program: after 1 min at 50 °C, the temperature was increased by 10 °C/min to 300 °C (hold time = 24 min); the total run time was 50 min. The carrier gas, helium (purity 5.0; Westfalen, Münster, Germany), was used at a flow rate of 1.2 mL/min. The transfer line temperature was held at 300 °C, and the ion source and quadrupole temperatures were maintained at 150 °C, respectively. Methane (purity 5.5; Air Liquide, Bopfingen, Germany) was used as reagent gas at 2 mL/min, which resulted in a source pressure of 1.6×10^{-4} Torr.

Analyses were performed in the selected ion monitoring (SIM) mode using four methods (SIM-01 to SIM-04). *SIM-01:* throughout the run m/z 79 and 81 of $[Br]^-$; m/z 158 and 160 of $[Br_2]^-$, m/z 159 and 161 of $[HBr_2]^-$,[36] m/z 440.6, 442.6, and 444.6 of $[C_6Br_4ClO]^-$, as well as m/z 486.6 and 488.6 of $[C_6Br_5O]^-$, that is, for the base peak of BDE-209.[37] *SIM-02:* m/z 79 and 81 of $[Br]^-$; m/z 639.5, 641.5, and 643.5 $[M]^-$ of Br_6DFs, and m/z 717.4, 719.4, and 721.4 of $[M]^-$ of Br_7DFs. *SIM-03:* m/z 79 and 81 of $[Br]^-$; m/z 406.7, 408.7, and 410.7 of $[C_6HBr_4O]^-$ and m/z 799.4, 801.4, and 803.4 of $[M]^-$ of Br_8DEs. *SIM-04:* m/z 79 and 81 of $[Br]^-$; m/z 158 and 160 of $[Br_2]^-$, m/z 159 and 161 of $[HBr_2]^-$, m/z 326.8, 328.8, 330.8, and 332.8 of $[C_6H_2Br_3O]^-$ [37] were recorded. Generally, a dwell time of 50 ms was used. Measurements in the full-scan mode covered m/z 30−800 at a scan rate of 1.94 scans/s.

Gas Chromatography with Electron Capture Detection. A Hewlett-Packard 5890 series II Plus system equipped with a GC PAL autosampler (CTC Analytics, Zwingen, Switzerland) was used for GC/ECD analyses. One microliter was injected in the splitless mode at 300 °C onto a 15 m × 0.25 mm internal diameter, 0.25 μm film thickness BGB-1 column (BGB-Analytik, Boeckten, Switzerland). The oven temperature was programmed for 2 min at 80 °C followed by 10 °C/min to 300 °C (20 min). The carrier gas flow of nitrogen (purity 5.0; Westfalen) was kept at a constant flow rate of 1.2 mL/min, and

the detector temperature was set to 300 °C. The makeup gas (nitrogen) was used with a flow rate of 60 mL/min.

Compounds not available as individual standards were semi-quantitatively assessed relative to the area of BDE-209 in the GC/ECD chromatogram of the unheated sample. Peaks were assigned to individual PBDEs present in technical pentaBDE and octaBDE according to the methods of La Guardia et al.,[38] Korytár et al.,[39] and Wei et al.[40] For all results presented, confirmatory measurements were conducted by GC/ECNI-MS.
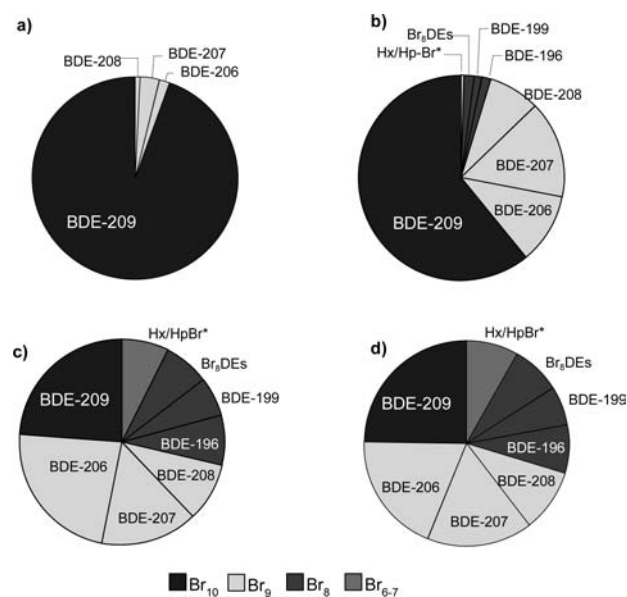
■ RESULTS AND DISCUSSION

