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Brominated flame retardants in Canadian chicken egg yolks

D.F.K. Rawn[a]*, A. Sadler[a], S.C. Quade[a], W.-F. Sun[a], B.P.-Y. Lau[a], I. Kosarac[a]†, S. Hayward[b] and J.J. Ryan[a]

[a]*Food Research Division and* [b]*Biostatisitcs and Computer Applications Division, Bureau of Chemical Safety, Health Products and Food Branch, Health Canada, Address Locator: 2203C, 251 Sir Frederick Banting Driveway, Tunney's Pasture, Ottawa, ON, Canada, K1A 0K9*

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Chicken eggs categorised as conventional, omega-3 enriched, free range and organic were collected at grading stations in three regions of Canada between 2005 and 2006. Free run eggs, which were only available for collection from two regions, were also sampled during this time frame. Egg yolks from each of these egg types ($n = 162$) were analysed to determine brominated flame retardant levels, specifically polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD). PBDEs were detected in 100% of the 162 samples tested, while HBCD was observed in 85% of the egg yolks. Total PBDE concentrations in egg yolks ranged from 0.018 to 20.9 ng g^{-1} lipid (median = 3.03 ng g^{-1} lipid), with PBDE 209 identified as being the major contributor to ΣPBDE concentrations. In addition to PBDE 209, PBDE 99, 47, 100, 183 and 153 were important contributors to ΣPBDE concentrations. Total HBCD concentrations ranged from below the limit of detection to a maximum concentration of 71.9 ng g^{-1} lipid (median = 0.053 ng g^{-1} lipid). The α-isomer was the dominant contributor to ΣHBCD levels in Canadian egg yolks and was the most frequently detected HBCD isomer. ΣPBDE levels exhibited large differences in variability between combinations of region and type. ΣHBCD concentrations were not significantly different among regions, although differences were observed between the different types of egg yolks analysed in the present study.

Keywords: gas chromatography/mass spectrometry (GC/MS); clean-up; exposure; environmental contaminants; eggs

Introduction

The research associated with brominated flame retardants (BFRs) has largely focused on the polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), in part because they are added to consumer products, rather than covalently bound to the products as is the case for tetrabromobisphenol-A (TBBPA) (de Wit 2002). As a result, they are subject to leaching during production and application processes, to volatilisation and leaching during use, and to loss following product disposal (Voorspoels et al. 2003). PBDEs and HBCD are detected in a wide variety of environmental compartments and biological tissues. North American concentrations are higher than observed in Europe with elevated levels being related to differences in registration status over time (Vorkamp et al. 2011). Human exposure to these compounds via ingestion of food, in addition to oral and dermal intake of dust and soil have been reported in the literature (Roosens et al. 2010). Exposure to BFRs is of concern because they are associated with negative health effects in experimental animals, including neurotoxic and reproductive effects, impacts on the thyroid system and liver enzyme activity (de Wit 2002; Birnbaum and Staskal 2004; Abdallah et al. 2008; Ema et al. 2008; Öberg et al. 2010).

PBDEs and HBCDs are amenable to analysis using existing sample preparation methodologies applied to other persistent organic pollutants (POPs) because of their similar physical–chemical properties. The PBDEs are bromine substituted aromatic ethers, structurally related to the polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs). The numbering system for individual PBDE congeners follows that of the PCBs. In contrast to PCBs, only a limited number of individual congeners are present in commercial PBDE mixtures (Birnbaum and Staskal 2004). HBCDs are not aromatic, but are rather cyclic aliphatic hydrocarbons (Covaci et al. 2006).

Foods of animal origin are generally thought to be the greatest source of exposure to humans of highly persistent, bioaccumulative compounds and, therefore, PBDEs and HBCDs have been studied to determine levels of these contaminants in a wide range of foods

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*Corresponding author. Email: thea.rawn@hc-sc.gc.ca
†Present address: Chemistry Research Division, Environmental Health Science and Research Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Address Locator, 0800C, Tunney's Pasture, Ottawa, ON, Canada, K1A 0K9.

