A Survey of Extractable Persistent Organochlorine Pollutants in Chinese Commercial Yogurt

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ABSTRACT

Eighteen Chinese commercial brands of yogurt were collected from supermarkets from December 2002 to April 2003, for characterization of organochlorine pesticides (OCP) and polychlorinated biphenyls (PCB). Besides monitoring OCP and PCB by gas chromatography, the levels of extractable persistent organochlorine (EPOCl; i.e., sulfuric acid-resistant EPOCl) were also determined by instrumental neutron activation analysis. The results indicated that the contamination pattern of the selected OCP and PCB were in the order of dichlorodiphenyltrichloroethanes (DDT) $\approx$ hexachlorocyclohexanes (HCH) $\gg$ aldrin $\geq$ chlordanes $\geq$ heptachlor epoxide and 4–6 chlorinated biphenyls (CB) $\gg$ 7–10 CB, respectively. Furthermore, β -HCH, and 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene were the predominant isomers of HCH and DDT residues in yogurt, and PCB with 4,4'- and 2,3,5- substitution patterns were the predominant congeners of PCB residues. Also, the results indicated that the mean level of total chlorine in the identified organochlorine species was below 4% of EPOCl in yogurt, which implied that more than 96% of EPOCl measured in yogurt samples could not be accounted for by selected OCP and PCB.

Key words: yogurt, extractable persistent organochlorine, organochlorine pesticide, polychlorinated biphenyl

INTRODUCTION

Dairy products supply lipophilic polychlorinated biphenyls (PCB) and organochlorinated pesticides (OCP) that accumulate in human tissues (Jacobs et al., 2004). Since the Stockholm Convention, a global treaty aiming to protect human health and the environment from persistent organic pollutants (POP) entered into force on May 17, 2004, the potential health risk to the public

from the residues of POP has raised a widespread international concern.

Currently, yogurt is considered a main component of the Chinese diet because of its health benefits and taste. Yogurt is not only an indicator of POP in pasture and forages, but also one of the major sources of POP entering the human body, thereby causing serious health problems (Wong and Lee, 1997). Thus, monitoring contaminant levels in dairy products is imperative for quantifying dietary exposure to POP. Although there is an extensive and growing body of data on the presence of POP in dairy products including milk and butter (Venant et al., 1991; Kalantzi et al., 2001), little information is available in the literature about the concentrations of OCP (α -, β -, γ - and δ -hexachlorocyclohexanes (HCH), 1,1,1-trichloro-2,2-bis (p-chloro-phenyl) ethane (p,p'-DDT), 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene (p,p'-DDE), and 1,1-dichloro-2,2-bis (p-chlorophenyl) ethane (p,p'-DDD), aldrin, heptachlor epoxide, *cis*- and *trans*-chlordanes) and PCB (PCB60, 103, 105, 128, 143, 154, 173, 202, 205, 208, and 209) in yogurt. In particular, concentrations of extractable persistent organochlorine (EPOCl) in the food supply are poorly understood. This study reports the levels of EPOCl and selected PCB and OCP in 18 commercial brands of yogurt, and discusses possible reasons for the occurrence of the predominant species of HCH, DDT, and PCB residues in yogurt.

MATERIALS AND METHODS

Sample Collection and Preparation

Eighteen Chinese commercial brands of yogurt were randomly collected from supermarkets of Beijing and Shenzhen, China, from December 2002 to April 2003. For each brand, 8 to 10 cups (about 1,000 to 1,250 g) were treated as soon as they were brought back to laboratory. Same-brand yogurt samples were pooled in petri dishes and freeze-dried until constant weight. The lyophilized yogurt was milled into a homogeneous powder, then stored in a brown glass bottle at -4°C until use.

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Figure 1. Flow chart for analysis of organohalogens in yogurt by a combination of instrumental neutron activation analysis (INAA), gas chromatography-electron capture detector (GC-ECD), and chemical separation. OCP = Organochlorine pesticides, PCB = polychlorinated biphenyls, EPOC1 = extractable persistent organochlorine.