Effects of Heating of BDE-47 and BDE-209 in Fish. Recoveries of BDE-47 and BDE-209 when spiked into fish without heating were high ($\sim$100% after correcting for recovery by the IS). When the spiked fish was heated for 15 min, the recoveries of BDE-209 and BDE-47 were $\sim$75 and $\sim$100%, respectively (Figure 1). The strong increase in the Br_9DE
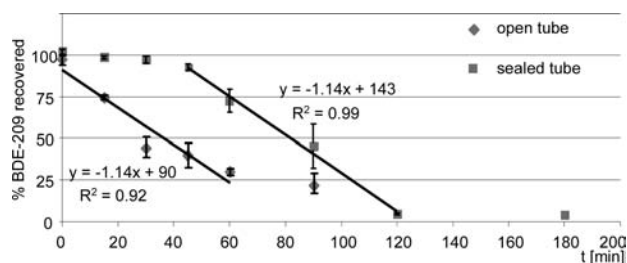
Figure 1. Decomposition kinetics of BDE-209 spiked in fish heated for 0–180 min in plant oil in open and sealed test tubes at 200 °C.

content and the formation of Br_8DEs (Figure 2) confirmed that BDE-209 was partly decomposed by hydrodebromination. Loss of BDE-209 by evaporation could be excluded because the more volatile BDE-47 was quantitatively recovered even after the longest heating period. Therefore, BDE-47 could be used as

an additional standard for quality control. Likewise, the repeated spiking of BDE-209 into a sample extract of a heated fish provided the same result after subtraction of the spiked amount (see Materials and Methods), and therefore GC related decomposition of BDE-209 was excluded. The decomposition of BDE-209 over time (15–90 min) progressed linearly (R^2 > 0.92) with a slope of −1.14%/min in the range of 0–60 min and seemed to slow between 60 and 90 min (Figure 1).

Heating of the fish samples was accompanied with an instant evaporation of water for 2–3 min. Because the reactions observed in the fish could be water content dependent, the experiment was repeated with sealed heating tubes. Under these conditions an induction phase of ~45 min of steady state was observed before the transformation of BDE-209 commenced and then progressed linearly (45–120 min) virtually parallel to the samples heated in open tubes (slope = −1.14%/min, R^2 = 0.99, Figure 1). Accordingly, the same process seemed to cause the debromination of BDE-209 in both the open- and closed-lid heated samples. It is worth noting that hydrodebromination of BDE-209 was not observed when heated in oil (without fish).[24] Hence, the transformation of BDE-209 must have been catalyzed by fish constituents and/or water. If and to what content the water itself (or its evaporation from the fish) was involved in the transformation of BDE-209 could not be elucidated.