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(Huwe et al. 2002; Domingo 2004; Huwe and Larsen 2005; Darnerud et al. 2006; Gómara et al. 2006; Voorspoels et al. 2007). Market basket studies, in addition to commodity-based studies, have been performed to determine dietary exposure to the BFRs. Eggs are an important commodity in Canada with the average Canadian consuming three to four eggs each week (Canadian Egg Marketing Agency 2007). They also are considered to be a good indicator of ambient POP levels (Windal et al. 2009). POPs in free range eggs (eggs from chickens allowed free access to outdoors) and eggs laid by home-raised chickens have been reported to have elevated levels relative to those produced commercially in some European countries (Schoeters and Hoogenboom 2006; de Vries et al. 2006; van Overmeire et al. 2006). Recently, a Belgian study reported elevated PCDD/F levels in home-produced eggs relative to commercially produced eggs (van Overmeire et al. 2009; Waegeneers et al. 2009). In contrast, PBDE and HBCD levels in the home-produced eggs were similar to levels reported in other regions of Europe and North America (Covaci et al. 2009).

Eggs from three discrete regions of Canada were collected to establish whether POP levels in Canadian organic eggs were higher than concentrations in eggs from other production types, similar to what has been observed in Europe. Commercial eggs from the four major production types (conventional, omega-3 enriched, free range, organic) in Canada were collected. When available, free-run eggs also were collected. Egg categories vary in Canada according to production type, with conventional eggs being produced by chickens raised in cages. Free range chickens are provided with access to the outdoors, while free run chickens have freedom to move around in the barn and are not restricted to cages. Organic chickens must be raised following certified organic production, allowed access to the outdoors and fed organic feed. Omega-3-enriched eggs are produced by chickens fed a diet enriched in omega-3 fatty acids.

Materials and methods

Sample collection

A minimum of ten large chicken eggs belonging to each of the four main categories of eggs on the Canadian market (i.e., conventional, omega-3 enriched, free range, and organic) were collected from separate producers in British Columbia (BC), Quebec and the Maritime provinces, representing, western, central and eastern Canada, respectively in 2005/06. Eggs identified as free run were only collected from Quebec and the Maritimes due to a lack in availability from BC. Egg collection was performed by Canadian Food Inspection Agency (CFIA) inspectors at grading stations. Upon collection, samples were shipped to the lab and frozen at −18°C until ready for analysis.

Reagents

HPLC-grade sulphuric acid as well as HPLC/GC residue-grade acetone, dichloromethane (DCM), hexane and toluene were purchased from EMD (Ottawa, ON, Canada). Distilled water was prepared using a Barnstead Nanopure Diamond water system (Thermo, Waltham, MA, USA). Anhydrous sodium sulphate (Na_2SO_4) was obtained from Fisher Scientific (Ottawa, ON, Canada). Silica gel (60–200 mesh) was obtained from J.T. Baker (Ottawa, ON, Canada), Florisil (60–100 mesh) and celite 545 were obtained from Fisher Scientific (Ottawa, ON, Canada). Carbopack C (60–80 mesh) was obtained from Supleco (Bellefonte, PA, USA). Analytical standards of analytes ($^{12}C_{12}$), surrogates ($^{13}C_{12}$) and performance standards ($^{12}C_{12}$ and $^{2}H_{18}$) were purchased from Wellington Laboratories (Guelph, ON, Canada) and Cambridge Isotope Laboratories (Andover, MA, USA), as available.