Chemicals

The quantitative standards of OCP (α -, β -, γ -, and δ -HCH, heptachlor epoxide, aldrin, *cis*-chlordane, *trans*-chlordane, p,p'-DDE, p,p'-DDD, and p,p'-DDT) and PCB (PCB60, 103, 105, 128, 143, 154, 173, 202, 205, 208, and 209) were authentic reference materials purchased from Supelco (Bellefonte, PA). The purity of each standard was greater than 99.3%. All solvents (analytical reagent grade) including acetone, cyclohexane, and n-hexane were redistilled before use. Concentrated sulfuric acid (guaranteed reagent grade) was extracted by cyclohexane before use. Anhydrous sodium sulfate (analytical reagent grade) was heated in an oven at 650°C for 5 h before use. Florisil (Supelco) was first heated in an oven at 675°C for 5 h, deactivated with 3 mL of distilled water, and then sealed in a beaker for 24 h before use. The Cl standard was prepared by dissolving the appropriate amount of KCl [guarantee reagent (content > 99.99%)] in redistilled water (1.0 $\mu\text{g/mL}$). The standard solutions of OCP and PCB were prepared by gradually diluting the original solutions of OCP and PCB in distilled n-hexane. None of the procedures were conducted in plastic ware to prevent contamination with external organic pollutants. Laboratory glassware was washed with acid and detergents, rinsed with distilled water and acetone, and then dried in an oven prior to use.

Analysis

Extraction and Cleanup. The entire experimental procedure, outlined in Figure 1, is based on a combination of instrumental neutron activation analysis (INAA) and gas chromatography (GC) with chemical separation (Xu et al., 2003). In brief, approximately 10

g of dried yogurt was weighed, and Soxhlet-extracted with 250 mL of a mixture of cyclohexane and acetone (1:1) for 14 h. The crude extract was washed with 1% sodium sulfate to remove acetone. The aqueous phases were again extracted with fresh cyclohexane, and the organic phases were combined and concentrated to approximately 15 to 20 mL by rotary evaporation. The raw extract was treated repeatedly with concentrated sulfuric acid until a clear and colorless cyclohexane extract was obtained, which was then washed with redistilled water, dried with anhydrous sodium sulfate, and concentrated to about 4 mL by rotary evaporation. A 1.5-mL aliquot of the 4-mL final extract was taken for determination of total EPOC1. The remaining extract was analyzed for OCP and PCB by Florisil column chromatography (Calamari et al., 1994). The column was prewashed with 20 mL of n-hexane; the remaining extract was eluted with 50 mL of n-hexane, concentrated by rotary evaporation, and evaporated to 0.5 mL under a gentle flow of nitrogen (99.999%).

Analysis of OCP and PCB. The GC analyses were carried out on a Varian 3800 gas chromatograph (Varian Ltd., Palo Alto, CA) equipped with a ^{63}Ni electron capture detector, using a fused silica capillary column (CP-Sil 5 CB Low Bleed/MS, 30 m $\times$ 0.25 mm i.d., with 0.25 μm film thickness). The temperature program was 130°C for 1 min, increased at 10°C/min to 200°C, increased at 3°C/min to 230°C, increased at 10°C/min to 270°C, and held for 7 min. Injector temperature was 270°C and detector temperature was 300°C. Helium and oxygen-free nitrogen (99.999%) were used as carrier and makeup gas, respectively. Peak identification was conducted by comparing the GC retention time with those of authentic standards, and quantification of OCP and PCB were made by external standard method calibrated with a 5-point calibration curve encompassing the entire concentration range. The detection limits, on the basis of a signal-to-noise ratio of 3:1, were between 0.01 to 0.06 and 0.002 to 0.06 $\mu\text{g/kg}$ for 11 OCP and 11 PCB standards, respectively; low enough to determine the selected OCP and PCB residues at the required levels in this study.