Transformation Product Spectrum. The decaBDE standard also contained traces of the three Br_9DEs (Figure 2a). In the course of the heating, their abundance increased in the order BDE-206 $\sim$ or > BDE-207 > BDE-208 (Figure 2b,c). A similar Br_9DE pattern was also observed after UV transformation of BDE-209 in sand and sediment[4] as well as during thermal decomposition and in wastewater treatment plants, sediment, or sludge.[4,41] After 15 min (i.e., the shortest heating period tested), the transformation product spectrum was dominated by the three Br_9DEs along with several Br_8DEs (Figure 2b). The sum of the transformation products exceeded the initial amount of decaBDE by ~15%, but this feature could be explained by the relative quantification of the Br_8- and Br_9DEs with the BDE-209 response, as along with the chromatographic performance of Br_8- and Br_9DEs the ECD response also improved. The Br_8DEs observed after 15 min of heating were dominated by the tri-*ortho*-substituted BDE-196 (1.7% of the initial BDE-209 amount) and BDE-199 (1.5%), which both were previously identified as the dominant products of sodium borohydride reduction of BDE-206.[12] It followed in abundance the tetra-*ortho*-substituted BDE-197 (0.8%), BDE-201 (0.6%), and BDE-202 (0.3%) and finally the di-*ortho*-substituted BDE-194 (0.3%) (Figure 3a). The presence of BDE-198, BDE-200, and BDE-203, which coelute with BDE-199, could be excluded due to the high response to m/z 408.7 ($[C_6HBr_4O]^-$; ~33% of m/z 79), which is typically for BDE-199 and the absence of the characteristic $[C_6Br_5O]^-$ fragment (typically for BDE-198, -200, and -203).[12] Accordingly, the second debromination step exclusively occurred in the fully brominated ring, as reported, and photolytic hydrodebromination of polybrominated biphenyls[42] and hydrodebromination of Br_9DEs with sodium borohydride.[12] For example, Br_8DEs, with four bromines on each ring moiety (tetra/tetra) were almost exclusively formed. In fact, all possible tetra/tetra-substituted Br_8DEs originating from BDE-206 (BDE-194, -196, -199), BDE-207 (BDE-196, -197, -201), and BDE-208 (BDE-199, -201, -202) were detected.
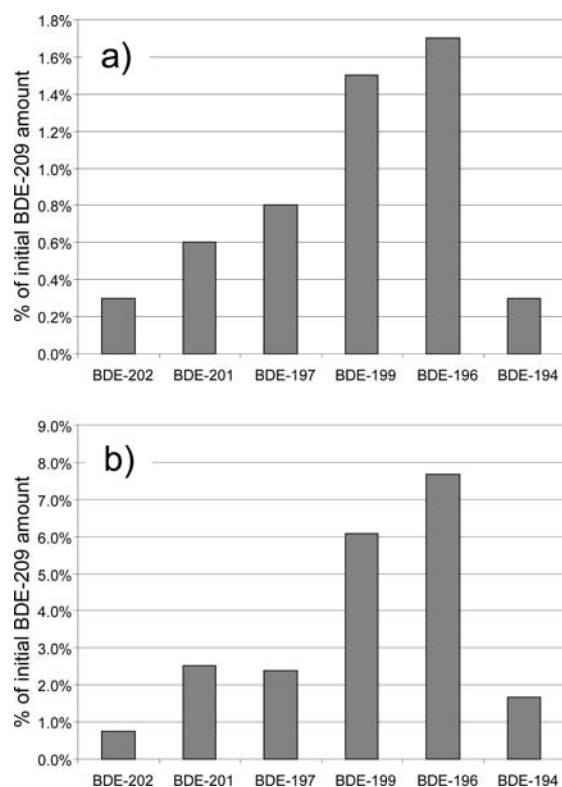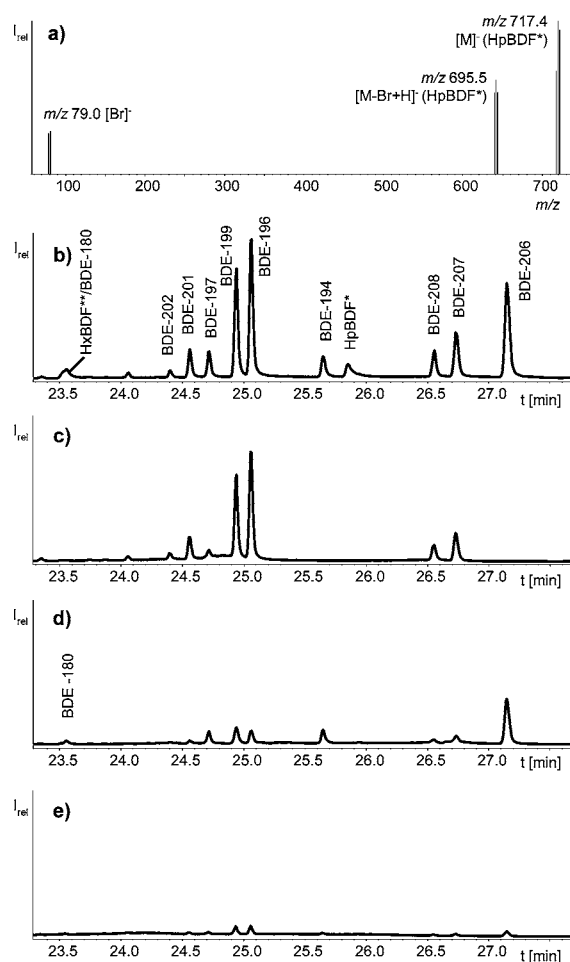

Figure 2. Residue pattern before and after the heating of fish spiked with 200 ng of decaBDE: sample extracts (a) before heating, (b) after 15 min of heating at 200 °C (open test tube), (c) after 60 min of heating at 200 °C (open test tube), and (d) after 90 min of heating (sealed test tube) at 200 °C. *Hx/Hp-Br, sum of all hexa- and heptabrominated compounds.

