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Determination of halogenated flame retardants in food: optimization and validation of a method based on a two-step clean-up and gas chromatography-mass spectrometry

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15 **Abstract**

16 In this work, a new simple method based on a two-step clean-up and gas chromatography-mass
17 spectrometry analysis for the determination of emerging halogenated flame retardants (HFRs), such
18 as dechlorane plus (DP) and brominated phthalates, and polybrominated diphenyl ethers (PBDEs)
19 in different food items was optimized and validated. Several types of food items, i.e. fish (smoked
20 salmon and cod fillet), meat (chicken breast), chicken eggs, cow milk, and extra virgin olive oil,
21 were chosen as representative matrices of the main food categories. After lyophilisation, the food
22 samples were extracted using acetonitrile:toluene (9:1, v/v). As interferences, such as lipids and
23 pigments, were co-extracted, a two-step clean-up (including Florisil and acid silica) was performed
24 to efficiently remove them prior to GC-MS analysis in electron capture negative ionization mode
25 (GC-ECNI/MS). The performance criteria established by the European Commission (2014/118/EU)
26 were achieved with this method for all target analytes, except for the LOQ achieved for BDE-209
27 (0.1 ng/g wet weight, ww). The trueness ranged between 75 and 125% for most compounds and the
28 matrices analyzed and the repeatability (expressed as RSD%) was <20%, within the set
29 performance criteria. The method was then used for the determination of PBDEs and emerging
30 HFRs in 20 different food items purchased from Antwerp supermarkets, revealing a prevalent
31 contamination with PBDEs (up to 2.02 ng/g ww) and tribromoanisole (up to 6.6 ng/g ww) in the
32 fish/seafood category.

33

34 **Keywords**

35 PBDEs; emerging halogenated flame retardants; TBA; Food analysis; Gas chromatography-mass
36 spectrometry (GC-MS); food market basket

1. Introduction

Brominated flame retardants (BFRs) are anthropogenic chemicals that are added to a wide variety of commercial products in order to improve their fire resistance. Polybrominated diphenyl ethers (PBDEs) are an important and widely used group of additive BFRs, generally used in plastics, textiles, electronic casings and circuitry. Concern has been raised due to the widespread occurrence of several PBDEs in the environment, food, human body, and biota (de Jourdan et al., 2013). Due to their lipophilic nature, PBDEs have been mainly found in lipid-rich food of animal origin, such as fish, meat, eggs, and dairy products (Voorspoels et al., 2007; Darnerud et al., 2006; Roosens et al., 2008). They are also persistent and potential effects on human health and the environment have been described (Domingo, 2012).

Several international agreements on the regulation and use of some PBDEs have been introduced. In particular, the Directive 2003/11 of the European Parliament ruled that the Penta-BDE and Octa-BDE technical formulations should not be used after 2004 and the European Court of Justice decided in 2008 that Deca-BDE could no longer be used in electronics and electrical applications. The reduction in the use of PBDEs has consequently opened the way for the introduction of other flame retardants, used as replacements to comply with fire safety regulations in commercial products (Covaci et al., 2011). These replacements include relatively new and previously known brominated and chlorinated FRs, such as dechlorane plus (DPs), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), bis(2-ethylhexyl) tetrabromophthalate (TBPH), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), and hexabromobenzene (HBB). DPs and BTBPE have been identified by the European Commission as possible replacements for the Deca-BDE and Octa-BDE formulations, respectively (European Commission report on potential alternatives to Deca-BDE, 2011). TBPH and TBB are used in the Firemaster 550 formulation as alternatives for the Penta-BDE mixture (Andersson et al., 2006; de Wit et al., 2011). HBB have been producing in Japan and China, in recent years, as an additive to paper, plastic, and electronic devices (Gauthier et al., 2007). Since these replacement FRs are highly brominated or chlorinated chemicals, they would have similar properties as PBDEs, e.g., low water solubility, high octanol-water partition coefficients, environmental persistence, potential for bioaccumulation, and have been detected in different food matrices, such as milk, eggs, meat, and fish (Tlustos et al., 2010; Kim et al., 2014; Kakimoto et al., 2012; Kalachova et al., 2013; Zhang et al., 2011; Zheng et al., 2012). No information on the presence of TBB and TBPH in food samples could be found in scientific literature, although the observations in wildlife, particularly in fish, indicate that these chemicals might also be present in foodstuffs (Zhou et al. 2010). 2,4,6-tribromoanisole (TBA) is naturally-produced by marine micro- and macroalgae, sponges, fungi, and/or bacteria (Moore et al., 2002; Vetter and Stoll, 2002).

Moreover, TBA has been also recognized as a fungal metabolite of 2,4,6-tribromophenol, which has been and is still used as a FR in plastics for packaging (Shim et al., 2006) and fungicide on lumber and cork (Koschier et al., 2011).

Considering the information given above, the residue levels of BFRs in food need to be better documented and to be included in food safety programs, as suggested by the European Food Safety Authority (EFSA) Panel on Contaminants in the Food Chain (CONTAM Panel, EFSA 2010). The traditional methods for determining BFR residues usually require large amounts of sample, are time-consuming, complicated, expensive, and produce considerable amount of (solvent) waste (Sapozhnikova and Lehotay, 2013; Na et al., 2013). Thus, simple, cheap, rapid, sensitive, and robust analytical methods, which enable the collection of a large set of reliable data in a short time, are needed to monitor the residues and ensure that the food is safe for consumption (Sapozhnikova and Lehotay, 2013; Kalachova et al., 2013).

The main goal of this study was to optimize and validate a method to follow-up the requirements of the EU draft regulation on the monitoring of BFRs in food (2014/118/EU) and to produce reliable data to fill the gap of information on the occurrence of emerging FRs in food. This method uses low sample amounts and solvent volumes, and involves a two-step clean-up, including Florisil and acid silica. The determination of PBDEs and other emerging halogenated FRs in different food samples was performed using gas chromatography-mass spectrometry (GC-ECNI/MS). The validated method was then used for the determination of BFRs in 20 different food items purchased from Antwerp supermarkets (including fish, meat, eggs, milk, grains, and vegetable oil), and will be used for the analysis of more than 200 samples in the frame of a Belgian food monitoring project (FLAREFOOD).