Analysis of EPOC1. The concentrations of EPOC1, expressed as chloride, were determined by INAA according to the methods reported by Xu et al. (2003). In brief, the samples and standards were sealed in polyethylene capsules and sent into the irradiation channel of the miniature neutron source reactor of the Institute of Atomic Energy, Beijing, China. To minimize the radioactivity background, the samples were transferred to a new counting vial after irradiation. The analyses were based on γ -peak from ^{38}Cl ($t_{1/2} = 37.24$ min, $E_\gamma = 1,642$ keV). For INAA, the samples were irradiated for 15 min, cooled for 2 min, and counted for 15 min. The

γ -energy spectra were measured with a high-purity germanium detector with associated electronics interfaced to a computer-controlled EG&G Ortec multichannel analyzer (EG&G Ortec, Oak Ridge, TN) for peak area calculations. The chlorine content was calculated by the relative method. The ^{24}Na ($t_{1/2}$ 15.0 h, E_γ = 2754 keV) was simultaneously determined as a control for the contamination caused by inorganic chlorine (Gether et al., 1979). In this study ^{24}Na was not found in the extracts. The detection limit of INAA for Cl was 50 ng.

Quality Control. Analyses were performed in a series of 5 samples and 1 blank. Each analysis of each brand of yogurt sample was performed in 2 to 4 replicates. For the recovery tests, the yogurt samples were spiked with the target analytes after thorough extraction with the mixture of cyclohexane and acetone (1:1) for 14 h, followed by the same processing as the real samples. The recovery (n = 3) of 11 OCP ranged from 81 to 99%, with relative standard deviations of 5.7 to 10.7%, and of 11 PCB ranged from 71 to 100%, with relative standard deviations of 7.1 to 10.8%. Laboratory blanks of all solvents and chemicals were also carefully checked. No significant peaks overlapping OCP and PCB standards appeared in the chromatogram of the blank run.

RESULTS AND DISCUSSION

OCP in 18 Commercial Yogurt Samples

The mean concentrations of the detectable target OCP in the yogurt samples are listed in Table 1. The contamination patterns of the selected OCP were in the order of DDT (detecting frequency = 100%) $\approx$ HCH (100%) $\gg$ aldrin (25%) $\geq$ chlordanes (65%) $\geq$ heptachlor epoxide (55%). Although levels of HCH and DDT residues are well below the China Dairy Guidelines (both HCH and DDT are ≤ 100 $\mu\text{g/L}$; GB6914-1986), they were still the predominant OCP in the yogurt samples; together, they accounted for 77.9 to 100% of total OCP.

The levels of HCH (mean value = 0.6 $\mu\text{g/kg}$ of fresh weight) and DDT residues (0.5 $\mu\text{g/kg}$) in yogurt samples were much lower than those previously reported in Chinese milk in 2001 (HCH = 35 $\mu\text{g/kg}$ of fresh weight and DDT = 46 $\mu\text{g/kg}$; Zhong et al., 2003) and in 1992 (HCH = 70 $\mu\text{g/kg}$ and DDT = 95 $\mu\text{g/kg}$; Zhang, 1995). The reasons for the remarkable reduction of HCH and DDT residues in yogurt can be generally attributed to the banning of HCH and DDT in agriculture practice, leading to a steady decline in residue levels in food (Chen and Gao, 1993). On the other hand, the manufacturing technology of yogurt, including heat treatments (pasteurization and sterilization), and the action of microorganisms during storage can result in reduction of HCH and DDT residues in yogurt. A reduction of lindane and

its metabolites have been observed in yogurt during pasteurization, boiling, and sterilization, and a gradual reduction of lindane was observed during storage (Abou-Arab, 1999). In addition, DDT residues were reduced by the isolated Ras cheese microorganisms, *Streptococci*, *Lactobacilli*, and yeast (Abou-Arab, 1997).