Sample preparation

A reagent blank and an internal laboratory QC subsample of homogenised butter from a sample that has been analysed many times, was included with each set of samples analysed. Eggs were thawed at room temperature and yolks were separated from whites. The first eggs to be tested ($n = 4$) were analysed separately (whites and yolks) to determine whether POPs were present in whites as well as the yolks. Following confirmation that POP levels in whites were below the limit of detection ($n = 4$), the lipid-rich yolks were retained for extraction and analysis. Individual yolks (12–36 g) were weighed into Erlenmeyer flasks and surrogate standards (500 pg $^{13}C_{12}$-labelled PBDE 15, 28, 47, 99, 100, 153, 154, 183, 200 and 209; and 10 ng $^{13}C_{12}$-labelled α, β- and γ-HBCD) were added. The samples were homogenised for 1 min with 80 ml acetone–hexane (2:1) using a Polytron®, the phases were allowed to separate and the hexane layer was transferred to a 250 ml separatory funnel. The samples were re-homogenised for 1 min with 40 ml hexane, and after phase separation the hexane layer was combined with the first hexane fraction. Deionised water (15 ml) was added to each separatory funnel and slowly mixed. The water phase was then removed and the hexane fraction was collected in a round-bottom flask after passing through a funnel filled with approximately 30 g anhydrous sodium sulphate and the volume was reduced to 100 ml. A subsample (5%) was retained for gravimetric lipid determination and the remaining extract was concentrated to allow for transfer of the extract and rinsing of the flask into a 10 ml volumetric flask.

Because egg yolks are known to contain cholesterol, the raw extracts were taken to a volume of 10 ml in hexane and added to silica gel (2 g) columns, preconditioned with 10 ml hexane. Extracts were eluted with 4 ml hexane to remove cholesterol, diluted to a volume of 80 ml and were further cleaned up through sequential washing in a 250 ml separatory funnel with eight fresh 20 ml volumes of concentrated sulphuric acid; 20 ml deionised water; 20 ml 1% KOH and a final rinse with 20 ml deionised water. The organic extracts were then dried on a bed of anhydrous Na_2SO_4 and collected in a round-bottom flask and reduced in volume to approximately 1 ml.

A 2 g acidic silica gel column (75 g silica gel: 50 g concentrated sulphuric acid) conditioned with 10 ml hexane, and a 100% activated Florisil column (1.5 g), conditioned with 10 ml DCM and 10 ml hexane, were set up in series. The extracts were added to the top of the silica column and 20 ml hexane was used to elute the column, the silica gel column was then removed and a second 20 ml aliquot of hexane was added to the Florisil column. This hexane fraction, containing PBDE 209, was removed and 60 ml DCM was added to the top of the Florisil column to elute the remaining PBDEs and HBCD. The extracts were evaporated to 1 ml under vacuum. A final clean-up step was performed on the DCM fraction using a 0.4 g 18% Carbopack C: Celite column (conditioned with 3 ml toluene and 1 ml 1:1 DCM: hexane) where the analytes were eluted with 1 ml (1:1) hexane: DCM, evaporated to dryness and reconstituted with 10 μl of a 20 pg μl^{-1} mixture of the performance standard containing PCB 200, 209 and decachlorodiphenyl ether in toluene and placed into v-vials for gas chromatographic-high resolution mass spectrometric analysis. Once the PBDE analyses were completed, samples were concentrated just to dryness using a gentle stream of nitrogen and reconstituted with 5 ng deuterated $C_{12}{}^2H_{18}Br_6$ HBCD performance standard in 100 μl methanol–water (80:20) in preparation for the liquid chromatographic-mass spectrometric analysis.

The hexane fraction, containing PBDE 209, was evaporated to dryness and re-constituted in 10 μl of 20 pg μl^{-1} decabromodiphenyl ether and sent for GC-MS analysis.

Analysis

A Micromass Autospec Ultima high-resolution mass spectrometer (Waters Corporation) coupled to an Agilent 6890 gas chromatograph was used in the PBDE analyses. A 15 m J&W DB-5MS, 0.25 mm i.d., 0.1 μm film thickness column was used and 1 μl of each sample was introduced via a cool on-column injector that was set to track the oven temperature. The initial temperature was set to 80°C and held for 1 min, followed by an increase in temperature to 225°C at a rate of 32°C min^{-1}. The temperature was held at 225°C for 1 min and increased at a rate of 3°C min^{-1} to 230°C and held for 8 min. The final increase was set at a rate of 40°C min^{-1} to 295°C. The head pressure initially was 28 kPa and held for 2 min, followed by an increase at a rate of 7 kPa min^{-1} to 83 kPa and held for 15 min with a final increase to 173 kPa at a rate of 69 kPa min^{-1}. Helium was used as the carrier gas and the mass spectrometer was operating in EI positive-ion mode at 50 eV, the trap current was 650 μA and the source temperature was 250°C. The resolution for all analytes was approximately 8000 (10% valley definition).