2. Materials and Methods

2.1 Chemicals

Standards of BDE-28, -49, -47, -99, -100, -153, -154, -138, -183, and -209, BTBPE, DP-s (*syn*- and *anti*- isomers), TBB, TBPH, HBB, and isotopically labelled internal standards (IS) ^{13}C -BDE-209, ^{13}C -TBPH, and ^{13}C -TBB were purchased from Wellington Laboratories (Guelph, ON, Canada). BDE-103 and BDE-128 (IS) were obtained from AccuStandard Inc. (New Haven, CT, USA). ^{13}C -DP-s and ^{13}C -DP-a (IS) were purchased from Cambridge Isotope Laboratories (Andover, MA, US). TBA (100 ng/ μL) was purchased from Sigma-Aldrich. Recovery standard (RS) CB-207 was purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). Polypropylene-PP tubes (15 mL) were obtained from Greiner Bio-one (Belgium). Empty polypropylene cartridges (25 mL) were

105 purchased from Grace (Lokeren, Belgium), while Florisil[®] cartridges (500 mg, 3 mL) and empty
106 propylene cartridges (6 mL) were purchased from Supelco (Bellefonte, PA, USA). Silica gel,
107 anhydrous sodium sulfate (Na₂SO₄) and concentrated sulfuric acid (H₂SO₄, 98%) were purchased
108 from Merck (Darmstadt, Germany). All solvents were chromatography grade: *n*-hexane was
109 purchased from Acros Organics (Belgium); dichloromethane (DCM), *iso*-octane, toluene and
110 acetonitrile (ACN) were purchased from Merck.

112 2.2 Sample preparation

113 Several types of food items, including fish (smoked salmon and cod fillet), meat (chicken breast),
114 chicken eggs, cow milk, and extra virgin olive oil (EVOO), were chosen as suitable matrices to
115 represent the main food categories and were purchased in the spring of 2015 at various
116 supermarkets from Antwerp (Belgium). The edible part of each sample was homogenized
117 individually with a blender, freeze-dried, and stored at -20°C until chemical analysis. The lipid
118 content of each sample was determined using a gravimetric method, as reported by Xu et al. (2015).
119 Based on the classification proposed by Lehotay et al. (2005), the food items could be divided into
120 non-fatty (<2% lipids), low fatty (2-20% lipids), and high fatty (>20% lipids), with lipid content
121 calculated on a wet weight basis. According to this classification, and based on the determined lipid
122 content of the food samples, it was decided to consider for the extraction 2 g dry weight (dw) for
123 non-fatty matrices (cod fillet and chicken breast), 1 g dw for low fatty matrices (chicken eggs, milk,
124 and smoked salmon), and 0.20 g for high fatty matrices (EVOO).

126 The sample was weighted in a pre-washed 15 mL polypropylene (PP) tube, and each sample was
127 spiked with the IS mixture (including BDE-103, BDE-128, ¹³C₁₂-BDE-209, ¹³C-TBPH, ¹³C-TBB,
128 ¹³C-DP-s, and ¹³C-DP-a). After spiking, 5 mL of ACN:toluene (9:1, v:v) was added to the samples.
129 The tubes were capped, vortexed for 1 min, and ultrasonicated for 10 min. The mixtures were then
130 loaded on empty SPE cartridges (25 mL) with a frit at the bottom. The eluting solvent was collected
131 in 15 mL glass tubes. After rinsing twice the PP tubes with 1 mL of the same solvent mixture and
132 combining all fractions, the cartridges were tightly packed to recover the maximum amount of
133 solvent. The extracts were evaporated to dryness, reconstituted in 0.5 mL *n*-hexane, and loaded on 3
134 mL Florisil[®] cartridges (pre-conditioned with 6 mL of *n*-hexane). The elution was achieved with 6
135 mL of *n*-hexane:DCM (4:1, v:v), followed by 6 mL of *n*-hexane:DCM (1:1, v:v). The solution was
136 then evaporated to 1 mL and loaded onto 6 mL cartridges containing 1.5 g of acidified silica (AS,
137 5%, w/w, prewashed with 6 mL *n*-hexane) for further clean-up, and eluted with 12 mL of *n*-
138 hexane:DCM (1:1, v:v). The final extract was concentrated to near dryness, reconstituted in 100 µL

139 of the recovery standard (RS) (CB-207 in iso-octane:toluene; 9:1, v/v) and transferred to amber
140 injection vials for GC-ECNI/MS analysis. The procedure of sample preparation is illustrated in Fig.
141 1.

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143 *2.3 Instrumental analysis*

144 Target analysis was performed with an Agilent 6890 GC (Palo Alto, CA, USA) coupled to an
145 Agilent 5973 MS operated in ECNI mode and equipped with a DB-5 capillary column (15 m×0.25
146 mm×0.10 μm) (J&W Scientific, Folsom, CA, USA). The GC system was equipped with electronic
147 pressure control and a programmable-temperature vaporizer (PTV) inlet. The injection temperature
148 was set at 90°C, held 0.04 min, ramped at 700°C/min to 295°C, held 25 min, ramped at 700°C/min
149 to 310°C, held 5 min. Injection (1 μL) was performed under a pressure of 2.10 psi until 1.25 min
150 and purge flow to split vent of 50 mL/min after 1.25 min. The GC temperature ramp started from
151 90°C, held 1 min, ramped at 20°C/min to 200°C, held 1 min, ramped at 5°C/min to 220°C, held 0.5
152 min, ramped at 5 °C/min to 242 °C, ramped at 30°C/min to 310°C, held 10 min. Helium was used
153 as a carrier gas with a flow rate of 1.0 mL/min until 18 min, then increased to 2 mL/min. The ion
154 source and quadrupole temperatures were set at 250°C and 150°C, respectively. The moderating gas
155 was methane. The mass spectrometer was operated in selected ion monitoring (SIM) for the
156 quantification of all the analytes of interest. BDE-103 and BDE-128 were used as IS for all PBDE
157 congeners (except BDE-209), TBA, HBB, and BTBPE. ¹³C-BDE-209 was used as IS for BDE-209.
158 ¹³C-TBB, ¹³C-TBPH, ¹³C-DP-s, and ¹³C-DP-a, were used as IS for TBB, TBPH, DP-s, and DP-a,
159 respectively. Details on the compound retention time and the quantifier/qualifier ions are provided
160 in Table 1.