HCH. The average levels of HCH isomers in 18 brands of yogurt specimens were in the order of β -HCH (12.8 $\mu\text{g/kg}$ of lipid) $\gg$ γ -HCH (5.8 $\mu\text{g/kg}$ of lipid) $\approx$ α -HCH (5.2 $\mu\text{g/kg}$ of lipid) $\geq$ δ -HCH (4.6 $\mu\text{g/kg}$ of lipid), which correlated with their bioconcentration factors in mammalian fat (β -HCH = 527 $\gg$ α -HCH = 20 $\approx$ γ -HCH = 19 $>$ δ -HCH = 8.5; Geyer et al., 1987). The high concentration of β -HCH was believed to be due to its comparatively high stability and low water solubility. Also, its all-equatorial configuration favors storage in biological media and affords it greater resistance to hydrolysis and enzymatic degradation. Willett et al. (1998) observed that β -HCH was also the major species in animal tissues and fluids and a similar finding was reported in human breast milk (Kumaran et al., 1990).

DDT. The predominant species in yogurt was p,p'-DDE, which comprised 84% of total DDT. The DDT individuals in yogurt samples, except for sample no. 6, decreased in the order of p,p'-DDE $\gg$ p,p'-DDT $>$ p,p'-DDD. This was in agreement with the half-lives of DDT individuals measured in cows by Fries (1977) who demonstrated that DDE was persistent, but not DDT, which was metabolized in the rumen to DDD. By a contaminant mass balance experiment of a lactating cow in its natural state, McLachlan (1993) also reported that virtually all of the cow's exposure to DDT was through feed (more than 98%), and 50 to 80% of the ingested p,p'-DDE were excreted via milk, and only 4% of the p,p'-DDT.

Risk Evaluation of Detected OCP to Human Health

To understand the magnitude of exposure to detected OCP via Chinese commercial yogurt, the mean daily intakes of HCH, DDT, heptachlor epoxide, chlordanes, and aldrin were estimated based on ingestion of 500 g/d of yogurt (according to the Chinese recommended 500 mL/d of milk ingestion for an adult). The estimated mean daily intakes of HCH (0.28 μg), DDT (0.27 μg), heptachlor epoxide (0.01 μg), chlordanes (0.02 μg), and aldrin (0.02 μg) are very low in comparison to the acceptable daily intakes of WHO/FAO (1978, 1998) for HCH (840 μg), DDT (1200 μg), heptachlor epoxide (30 μg), chlordanes (60 μg), and aldrin (6 μg). Such a low daily intake of these pollutants via yogurt indicates the insignificant exposure of OCP from yogurt to local residents. However, the acceptable daily intakes are based on an "acceptable" risk to human health. This

Table 1. The average concentrations (and range) of organochlorine pesticides (OCP) in 18 Chinese commercial yogurt samples