HBCD was quantified using an Acquity UPLC coupled to a Quattro Premier XE triple quadrupole MS/MS (Waters) with electrospray ionisation in the negative ion detection mode using a 2.1×100 mm, Hypersil Gold C18, 1.9 μm column (Thermo Scientific). Water (mobile phase A) and acetonitrile–methanol (2:1) (mobile phase B) were used in separation of the HBCD isomers and the gradient was as follows: 40% mobile phase B for 1 min, 40–80% mobile phase B by 4 min, 80–90% B by 13 min, then returned to 40% B over 0.5 min where it remained until 18 min. The flow rate was maintained at 0.175 ml min^{-1} and the column temperature was maintained at 15°C to resolve completely the deuterated HBCD analogues from the ^{13}C-labelled and native analogues. The capillary and cone voltage were −3.5 kV and 20 V, respectively. The source temperature and desolvation temperature were 140°C and 400°C, respectively. Cone gas flow and desolvation gas flow were 47 and 947 l h^{-1}, respectively. Argon was the collision gas set at 5×10^{-3} mbar and resolution was established at 90% valley at base for both quadrupole analysers. Transitions monitored for native HBCD, ^{13}C HBCD isomers and deuterated HBCD were $639 \rightarrow 79$, $641 \rightarrow 79$, $641 \rightarrow 81$ and $643 \rightarrow 81$; $651 \rightarrow 79$, $653 \rightarrow 79$, $653 \rightarrow 81$ and $655 \rightarrow 81$; and $656 \rightarrow 79$, $658 \rightarrow 79$, $658 \rightarrow 81$ and $660 \rightarrow 81$, respectively. Dwell times were set to 5 ms.

Statistical analysis

Analytes below the limit of detection were reported as zero for statistical analysis. Statistical analysis of PBDEs and HBCD levels was performed using SigmaStat for Windows 3.11. Because of the lack of homogeneity of variance for the PBDEs, however, it was necessary to analyse the data using non-parametric techniques, and because of the interaction between region and type, it was necessary to assess the effect of each factor within the levels of the other factor. The non-parametric Kruskal–Wallis test was used to assess the overall significance of each factor (e.g., region of collection, production type). The results were sorted by the mean rank score and contingent groups with no significant differences in score were found.

Results and discussion

Quality assurance/quality control

PBDE amounts that were observed in the reagent blanks analysed with each set of samples were subtracted from the samples in the corresponding set, prior to determination of levels in individual egg yolk samples. Generally, only PBDE 47, 99 and 209 were detected in the reagent blanks. The reagent blanks tested for HBCD levels were consistently observed to have non-detected or negligible levels of all three HBCD analogues.

Average surrogate recoveries in egg yolks ranged from 22% to 70%, for PBDE 209 and PBDE 100, respectively, while average, recoveries for α-HBCD, β-HBCD, γ-HBCD were 36%, 15% and 17%, respectively. Because the method used was optimised for polychlorinated dibenzo-*p*-dioxins, dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), lower recoveries observed for these analytes was not unexpected. PCDD/F and PCB concentrations will be reported elsewhere. Reported concentrations were recovery corrected.

The average instrumental limit of detection for the PBDEs, determined based on a signal-to-noise ratio of (S/N) 3:1, ranged from 0.045 pg (0.001 ng g^{-1} lipid) to 13.9 pg (0.228 ng g^{-1} lipid) for PBDE 15 and PBDE 209, respectively. All samples were blank subtracted for all congeners, although only PBDE 47, 99 and 209 were consistently observed in the reagent blank samples. The average instrumental limit of detection was 5.4 pg (0.010 ng g^{-1} lipid), 3.2 pg (0.006 ng g^{-1} lipid) and 2.8 pg (0.006 ng g^{-1} lipid) for α-, β-, and γ-HBCD, respectively, based on 15 µl injection volumes. HBCD was not observed in any reagent blank samples.