161

162 *2.4 Assessment of measurement uncertainty*

163 To assess the reliability and the quality of the results obtained by using this method, the
164 measurement uncertainty (U) was estimated based on the measurements performed during the
165 method validation (Eq. 1).

$$166 \quad U = u_c * k \quad (\text{Eq. 1})$$

167 where u_c is the combined standard uncertainty, and k is the coverage factor ($k=2$ for 95%
168 confidence). The combined uncertainty, u_c , is given by the combination of all the contributing
169 component uncertainties (here identified as repeatability and trueness) and can, thus, be estimated
170 as follows (Eq. 2):

$$171 \quad u_c = \sqrt{u_r^2 + u_t^2} \quad (\text{Eq. 2})$$

172 where u_r , uncertainty of repeatability, is determined as the standard deviation of the replicated
173 measurements, and u_t is the uncertainty of trueness. When a suitable standard reference material
174 (SRM) is available, u_t can be estimated using (Eq. 3):

$$175 \quad u_t = \sqrt{\frac{s_t^2}{n_t} + u_{\text{SRM}}^2} \quad (\text{Eq. 3})$$

176 where s_t is the standard deviation and n_t the square root of the number of measurements, and u_{SRM} is
177 the standard uncertainty of the certified value (ERM, 2005). For those analytes lacking a suitable
178 SRM, fortification experiments were performed and, in this case, u_t was determined as the ratio
179 between the standard deviation of the replicate measurements and the square root of the number of
180 measurements.

181

182 **3. Results and discussion**

183 *3.1 Method optimization*

184 In this method, the food samples were first freeze-dried and homogenized before analysis, allowing
185 the extraction of a limited amount of sample, and consequently the use of a reduced volume of
186 solvent. The extraction solvent acetonitrile was added with a 10% of toluene, to improve the
187 extraction of the lipophilic and highly brominated compounds (BDE-209), and to simplify the
188 solvent exchange to hexane. However, such extraction technique can cause the co-extraction of
189 interferences typically present in food items (mainly lipids and pigments). Thus, considering the
190 wide variety of food items analyzed and their different lipid content, a two-step clean-up (including
191 Florisil and acidified silica) was performed to efficiently remove the interfering substances prior to
192 GC-MS analysis. The silica was acidified only slightly using H_2SO_4 (to 5%, w/w) to avoid the
193 degradation of TBPH. However, taking into account the lipid capacity of the SPE cartridge (200 mg
194 of fat), this low percentage of acid strongly limits the amount of sample that can be purified (strictly
195 related to the lipid content) to a maximum of 0.2 g for high fatty, 1 g for low fatty, and 2 g for non-
196 fatty matrices.

197 Using the instrumental parameters described in Section 2.3, nearly all the chromatographic peaks
198 were baseline separated (Fig. 2), but the co-elution of BDE-99 with ^{13}C -TBB could not be
199 prevented. This co-elution could not be resolved by the mass spectrometer as the Br^- ion (m/z 79
200 and 81) of ^{13}C -TBB interfered with the quantification of BDE-99. The co-elution does not influence
201 the quantification of ^{13}C -TBB, as it is based on different ions (m/z 363 and 365). Therefore, this
202 effect was compensated in the calibration, in which ^{13}C -TBB was present at the same amount in
203 each calibration level and its contribution to the Br^- ion (m/z 79 and 81) of BDE-99 was constant
204 throughout the calibration range.

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3.2 Method validation

3.2.1 Linearity

The linearity was assessed via the average response factor of the whole calibration range (Table 1). Six matrix-matched calibration points (prepared from a BFR-free material, such as vegetable oil) for each compound were prepared and injected 3 times in random order. Calibration curves were best fitted to a linear model and were constructed by plotting the analyte/IS ratio against the concentration ratio of each analyte/IS. The curves showed a good correlation for all the target compounds within the tested interval and for all the analyzed food matrices, with coefficients of determination higher or equal to 0.98 (relative standard deviation, RSD, of 0.40%).

3.2.2 Limits of quantification (LOQ)

A number of 6 procedural blanks were analyzed for the LOQ estimation (Table 1). When the HFR concentration in the blanks were negligible, LOQs were determined by the instrument performance ($S/N = 5$). In this case, the lowest calibration point was used as LOQ. The injection precision at LOQ was below 3 %.

TBPH and BDE-209 could be detected in the blanks and thus, for these analytes, the LOQs were based on the standard deviation of the procedural blanks. Average blank levels were subtracted from the sample results and a value equal to $3 \times SD$ of the blank measurement was used as cut-off before reporting results. Determined LOQs were 0.2 ng/g ww for TBPH, and 0.1 ng/g ww for BDE-209. The RSD of repeated determinations ($n=6$) was 26% for TBPH and 18% for BDE-209.

The LOQ values specified in the European Commission recommendation (2014/118/EU) are the following: 0.01 ng/g ww for PBDEs, 0.10 ng/g ww for TBA, and 1 ng/g ww for other BFRs. These requirements are fulfilled with this method, with the only exception of BDE-209, having a LOQ approximately ten times higher than the requested limit. However, this was expected, due to the lower instrumental sensitivity for this compound (Covaci et al., 2007; Björklund et al., 2004), combined with the expected presence in the procedural blanks. It is likely that the expected differences in sensitivity of various PBDE congeners were not taken into account in the EC recommendation, leading to an unrealistic LOQ requirement.