Sample no.	OCP ¹ (μg/kg of lipid)												
	α-HCH	β-HCH	γ-HCH	δ-HCH	HCH	p,p'-DDE	p,p'-DDT	p,p'-DDD	DDT	Heptachlor epoxide	Cis-chlordan	Trans-chlordan	Aldrin
1	3.5	9.7	5.0	1.6	19.9	54.4	2.1	1.0	57.5	ND	ND	1.2	ND
	3.4–3.6	9.2–10.2	4.9–5.2	ND–3.2	17.4–22.2	50.7–58.2	2.1–2.1	0.9–1.0	53.8–61.3			1.2–1.2	
2	18.8	46.4	9.5	16.3	91.1	71.7	4.7	3.3	79.7	0.6	ND	ND	2.1
	18.7–19.0	46.2–46.7	9.0–10.0	16.2–16.4	90.6–91.6	69.1–74.3	4.7–4.7	3.3–3.3	77.1–82.3	ND–1.2			2.0–2.2
3	3.3	0.2	4.0	3.3	10.8	3.1	0.5	0.4	4.0	ND	1.3	ND	1.7
	2.7–5.3	ND–0.3	3.0–5.8	2.1–6.1	8.3–17.2	2.4–4.4	ND–1.8	ND–0.8	2.4–5.3		ND–3.4		ND–4.3
4	7.3	15.8	6.4	5.4	34.9	22.7	4.2	1.5	28.4	ND	1.8	0.5	3.5
	6.2–8.6	14.0–17.6	5.7–6.7	4.1–6.7	31.4–39.0	20.0–26.1	3.4–4.9	1.3–1.7	24.9–32.5		ND–3.6	ND–1.9	2.3–4.5
5	3.1	2.7	3.4	3.1	12.2	6.9	0.9	0.2	8	0.9	ND	ND	ND
	2.0–3.7	2.2–3.4	2.3–3.9	2.0–3.7	8.5–14.7	4.5–8.8	ND–2.6	ND–0.3	4.8–10.0	ND–1.7			
6	2.0	1.7	2.3	1.0	7.2	4.8	0.04	0.2	5.0	0.6	ND	ND	ND
	1.4–2.6	0.1–2.6	1.7–3.2	ND–2.0	6.0–8.0	3.5–5.8	ND–0.06	ND–0.3	3.5–5.8	ND–0.9			
7	3.5	29.4	4.9	2.5	40.4	31.8	3.8	2.8	38.3	ND	ND	1.3	ND
	3.3–3.8	26.8–32.1	4.6–5.2	2.3–2.7	37.0–43.8	28.4–35.2	3.5–4.0	2.5–3.0	34.4–42.2			1.2–1.4	
8	5.8	18.4	6.7	6.1	37	19.4	4.1	1.5	25.0	1.3	ND	ND	ND
	5.3–6.2	16.4–20.5	6.6–6.8	5.8–6.3	4.4–39.6	17.9–20.9	3.8–4.4	1.4–1.6	23.1–27.0	1.3–1.3			
9	4.9	13.5	5.6	5.8	29.8	22.2	2.6	1.4	26.2	1.1	ND	0.6	1.9
	4.4–5.5	12.6–14.5	4.6–6.5	5.0–6.6	26.6–33.1	21.3–23.1	2.1–3.1	1.2–1.5	24.6–27.7	1.0–1.3		ND–1.2	1.7–2.2
10	12.4	39.2	10.6	9.1	71.2	40.1	6.9	2.6	49.6	ND	ND	ND	ND
	11.9–12.9	37.7–40.8	10.1–11.0	8.8–9.4	68.4–74.1	39.6–40.5	6.8–7.1	2.6–2.6	49.0–50.2				
11	2.6	0.6	4.0	ND	7.2	4.1	1.5	0.4	6.0	1.0	ND	ND	ND
	2.6–2.6	0.6–0.6	3.9–4.1		7.1–7.2	4.0–4.3	1.4–1.5	0.4–0.4	5.8–6.2	0.9–1.0			
12	3.2	3.6	4.6	ND	11.4	11.7	1.9	1.2	14.8	1.2	ND	ND	ND
	3.1–3.2	3.6–3.6	4.5–4.7		11.3–11.4	11.1–12.2	1.8–2.0	1.2–1.3	14.1–15.5	1.1–1.3			
13	3.8	ND	8.5	3.5	15.8	12.5	2.4	0.5	15.5	ND	ND	1.6	ND
	3.5–4.1		8.0–8.9	3.0–3.9	14.6–17.0	11.6–13.4	2.2–2.7	0.5–0.6	14.8–16.1			1.4–1.8	
14	4	ND	7.4	3.6	15.1	26.8	2.4	0.9	30.1	ND	1.4	1.6	ND
	2.8–5.3		6.0–8.7	2.5–4.8	11.2–18.9	24.4–29.3	2.0–2.8	0.4–1.3	26.8–33.4		ND–2.7	ND–3.2	
15	5.2	2.8	8.6	3.7	20.2	32.0	3.4	0.7	36.0	ND	ND	2.2	3.5
	4.6–5.7	2.5–3.0	8.1–9.1	3.2–4.2	18.5–22.0	29.6–34.4	2.9–3.8	0.6–0.8	33.0–39.0			1.9–2.5	2.9–4.1
16	3	7.3	3.7	2.6	16.6	10.7	1.7	0.6	13	0.7	ND	1.0	ND
	2.7–3.2	6.6–8.1	3.6–3.8	2.4–2.7	15.3–17.8	9.1–12.3	1.6–1.8	0.5–0.7	11.2–14.8	0.7–0.7		0.9–1.1	
17	2.7	5.1	3.4	2.4	13.6	12	1.2	0.5	13.8	0.8	ND	1.0	ND
	2.6–2.7	5.1–5.1	3.4–3.5	2.1–2.7	13.2–14.0	11.0–13.1	1.2–1.3	0.4–0.5	12.6–14.9	0.8–0.9		0.9–1.1	
18	3.9	8.1	6.2	3.1	21.4	13.7	2.0	0.7	16.4	0.9	ND	1.1	ND
	3.6–4.2	7.8–8.4	5.8–6.6	3.0–3.2	20.2–22.5	13.0–14.4	1.9–2.1	0.6–0.7	15.6–17.2	0.6–1.2		0.8–1.4	