The internal quality assurance system employed in the laboratory was confirmed through the successful participation in the Norwegian Institute of Public Health international interlaboratory study, where several classes of POPs, including PBDEs and HBCD in various foods including eggs are examined (Haug and Becher 2006; Haug et al. 2008). PBDE and HBCD levels observed in the in-house internal quality control sample also were found to range within the expected values.

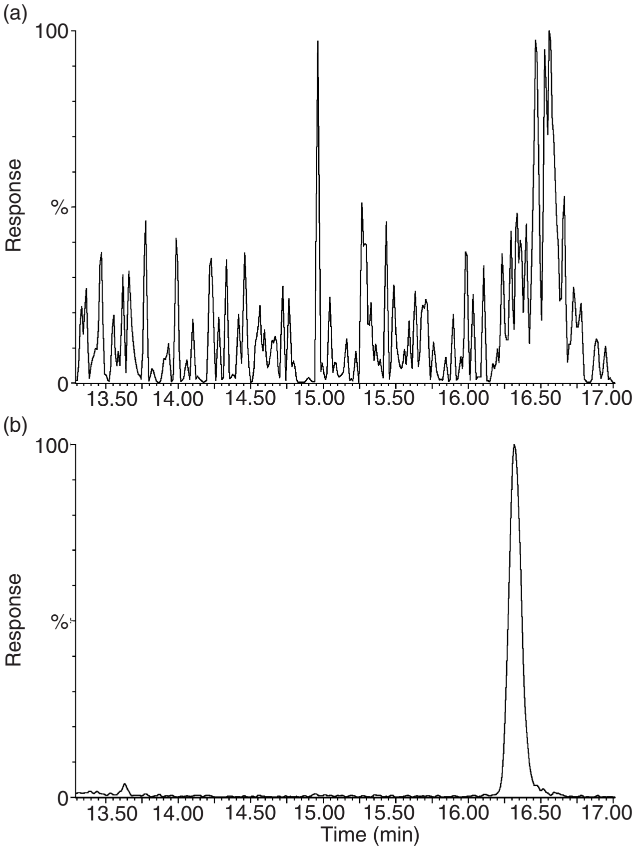

Figure 1. Traces for [M-2Br] ion (m/z 799.333) corresponding to PBDE 209 in (a) egg white and (b) egg yolk from a conventionally produced egg.

PBDE levels and profiles

PBDE and HBCD levels were below the limit of detection in the egg whites ($n = 4$) analysed during confirmation activities to ensure that the correct egg fraction would be the focus of investigation in the present study. Although there has been discussion related to whether PBDE 209 would be associated with lipid rich yolk or present in egg white, in the present study PBDE 209 was not observed in any of the egg whites tested but present above the average limit of detection in 66% of the egg yolks analysed (Figure 1). PBDE 209 was the dominant contributor to ΣPBDE concentrations, when present. The other congeners contributing to ΣPBDE levels in egg yolks were 99 > 47 > 100 > 183 and 153. The detection frequency of these congeners ranged from 96% (PBDE 47 and 99) to 99% (PBDE 100). The very high contribution of PBDE 209 to ΣPBDE levels is consistent with reports obtained from other studies (Gómara et al. 2006; Covaci et al. 2009).

PBDEs were detected in all egg yolks ($n = 162$) analysed in the present study. ΣPBDE concentrations ranged from 0.018 ng g^{-1} lipid to 20.9 ng g^{-1} lipid, the maximum and minimum concentration were both observed in yolks from free run eggs, although

Table 1. Blank-corrected PBDE concentration range (median) in Canadian egg yolks (ng g^{-1} lipid).