3.2.3 Trueness

For PBDEs, trueness was assessed by means of five replicate analyses of a certified reference material (SRM 1945, Organics in whale blubber) (Table 2). This CRM was also used as a control sample throughout the analyses. For those compounds lacking a suitable CRM, fortification

experiments and subsequent recovery calculation were the basis for trueness assessment. In this case, an analyte-free matrix (EVOO) was spiked at two levels relevant for the analysis (Table 2). Each test was performed in triplicate and the average recovery value was calculated. The trueness for the CRM ranged between 74 and 113%, which was within the performance criteria proposed by SANCO/12495/2011. The comparison of the results obtained for SRM with the certified values was done according to the European Reference Materials Application Note 1 (ERM, 2005). No significant differences among the obtained results and the certified values were observed, with the only exception of BDE-99, for which the absolute difference between the mean measured value and the certified value was higher than the uncertainty of the measurement (ERM, 2005). The recoveries for the spiked samples ranged between 75 and 121% for the majority of compounds, with the exception of BDE-99 and TBA (recovery of 204% and 59%, respectively, at the low spiking level). In the case of BDE-99, the higher recovery is likely due to the incomplete separation between BDE-99 and ¹³C-TBB by GC, while the lower recovery for TBA could be attributed to its higher volatility compared to the other compounds (vapor pressure of 0.065 Pa, Vetter et al., 2004), leading to losses during sample preparation.

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3.2.4 Repeatability

The repeatability was calculated as the relative standard deviation of three-replicate analyses within one day under repeatability conditions (Table 3). Fortified samples were used for the validation; each analytical batch contained calibration standards, fortified samples, method blanks, and a CRM sample. The obtained RSD values ranged between 0.10 and 22%. With 98% of the RSD values ≤ 15%, the repeatability obtained by applying this method lies well within the proposed range (Commission Regulation (EU) No. 589/2014). The recoveries of tri- to penta-PBDEs, BDE-209, and of the other FRs in the fortified samples generally ranged between 75 and 125%, while the recoveries of hexa- and hepta-BDEs were mostly below 75%, probably due to matrix suppression effect.

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3.2.5 Uncertainty of the method

Based on the equations listed in Section 2.4, the expanded uncertainty, U, was calculated for the different food items and the mean expanded uncertainty ($\bar{U}$) of the method was determined (Table 4). No statistically significant difference was found among the U results for the considered matrices (with ANOVA test, $p > 0.05$), indicating that the different characteristics of the food items (i.e. lipid content and pigments) did not affect the reliability of the analysis. The obtained values of $\bar{U}$ ranged

272 between 4 and 37%, fitting well with the commonly accepted performance criteria
273 (SANCO/12495/2011).

274

275 *3.3 Analysis of PBDEs and emerging HFRs in food samples*

276 To evaluate the applicability of this method, the presence of PBDEs and other FRs was investigated
277 in food samples purchased from Antwerp supermarkets, including fish/seafood (tuna fillet, trout,
278 prawn, sardine, mackerel, mussels, herring, anchovy, and salmon fillet), rabbit meat, turkey breast,
279 quail eggs, potato chips, and biscuits (Table 5).

280 In all considered food categories, PBDEs were the most frequently detected chemicals and the
281 fish/seafood was the most PBDE contaminated food group among all. In this category, the total
282 PBDE concentration, calculated as the sum of the considered congeners, ranged from 0.01 ng/g ww
283 in prawn to 2.02 ng/g ww in blue mussels. BDE-47 was the predominant congener detected in all
284 the fish/seafood samples, with an average contribution to the sum of considered congeners up to
285 42%, and with concentrations between 0.010 and 1.20 ng/g ww, whereas many of the other
286 congeners showed concentrations below LOQ. Similar PBDE levels were found in various food
287 items purchased from Sweden (Törnkvist et al., 2011), Hong Kong (Chen et al., 2013), different
288 cities in China (Zhang et al., 2013), Belgium (Xu et al., 2015), and the USA (Schechter et al., 2004).
289 Among the other FRs, TBA was detected only in fish/seafood, with concentrations up to 6.6 ng/g
290 ww (salmon fillet). The fact that TBA was measured exclusively in this food category can indicate
291 its primary natural origin from the marine environment (Moore et al., 2002; Vetter and Stoll, 2002),
292 rather than its transfer from plastic used for packaging. For the other compounds, the results pointed
293 out a generally low contamination, with all values < LOQ.

294

295 **4. Conclusions**

296 A reliable method for the quantification of PBDEs and other HFRs in food was optimized and
297 validated. A high extraction performance and an efficient two-step clean-up procedure enabled the
298 accurate determination and quantification of the target compounds in a wide variety of food
299 matrices, with different characteristics and lipid content. This method has been successfully applied
300 to the determination of PBDEs and other FRs in 20 types of food items purchased in Belgian
301 supermarkets. PBDEs were found as the prevalent contaminants among the different food
302 categories and the highest FR contamination were found in fish/seafood.