Figure 3. Detailed pattern of the octabromo diphenyl ethers transformation products after heating of fish spiked with 200 ng of decaBDE for (a) 15 min and (b) 60 min at 200 °C (open test tube).


Figure 4. (a) Reconstructed GC/ECNI-SIM mass spectrum of the suspected heptabromodibenzofuran (SIM-01 + SIM-02 + SIM-03) and (b) GC/ECNI-SIM selected ion chromatograms (m/z 79, SIM-02) of a fish extract spiked with decaBDE heated in plant oil at 200 °C for 120 min. Fractions of the sample are shown in (b) on a activated carbon column (c) first fraction (n-hexane), (d) second fraction (n-hexane/toluene 95:5 (v/v)), and (e) third fraction (toluene). *HpBDF, heptabromodibenzofuran; **HxBDF, hexabromodibenzofuran.

The Br_8DE pattern observed after 15 min proved to be characteristic as it was also observed after longer heating periods. After 60 min, the abundance of the Br_8DEs was ~4-fold higher than after 15 min (Figure 2b,c). A linear increase of the amount of Br_8DEs was observed during the heating experiment. After 60 min, BDE-206 reached the level of BDE-209 (Figure 2c). Longer heating times were also accompanied with the increase in the abundance of Br_7DEs. The Br_7DE pattern was dominated by BDE-183, followed by BDE-182 and an isomer not available as reference standard, which eluted just before BDE-183. Likewise, traces of BDE-184, BDE-171 (its potential coeluters BDE-173 and BDE-190 were excluded because they have an unfavored di/penta distribution of Br on the two ring moieties), and BDE-191 could be detected (Figure S1, Supporting Information). Patterns of the transformation products after heating fish in the open tube for 60 min compared well with the pattern obtained after heating for 90 min in the closed tube (Pearson correlation coefficient = 0.987) (Figure 2c,d). This also supported the previous observation that the reaction pathway was the same for the heating of samples with open and closed tubes (except for the delayed start of the PBDE transformation in the closed tubes). Traces of Br_6DEs BDE-153 (di-ortho-substituted) and BDE-154 (tri-ortho-substituted, tri/tri) were detected only when BDE-209 was heated for an extremely long time (3 h) in fish with a sealed tube (Figure S1, Supporting Information). However, a further polybrominated compound was detected in the GC/ECNI-MS chromatograms, which eluted between the last Br_8DE and the first Br_9DE. The mass spectrum with the base peak m/z 719.4 ([M]$^-$) showed response neither to the characteristic ring fragment of Br_8DEs ([C_6HBr_4O]$^-$ at m/z 408.7 (or m/z 486.7) nor to m/z 161 [HBr_2]$^-$ (Figure 4a).[37,43]

This feature substantiated the detection of a heptabrominated dibenzofuran congener in our sample. Planar polybrominated dibenzofurans (PBDFs) can be absorbed with charcoal. Thus, we used the sample heated for 3 h (Figure 4b) and fractionated it by means of activated carbon column chromatography (see Materials and Methods). With this method, 96 ± 6% of most PBDEs (BDE-196, -197, -201, -199, -207, -208) eluted into fraction 1 (Figure 4c), whereas ~50% of BDE-209 and -206 eluted into fractions 2 and 3 (Figure 4d,e). However, the unknown compound was not eluted, and this confirmed the presence of the heptabromodibenzofuran congener in our heated samples. The charcoal fractionation and subsequent GC/ECNI-MS analysis also showed the presence of a hexabromodibenzofuran congener, which coeluted with BDE-180 (Figure S2, Supporting Information).