Type of egg yolk	Lipid (%)	*n*	PBDE 47	PBDE 99	PBDE 100	PBDE 183	PBDE 209	ΣPBDE[a]
Conventional	12.8–27.0	41	0.039–0.249 (0.096)	0.087–0.442 (0.211)	0.019–0.112 (0.049)	0.001–2.52 (0.076)	<0.228–19.1 (5.15)	0.751–19.7 (5.83)
Omega-3 enriched	13.0–25.2	30	0.038–0.643 (0.125)	0.080–0.841 (0.393)	0.016–0.284 (0.086)	0.068–0.293 (0.032)	<0.228–16.7 (2.87)	0.379–18.3 (3.25)
Free range	15.8–25.0	30	0.016–0.665 (0.078)	0.027–1.92 (0.208)	0.007–0.340 (0.052)	0.006–0.281 (0.047)	<0.228–11.6 (2.69)	0.249–14.6 (2.68)
Organic	17.7–27.9	30	<0.001–0.669 (0.080)	<0.002–1.95 (0.175)	0.001–0.357 (0.040)	0.003–0.055 (0.010)	<0.228–15.7 (0.597)	0.120–16.0 (1.07)
Free run	13.4–27.0	31	<0.001–0.148 (0.090)	<0.002–0.338 (0.205)	<0.001–0.083 (0.043)	0.009–0.182 (0.039)	<0.228–20.4 (11.8)	0.018–20.9 (1.28)

Note: [a]Σ of PBDE 15, 17, 28, 37, 47, 66, 71, 75, 77, 85, 99, 100, 119, 126, 138, 153, 154, 160, 181, 183, 190, 205 and 209.

the low concentration was observed in a yolk collected in Quebec while the yolk from an Atlantic free run egg had the highest observed ΣPBDE concentrations (Table 1). The mean and median ΣPBDE concentrations based on all egg yolks analysed were 5.49 ng g^{-1} lipid and 3.03 ng g^{-1} lipid, respectively.

The PBDE levels in eggs exhibited large differences in variability between various combinations of region and type, and the effects of region and type were not additive (i.e., there was evidence of an interaction) (Figure 2). No one type of yolk from BC had significantly different ΣPBDE levels than yolks from another type. Conventional and free run yolks from the Maritimes, however, had higher ΣPBDE concentrations than other egg types from that region ($p < 0.05$) and free range yolks had lower ΣPBDE concentrations ($p < 0.05$). In eggs collected from Quebec, ΣPBDE concentrations were significantly highest in omega-3-enriched yolks ($p < 0.05$). There was no evidence of an effect of region on levels for free run eggs.

HBCD levels and profiles

HBCD was detected in 85% of the egg yolks analysed in the present study. Concentrations ranged from below the limit of detection to 71.9 ng g^{-1} lipid, although most yolks ($n = 142$) had ΣHBCD concentrations below 1 ng g^{-1} lipid (Table 2). In addition to being the most frequently detected HBCD isomer (83%), α-HBCD was the predominant isomer, contributing 87% to ΣHBCD concentrations in Canadian egg yolks, while β- and γ-contributed less than 1% and 13%, respectively. The β- and γ-isomers were detected in 9% and 27% of the egg yolks analysed in the present study.

HBCD concentrations were not significantly different among regions of collection. Concentrations observed in organic egg yolks collected from the Maritimes, however, were significantly higher than those observed in yolks collected from other production types ($p < 0.001$) (Figure 3).

Comparison of BFR levels with other studies

The inclusion of PBDE 209 does have a major impact on the ΣPBDE levels observed in food samples, including eggs (Covaci et al. 2009, Fernandes et al. 2009). The variability between programs does somewhat limit the comparison of levels obtained by