303

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307

308 **References**

- 309 Andersson, P. L., Öberg, K., Örn, U. (2006). Chemical characterization of brominated flame
310 retardants and identification of structurally representative compounds. *Environmental Toxicology*
311 *and Chemistry*, 25, 1275-1282.
- 312 Birnbaum, L. S., Staskal, D. F. (2004). Brominated flame retardants: cause for concern?
313 *Environmental Health Perspective*, 112, 9-17.
- 314 Björklund, J., Tollbäck, P., Hiärne, C., Dyremark, E., Östman, C. (2004). Influence of the injection
315 technique and the column system on gas chromatographic determination of polybrominated
316 diphenyl ethers. *Journal of Chromatography A*, 1041, 201-210.
- 317 Chen, M. Y. Y., Wong, W. W. K., Choi, K. K., Yip, Y. C., Ho, Y. Y., Xiao, Y. (2013). Dietary
318 exposure of the Hong Kong adult population to polybrominated diphenyl ethers (PBDEs): results
319 of the first Hong Kong Total Diet Study. *Food Additives & Contaminants*, 30, 1780-1787.
- 320 Commission Recommendation (2014/118/EU) on the monitoring of traces of brominated flame
321 retardants in food.
- 322 Commission Regulation No 589/2014 laying down methods of sampling and analysis for the control
323 of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain food stuff and
324 repealing Regulation (EU) No 252/2012.
- 325 Covaci, A., Voorspoels, S., Ramos, L., Neels, H., Blust, R. (2007). Recent developments in the
326 analysis of brominated flame retardants and brominated natural compounds. *Journal of*
327 *Chromatography A*, 1153, 145-171.
- 328 Covaci, A., Harrad, S., Abdallah, M. A., Ali, N., Law, R. J., Herzke, D., de Wit, C. A. (2011).
329 Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour
330 *Environment International*, 37, 532-556.
- 331 Darnerud, P. O., Atuma, S., Aune, M., Bjerselius, R., Glynn, A., Petersson, K. G., et al. (2006).
332 Dietary intake estimations of organohalogen contaminants (dioxins, PCB, PBDE and chlorinated
333 pesticides, e.g. DDT) based on Swedish market basket data. *Food Chemistry and Toxicology*, 44,
334 1597-606.
- 335 De Jourdan, B., Hanson, M., Muir, D.C. G., Solomon, K. R. (2013). Environmental fate of three
336 novel brominated flame retardants in aquatic mesocosms. *Environmental Toxicology and*
337 *Chemistry*, 32, 1060-8.
- 338 de Wit, C.A., Kierkegaard, A., Ricklund, N., Sellström. (2011). Emerging Brominated Flame
339 Retardants in the Environment. In: Brominated flame retardants in the environment. Eds Eljarrat
340 E and Barceló D. *The Handbook of Environmental Chemistry*. Springer.
- 341 Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending
342 for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use
343 of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromo-
344 diphenyl ether).
- 345 Domingo, J. L. (2012). Polybrominated diphenyl ethers in food and human dietary exposure: A
346 review of the recent scientific literature. *Food and Chemical Toxicology*, 50, 238-249.

EFSA Panel on Contaminants in the Food Chain (CONTAM) (2010). Scientific Opinion on Polybrominated Biphenyls (PBBs) in Food. 8 (10)1789 <www.efsa.europa.eu/en/scdocs/doc/1789.pdf>.

European Court of Justice. Cases C-14/06 and C-295/06, Judgement of the Court, 1 April 2008, Directive 2002/95/EC and Commission Decision 2005/717/EC.

European Commission report on potential alternatives to deca-BDE. http://ecb.jrc.ec.europa.eu/documents/Existingchemicals/Review_on_production_process_of_decaBDE (accessed January 16, 2011).

Gauthier, L. T., Hebert, C. E., Weseloh, D. V. C., Letcher, R.J. (2007). Current-use flame retardants in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes. *Environmental Science and Technology*, 41, 4561–4567.

Kalachova, K., Cajka, T., Sandy, C., Hajslova, J., Pulkrabova, J. (2013). High throughput sample preparation in combination with gas chromatography coupled to triple quadrupole tandem massspectrometry (GC–MS/MS): A smart procedure for (ultra) trace analysis of brominated flame retardants in fish. *Talanta*, 105, 109–116.

Kakimoto, K., Nagayoshi, H., Yoshida, J., Akutsu, K., Konishi, Y., Toriba, A., Hayakawa, K. (2012). Detection of Dechlorane Plus and brominated flame retardants in marketed fish in Japan, *Chemosphere*, 89, 416–419.

Kim, J., Son, M., Kim, J., Suh, J., Kang, Y., Chang, Y. S. (2014). Assessment of Dechlorane compounds in foodstuffs obtained from retail markets and estimates of dietary intake in Korean population. *Journal of Hazardous Materials*, 275, 19–25.

Koschier, F., Gallo, M. A., Feng, X., Baxter, G. E., Preston, R., Stevens, K., Powers, W. (2011). Toxicological studies on 2,4,6-tribromoanisole. *Food and Chemical Toxicology*, 49, 2074–2080.

Lehotay, S. J., Mañtovská, K., Yun, S.J. (2005). Evaluation of Two Fast and Easy Methods for Pesticide Residue Analysis in Fatty Food Matrixes. *Journal of AOAC International*, 88, 630–638.

Moore, M. R., Vetter, W., Gaus, C., Shaw, G. R., Muller, J. F. (2002). Trace organic compounds in the marine environment. *Marine Pollution Bulletin*, 45, 62–68.

Na, S., Kim, M., Paek, O., Kim, Y. (2013). Dietary assessment of human exposure to PBDEs in South Korea. *Chemosphere*, 90, 1736–1741.

Roosens, L., Dirtu, A., Goemans, G., Belpair, C., Gheorghe, A., Neels, H., Blust, R., Covaci, A. (2008). Brominated flame retardants and organochlorine contaminants in fish samples along Scheldt River, Belgium. *Environment International*, 34, 976–83.

SANCO, Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed, Doc. N°SANCO/12495/2011 (2011).

Sapozhnikova, Y., Lehotay, S. J. (2013). Multi-class, multi-residue analysis of pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers and novel flame retardants in fish using fast, low-pressure gas chromatography–tandem mass spectrometry. *Analytica Chimica Acta*, 758, 80–92.

Schecter, A., Papke, O., Tung, K. C., Staskal, D., Birnbaum, L. (2004). Polybrominated Diphenyl Ethers Contamination of United States Food. *Environmental Science and Technology*, 38, 5306–5311.

Shim, I. W., Jo, H. J., Park, H.S., Kim, S. K., Kim, Y. G. (2006). Preparation and flame retardancy effect of polyurethane coatings containing phosphorus and chlorine. *Polymer-Korea*, 30, 238–246.