Heating of Different Highly Brominated PBDE Congeners in Fish. Heating of BDE-209 in fish resulted in several hydrodebromination products (Br_9DEs to Br_6DEs), whereas BDE-47 was neither reacting nor formed from BDE-209. In the following, we aimed to determine until what degree

of bromination hydrodebromination occurred. For this purpose, a mixture of Br_6- to Br_8DEs isolated from technical octaBDE was spiked into fish (Figure 5). In the course of the
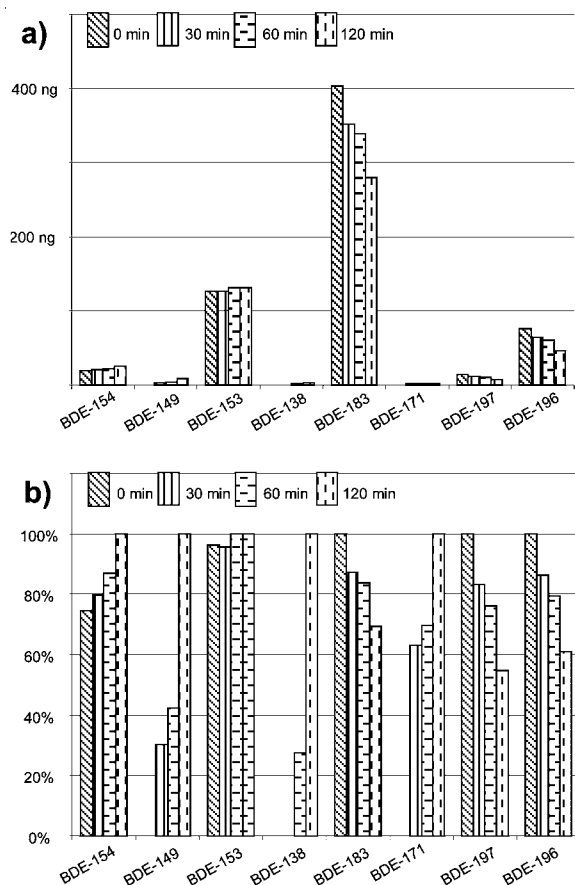
Figure 5. Fate of a mixture of BDE-154, BDE-149, BDE-153, BDE-138, BDE-183, BDE-171, BDE-197, and BDE-196 spiked into fish after heating for 0, 30, 60, and 120 min at 200 °C in plant oil in open test tubes: (a) distribution by mass in test tube; (b) PBDE pattern normalized to the most intensive detection recorded with SIM-04.

heating the amount of the Br_7- and Br_8DEs was continuously reduced. However, after 120 min, only ∼40% of the degraded PBDE amount could be traced back to the lower brominated PBDE congeners shown in Figure 5. The Br_6DEs approximately remained on the same level (BDE-153) or even increased (BDE-154 and BDE-149) with time. BDE-149 was not available as an individual reference standard, and its structural assignment was based on the GC retention time and its occurrence in DE-79 as demonstrated by Konstantinov et al.[44] BDE-149 had been identified as a key metabolite of BDE-183 in zebrafish together with BDE-154 (most abundant) and BDE-153.[45] Interestingly, the pattern and the relative abundance of the three Br_6DEs were similar in our study. Next to these three Br_6DEs, traces of BDE-138 were identified at longer heating times. In accordance with the observations above, all Br_6DEs detected had a symmetrical tri/tri-substitution in the two phenyl moieties. Br_5DEs or less brominated diphenyl ethers were not detected in this experimental setup. This was also verified the quantitative recovery of BDE-47 (see above). Obviously, the hydrodebromination ended with Br_6DEs, similar to the fact that

Br_6DEs were not accessible to sodium borohydride mediated hydrodebromination.[46]

Our model system was based on the heating of BDE-209 in fish to 200 °C for periods of 15−60 min (and longer). These conditions are more drastic than those typically used for the roasting, broiling, or frying of fish. Accordingly, the transformation rate of the PBDEs during the cooking of fish in households could be smaller. However, our experiments clearly indicate that the transformation of BDE-209 is an important issue and underscored the particular behavior of this flame retardant in the environment and food.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Additional information as noted in text (Figures S-1 and S-2 and Table S-1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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