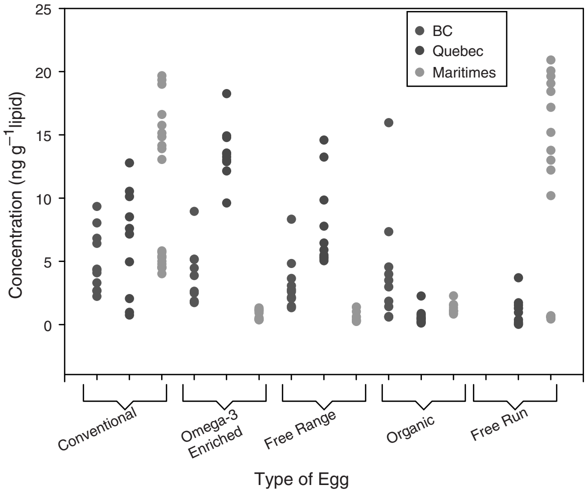

Figure 2. ΣPBDE concentrations in Canadian chicken egg yolks (ng g^{-1} lipid) based on the type of egg, identified by region.

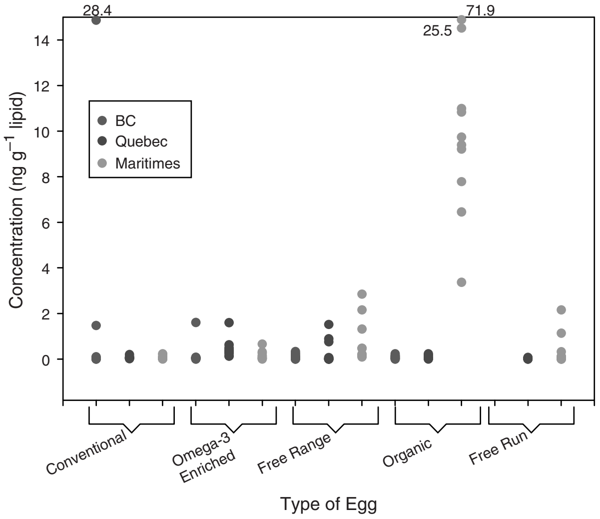

Figure 3. ΣHBCD concentrations in Canadian chicken egg yolks (ng g^{-1} lipid) based on the type of egg, identified by region.

Table 2. HBCD concentration range (median) in Canadian egg yolks (ng g^{-1} lipid).

Type of egg yolk	*n*	α-HBCD	β-HBCD	γ-HBCD	Σ-HBCD
Conventional	41	<0.010–0.307 (0.025)	<0.006–0.022 (<0.006)	<0.006–28.1 (<0.006)	<0.006–28.4 (0.036)
Free range	30	<0.010–2.85 (0.131)	<0.006–0.112 (<0.006)	<0.006–0.645 (<0.006)	<0.006–2.85 (0.134)
Omega-3 enriched	30	<0.010–1.60 (0.121)	<0.006 (<0.006)	<0.006–1.13 (<0.006)	<0.006–1.60 (0.129)
Organic	30	<0.010–70.7 (0.128)	<0.006–0.524 (<0.006)	<0.006–7.05 (<0.006)	<0.006–71.9 (0.137)
Free run	31	<0.010–2.15 (0.028)	<0.006–0.959 (<0.006)	<0.006–0.043 (<0.006)	<0.006–2.15 (0.029)

Table 3. ΣPBDE concentrations ($ng\,g^{-1}$ lipid) in literature studies relative to levels observed in the present work.

Fraction of egg analysed	*n*	ΣPBDE	Congeners measured	Percentage lipid	Country and year of study	Reference
Whole egg	2	0.482–0.530[a]	47, 99, 153, 154, 183	12.0	Spain (2000)	Bocio et al. (2003)
Liquid yolk	1	2.3	17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183	n.a.[b]	Germany (n.a.)	Tritscher et al. (2003)
Whole egg + meat	n.a.	0.136	47, 99, 100, 153, 154	11.0	Finland (1997–1999)	Kiviranta et al. (2004)
Whole egg	5	0.412[c]	47, 99, 100, 153, 154	10.2	Sweden (1999)	Darnerud et al. (2006)
Whole egg	5	0.680[d]	17, 28, 47, 66, 85, 99, 100, 153, 154, 183, 184, 191, 196, 197, 209	10.8	Spain (2003–2005)	Gómara et al. (2006)
Whole egg	n.a.	0.350–1.70[e]	28, 47, 99, 100, 153, 154, 183	10.0	Belgium (2005)	Voorspoels et al. (2007)
Whole egg	1	0. 739	17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183, 209	11.5	USA (2003–2004)	Schecter et al. (2006)
Whole egg	10 pools 10 pools	3.04–13.3[f] $<$LOQ–32.2	28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 209	11.5, 10.4	Belgium (2006) Belgium (2007)	Covaci et al. (2009)
Whole egg	20	0.87–4.43	17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183, 209	n.a.	Ireland (2006–2007)	Fernandes et al. (2009)
Yolk only	162	0.018–20.9	15, 17, 28, 37, 47, 66, 71, 75, 77, 85, 99, 100, 119, 126, 138, 153, 154, 160, 181, 183, 190, 205, 209	21.1	Canada	Present study