391 Tlustos, C., Fernandes, A., Rose, M. (2010). The emerging BFRs – hexabromobenzene (HBB),
 392 bis(246-tribromophenoxy) ethane (BTBPE) and decabromodiphenylethane (DBDPE) – in Irish
 393 foods. *Organohalogen Compounds*, 72, 1577-1579.

394 Törnkvist, A., Glynn, A., Aune, M., Darnerud, P. O., Ankarberg, E. H. (2011). PCDD/F, PCB,
 395 PBDE, HBCD and chlorinated pesticides in a Swedish market basket from 2005 – Levels and
 396 dietary intake estimations. *Chemosphere*, 83, 193–199.

397 Verreault, J., Gebbink, W. A., Gauthier, L. T., Gabrielsen, G. W., Letcher, R. J. (2007). Brominated
 398 Flame Retardants in Glaucous Gulls from the Norwegian Arctic: More Than Just an Issue of
 399 Polybrominated Diphenyl Ethers. *Environmental Science and Technology*, 41, 4925-4931.

400 Vetter, W., Stoll, E. (2002). Qualitative determination of bioaccumulative halogenated natural
 401 products in food and novel food. *European Food Research Technology*, 215, 523–528.

402 Vetter, W., Hahn, M. E., Tomy, G., Ruppe, S., Vatter, S., Chahbane, N., Lenoir, D., Schramm, K.
 403 W., Scherer, G. (2004). Biological Activity and Physicochemical Parameters of Marine
 404 Halogenated Natural Products 2,3,3',4,4',5,5'-Heptachloro-1'-Methyl-1,2'-Bipyrrole and 2,4,6-
 405 Tribromoanisole. *Arch. Environ. Contam. Toxicol*, 48, 1–9.

406 Voorspoels, S., Covaci, A., Neels, H., Schepens, P. (2007). Dietary PBDE intake: a market-basket
 407 study in Belgium. *Environment International*, 33, 93–7.

408 Watanabe, I., Sakai, S. (2003). Environmental release and behavior of brominated flame retardants.
 409 *Environment International*, 29, 665–682.

410 Xu, F., García-Bermejo, A., Malarvannan, G., Gómara, B., Neels, H., Covaci, A. (2015). Multi-
 411 contaminant analysis of organophosphate and halogenated flame retardants in food matrices
 412 using ultrasonication and vacuum assisted extraction, multi-stage cleanup and gas
 413 chromatography–mass spectrometry. *Journal of Chromatography A*, 1401, 33–41.

414 Zhou, S. N., Reiner, E. J., Marvin, C., Kolic, T., Riddell, N., Helm, P., Dorman, F., Misselwitz, M.,
 415 Brindle, I. D. (2010). Liquid chromatography–atmospheric pressure photoionization tandem
 416 mass spectrometry for analysis of 36 halogenated flame retardants in fish. *Journal of*
 417 *Chromatography A*, 1217, 633-641.

418 Zheng, X. B., Wu, J. P., Luo, X. J., Zeng, Y. H., She, y. Z., Mai, B. X. (2012). Halogenated flame
 419 retardants in home-produced eggs from an electronic waste recycling region in South China:
 420 levels, composition profiles, and human dietary expo-sure assessment, *Environment*
 421 *International*, 45, 122-128.

422 Zhang, L., Luo, X. J., Liu, H. Y., Yu, L. H., Chen, S. J., Mai, B. X. (2011). Bioaccumulation of
 423 several brominated flame retardants and dechlorane plus in water birds from an e-waste
 424 recycling region in South China: associated with trophic level and diet sources, *Environmental*
 425 *Science and Technology*, 45, 400-405.

426 Zhang, L., Li, J., Zhao, Y., Li, X., Wen, S., Shen, H., Wu, Y. (2013). Polybrominated Diphenyl
 427 Ethers (PBDEs) and Indicator Polychlorinated Biphenyls (PCBs) in Foods from China: Levels,
 428 Dietary Intake, and Risk Assessment. *Journal of Agricultural and Food Chemistry*, 61, 6544-
 429 6551.

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Fig. 1. Overview of the sample preparation procedure for halogenated flame retardant in food

Fig. 2. Chromatograms of a standard mixture of (A) PBDEs (1 ng), (B) other HFRs (2 ng), and (C) TBA (1 ng) on GC-ECNI/MS.

Table 1. Retention times (RT), quantifier and qualifier ions, regression data, and LOQ of the target compounds.

Compounds	RT min	quantifier and qualifier ions (m/z)	begin time windows (min)	R ²	working range ng	LOQ*** ng/g ww
BDE-103 (<i>IS</i> [*])	11.58	79/81	4	-	1	-
TBA	4.41	79/81		0.998	0.032-1	0.05
BDE-28	8.06	79/81		0.999	0.032-1	0.005
HBB	9.54	79/81		0.999	0.064-2	0.02
BDE-49	9.91	79/81		1	0.032-1	0.005
BDE-47	10.29	79/81		0.999	0.032-1	0.005
BDE-100	12.41	79/81		0.999	0.032-1	0.005
BDE-99	13.25	79/81		0.983	0.032-1	0.005
BDE-128 (<i>IS</i>)	17.96	79/81	17	-	1	-
BDE-154	15.25	79/81		0.996	0.032-1	0.005
BDE-153	16.42	79/81		0.999	0.032-1	0.005
BDE-138	17.36	79/81		0.998	0.032-1	0.005
BDE-183	18.03	79/81		0.997	0.032-1	0.005
BTBPE	18.29	79/81		0.997	0.064-2	0.01
¹³ C-TBB (<i>IS</i>)	13.32	363/365	21	-	10	-
TBB	13.5	357/359		0.998	0.064-2	0.2
¹³ C-TBPH (<i>IS</i>)	18.55	470/390		-	10	-
TBPH	18.61	464/384		0.999	0.064-2	0.2
¹³ C-DP-s (<i>IS</i>)	18.66	662/664		-	2.5	-
s-DP	18.66	652/654		0.997	0.064-2	0.02
¹³ C-DP-a (<i>IS</i>)	18.85	662/664		-	2.5	-
a-DP	18.85	652/654		0.999	0.064-2	0.02
¹³ C-BDE-209 (<i>IS</i>)	21.83	495/497		-	6.25	-
BDE-209	21.83	485/487		0.999	0.32-10	0.1
CB-207 (<i>RS</i> ^{**})	12.03	462/464		-	5	-

^{*}*IS* = internal standard

^{**}*RS* = recovery standard

^{***}as estimated from the sample intake of 2 g

Table 2. Trueness data of the spiking experiments (extra virgin olive oil – EVOO) and using SRM 1945.

	Spiking experiments on EVOO ^a						SRM 1945 ^b	
	low level (ng)	Accuracy %	RSD %	high level (ng)	Accuracy %	RSD %	Accuracy %	RSD %
BDE 28	0.16	109	3	0.80	107	1	-	-
BDE 49	0.16	121	7	0.80	119	4	-	-
BDE 47	0.16	101	2	0.80	103	3	101	13
BDE 100	0.16	127	4	0.80	115	4	102	9
BDE 99	0.16	104	2	0.80	121	5	74	11
BDE154	0.16	91	4	0.80	88	3	113	23
BDE153	0.16	113	7	0.80	106	2	109	14
BDE 138	0.16	76	3	0.80	65	3	-	-
BDE183	0.16	115	12	0.80	93	7	-	-
BDE 209	1.6	106	1	8	103	2	-	-
TBA	0.16	59	28	0.80	85	16	-	-
HBB	0.32	93	2	1.6	94	2	-	-
TBB	0.32	107	2	1.6	87	6	-	-
BTBPE	0.32	75	6	1.6	76	1	-	-
TBPH	0.32	118	14	1.6	121	1	-	-
s-DP	0.32	117	11	1.6	95	3	-	-
a-DP	0.32	105	2	1.6	91	1	-	-

^a $n = 3$

^b $n = 5$

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Table 3. Repeatability data for BFRs in different food matrices (in each case n=3).

	CHICKEN EGG					SMOKED SALMON				MILK			
	6.4% lipid ^a					6.2% lipid				10% lipid			
	spiking level ng	mean conc. ng/g	sd ng/g	RSD %	accuracy %	mean conc. ng/g	sd ng/g	RSD %	accuracy %	mean conc. ng/g	sd ng/g	RSD %	accuracy %
BDE 28	0.80	1.09	0.02	2	136	1.19	0.03	2	149	1.09	0.01	1	136
BDE 49	0.80	0.98	0.03	3	122	1.04	0.02	2	130	0.92	0.01	1	115
BDE 47	0.80	0.90	0.01	0.1	113	1.28	0.03	2	160	0.87	0.05	5	109
BDE 100	0.80	0.83	0.03	4	104	0.96	0.05	5	120	0.86	0.01	0.5	108
BDE 99	0.80	0.64	0.06	10	81	0.91	0.02	3	114	0.50	0.03	6	74
BDE154	0.80	0.37	0.02	6	47	0.40	0.01	1	50	0.41	0.01	2	51
BDE153	0.80	0.42	0.05	11	52	0.47	0.01	2	59	0.45	0.02	5	56
BDE 138	0.80	0.49	0.02	5	62	0.51	0.02	4	64	0.52	0.02	5	65
BDE183	0.80	0.34	0.04	11	42	0.32	0.01	2	40	0.35	0.02	5	44
BDE 209	8	8.21	0.05	1	103	7.92	0.17	2	99	7.89	0.06	1	99
TBA	0.80	0.58	0.05	9	73	0.54	0.16	9	68	0.69	0.15	22	87
HBB	1.6	1.17	0.02	2	73	1.51	0.06	4	94	1.49	0.04	3	93
TBB	1.6	1.48	0.10	7	93	1.54	0.02	1	96	1.48	0.05	3	92
BTBPE	1.6	1.11	0.06	5	69	1.13	0.02	2	71	1.22	0.16	13	76
TBPH	1.6	1.51	0.07	5	94	1.52	0.02	1	95	1.74	0.11	6	109
s-DP	1.6	1.44	0.07	5	90	1.48	0.10	7	93	1.47	0.11	7	92
a-DP	1.6	1.45	0.02	1	91	1.44	0.08	6	90	1.46	0.10	7	91

	COD					CHICKEN BREAST				EVOO			
	0.1% lipid					0.6% lipid				91% lipid			
	spiking level ng	mean conc. ng/g	sd ng/g	RSD %	accuracy %	mean conc. ng/g	sd ng/g	RSD %	accuracy %	mean conc. ng/g	sd ng/g	RSD %	accuracy %
BDE 28	0.80	0.50	0.01	1	125	0.48	0.02	4	120	5.16	0.17	3	129
BDE 49	0.80	0.46	0.02	3	115	0.45	0.00	1	113	4.40	0.14	3	110
BDE 47	0.80	0.45	0.02	5	111	0.41	0.01	2	103	4.27	0.22	5	107
BDE 100	0.80	0.43	0.01	3	107	0.41	0.01	3	103	4.33	0.34	8	108
BDE 99	0.80	0.48	0.03	6	119	0.17	0.03	15	80	9.07	1.05	12	138
BDE154	0.80	0.22	0.01	6	55	0.20	0.01	3	51	1.90	0.13	7	47
BDE153	0.80	0.25	0.02	7	63	0.23	0.02	7	59	1.99	0.16	8	50
BDE 138	0.80	0.27	0.02	6	69	0.26	0.01	4	64	2.46	0.11	4	62
BDE183	0.80	0.20	0.01	5	51	0.19	0.01	4	48	1.64	0.09	6	41
BDE 209	8	3.91	0.10	3	98	3.83	0.13	3	96	38.27	0.19	0.5	96
TBA	0.80	0.30	0.05	16	75	0.41	0.03	8	104	3.15	0.44	14	79
HBB	1.6	0.75	0.03	5	94	0.73	0.01	1	91	6.73	0.46	7	84
TBB	1.6	0.77	0.03	4	96	0.76	0.04	5	95	6.70	0.24	4	84
BTBPE	1.6	0.77	0.08	10	96	0.72	0.01	1	89	5.35	0.08	1	67
TBPH	1.6	0.76	0.04	5	95	0.77	0.01	1	96	8.88	0.20	2	111
s-DP	1.6	0.75	0.05	7	93	0.69	0.03	4	87	6.84	0.62	9	85
a-DP	1.6	0.73	0.03	4	92	0.74	0.01	1	92	7.01	0.46	7	88

^a% lipids is given on wet weight basis.