Notes: [a]Concentration range based on levels < LOD reported as zero to < LOD reported as 0.5 LOD.
[b]Not available.
[c]Mean.
[d]Median.
[e]Concentration range based on levels < LOD reported as zero to < LOD reported as the LOD.
[f]Median and maximum.

different researchers. Additionally, most researchers analyse the whole egg, rather than yolks only, however, a comparison of results on a lipid weight basis does allow for comparison of PBDE levels among different research groups.

The ΣPBDE concentrations observed in the present study are within the range reported in the literature for eggs (Table 3). The range in ΣPBDE concentrations observed in Canadian egg yolks is greater than reported by most researchers (Table 3), although a larger number of individual egg yolks were measured than is generally reported. The highest concentration observed in the present study (20.9 $\mathrm{ng\,g^{-1}}$ lipid) was in a commercially produced free run egg yolk collected from the Maritimes, but was below the maximum level reported by Covaci et al. (2009) (39.3 $\mathrm{ng\,g^{-1}}$ lipid) in eggs from home produced chickens that were fed kitchen waste.

Although HBCD has been reported at concentrations from below the limit of detection to levels in excess of 5000 $\mathrm{ng\,g^{-1}}$ lipid in eggs of predatory bird species (Lindberg et al. 2004; Jaspers et al. 2005; Gauthier et al. 2007; Janák et al. 2008), reported levels of HBCD in chicken eggs or egg yolks are rare in the literature (Driffield et al. 2008; Covaci et al. 2009). HBCD can be measured as a total using gas chromatography-mass spectrometry, however, isomer separation can only be achieved using liquid chromatography-mass spectrometry (Janák et al. 2008). Covaci et al. (2009) reported ΣHBCD levels ranging from 0.06 to 23.9 $\mathrm{ng\,g^{-1}}$ lipid in Belgian home-produced eggs, which is below the maximum observed in an organic egg yolk analysed in the present study (71.9 $\mathrm{ng\,g^{-1}}$ lipid). Driffield et al. (2008) reported HBCD levels below the limit of detection in eggs (0.19, 0.078 and 0.110 $\mathrm{ng\,g^{-1}}$ fresh weight, for α-HBCD, β-HBCD, γ-HBCD, respectively) collected as part of the UK Total Diet Study in 2004, where the number of eggs sampled was limited in number. Despite the high maximum concentration observed in yolks in the present study, the mean (1.39 $\mathrm{ng\,g^{-1}}$ lipid) and median (0.052 $\mathrm{ng\,g^{-1}}$ lipid) ΣHBCD concentrations were similar to the levels reported by others.

No statistical ($r^2 = 0.012$) relationship between ΣPBDE concentrations and ΣHBCD concentrations were observed in the yolks analysed as part of the present study.

Conclusions

The brominated flame retardants PBDEs and HBCD are present in Canadian egg yolks at levels similar to those observed throughout the world. The inclusion of PBDE 209 in routine analysis of foods has only recently been performed; however, this congener has a large contribution to ΣPBDE concentrations. HBCD is generally present in Canadian egg yolks at detectable levels with α-HBCD being the most frequently detected isomer, with the others (β- and γ-HBCD) observed infrequently. Currently, Canada has no established guidelines for PBDE and HBCD residues in foods.

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