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458 **Table 4.** Estimation of measurement uncertainty.
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	CHICKEN EGG				SMOKED SALMON				MILK				COD				CHICKEN BREAST				EVOO				$\bar{U}^e$
	u_r^a	u_t^b	u_c^c	U^d	u_r	u_t	u_c	U	u_r	u_t	u_c	U	u_r	u_t	u_c	U	u_r	u_t	u_c	U	u_r	u_t	u_c	U	
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	
BDE 28	2	1	3	5	2	1	3	5	1	1	2	3	1	1	2	3	4	1	4	9	3	1	4	7	6
BDE 49	3	3	4	8	2	3	4	8	1	3	3	7	3	3	5	9	1	3	3	6	3	3	4	9	8
BDE 47	0	6	6	12	2	6	6	13	5	6	8	16	5	6	8	16	2	6	6	13	5	6	8	16	14
BDE 100	4	7	8	16	5	7	9	17	0	7	7	14	3	7	8	16	3	7	8	15	8	7	11	21	16
BDE 99	10	10	14	28	3	10	10	21	6	10	12	23	6	10	12	23	15	10	18	37	12	10	15	31	27
BDE154	6	12	13	27	1	12	12	24	2	12	12	24	6	12	13	27	3	12	12	25	7	12	14	28	26
BDE153	11	7	13	27	2	7	7	14	5	7	8	17	7	7	10	20	7	7	10	19	8	7	11	21	20
BDE 138	5	2	5	10	4	2	5	9	5	2	5	10	6	2	7	13	4	2	5	9	4	2	5	9	10
BDE183	11	5	12	24	2	5	6	12	5	5	7	14	5	5	7	15	4	5	7	13	6	5	8	16	16
BDE 209	1	1	1	2	2	1	2	4	1	1	1	2	3	1	3	6	3	1	4	7	0	1	1	2	4
TBA	9	13	16	31	7	13	15	29	22	13	25	51	16	13	21	41	8	13	15	30	14	13	19	38	37
HBB	2	1	2	4	4	1	4	8	3	1	3	6	5	1	5	9	1	1	2	3	7	1	7	14	7
TBB	7	2	7	14	1	2	3	5	3	2	4	8	4	2	4	9	5	2	5	11	4	2	4	9	9
BTBPE	5	2	6	11	2	2	3	5	13	2	13	27	10	2	10	20	1	2	2	4	1	2	2	5	12
TBPH	5	5	6	13	1	5	5	10	6	5	8	15	5	5	7	13	1	5	5	9	2	5	5	10	12
s-DP	5	4	6	13	7	4	8	16	7	4	8	16	7	4	8	16	4	4	6	12	9	4	10	20	16
a-DP	1	1	2	3	6	1	6	12	7	1	7	14	4	1	5	9	1	1	1	2	7	1	7	13	9

460 ^a u_r : uncertainty of repeatability
 461 ^b u_t : uncertainty of trueness
 462 ^c u_c : combined uncertainty
 463 ^d U : expanded uncertainty
 464 ^e $\bar{U}$: mean expanded uncertainty of the method

465 **Table 5.** Concentrations of PBDEs and other emerging FRs (ng/g ww) in the analyzed food samples.

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	BDE 28	BDE 49	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 138	BDE 183	BDE 209	Σ PBDEs	TBA	HBB	TBB	BTBPE	TBPH	s-DP	a-DP
<i>Validation matrices</i>																		
Smoked salmon	<0.005	0.03	0.10	0.03	<0.005	0.02	<0.005	<0.005	<0.005	<0.10	0.18	0.88	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Cod	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Chicken Eggs	<0.005	<0.005	0.04	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	0.04	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Chicken Breast	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Cow Milk	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
EVOO	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
<i>Fish/seafood</i>																		
Tuna fillet	0.03	0.01	0.04	0.01	<0.005	0.02	<0.005	<0.005	<0.005	<0.10	0.10	0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Trout	0.01	0.03	0.16	0.04	<0.005	0.02	<0.005	<0.005	<0.005	0.11	0.37	1.96	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Prawn	<0.005	<0.005	0.01	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	0.01	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Sardine	0.03	<0.005	0.05	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.20	0.27	0.23	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Mackerel	0.01	<0.005	0.03	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.25	0.29	0.06	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Mussel	<0.005	0.46	1.20	0.36	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	2.02	2.76	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Herring	0.24	0.16	0.44	0.12	<0.005	0.03	0.02	<0.005	<0.005	<0.10	1.02	0.51	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Anchovy	0.04	<0.005	0.06	<0.005	<0.005	<0.005	0.06	<0.005	<0.005	0.18	0.34	0.14	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Salmon fillet	<0.005	0.03	0.16	0.03	<0.005	0.01	<0.005	<0.005	<0.005	0.10	0.33	6.66	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
<i>Other categories</i>																		
Rabbit	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Turkey Breast	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Quail eggs	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Potato chips	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	<LOQ	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02
Biscuits	<0.005	<0.005	0.04	0.01	<0.005	<0.005	<0.005	<0.005	<0.005	<0.10	0.06	<0.05	<0.02	<0.20	<0.01	<0.20	<0.02	<0.02

467