¹OCP: organochlorine pesticides; α-,β-,γ-,δ-HCH: α-,β-,γ-,δ-hexachlorocyclohexane; p,p'-DDEE: 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene; p,p'-DDT: 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane; p,p'-DDD: 1,1-dichloro-2,2-bis (p-chlorophenyl) ethane; HCH = α- + β- + γ- + δ-HCH; DDT = p,p'-DDE + p,p'-DDT + p,p'-DDD; ND = Not detected.

Table 2. The average concentrations (and range) of selected polychlorinated biphenyls (PCB) in 18 Chinese commercial yogurt sample

Sample no.	PCB ¹ (µg/kg of lipid)										
	PCB60	PCB103	PCB105	PCB128	PCB143	PCB154	PCB173	PCB202	PCB205	PCB208	PCB209
1	ND ¹	3.8 3.7–3.9	ND	1.6 1.6–1.7	1.0 1.0–1.1	ND	ND	0.7 0.6–0.7	ND	ND	ND
2	ND	6.0 4.4–7.6	1.2 0.8–1.4	3.1 2.5–3.7	ND	ND	0.2 0.2–0.2	1.3 1.0–1.6	1.4 1.1–1.8	ND	0.5 0.4–0.6
3	1.8 1.2–2.4	4.5 2.6–5.9	ND	1.2 0.9–1.4	ND	ND	ND	0.8 0.6–1.2	1.2 0.8–1.6	0.3 0.2–0.4	ND
4	2.8 2.6–3.0	10.9 10.1–11.6	2.2 1.2–3.1	2.6 1.9–3.1	2.1 2.0–2.2	ND	ND	1.0 0.9–1.0	1.2 0.06–2.4	0.7 0.6–0.7	ND
5	0.8 0.6–1.1	ND	ND	ND	0.8 0.6–1.0	ND	ND	ND	ND	ND	ND
6	ND	ND	ND	ND	0.6 0.4–0.9	ND	ND	ND	ND	ND	1.2 0.8–1.5
7	0.8 0.6–1.0	3.9 3.5–4.3	ND	ND	2.3 2.1–2.6	0.4 0.4–0.5	ND	1.3 1.2–1.4	ND	ND	0.1 0.09–0.1
8	ND	ND	1.5 1.4–1.5	2.5 2.4–2.5	ND	ND	ND	1.4 1.4–1.4	0.3 0.3–0.3	ND	ND
9	ND	ND	ND	2.1 1.8–2.4	ND	ND	ND	0.8 0.8–0.9	0.01 0.009–0.01	ND	ND
10	ND	ND	ND	8.0 7.6–8.4	ND	ND	ND	ND	ND	ND	ND
11	ND	ND	ND	3.0 2.3–3.7	ND	ND	ND	ND	ND	ND	ND
12	ND	ND	ND	ND	ND	ND	0.2 0.1–0.2	0.6 0.4–0.8	ND	ND	ND
13	ND	6.2 5.6–6.9	ND	ND	ND	ND	ND	2.2 1.2–3.2	ND	ND	ND
14	2.1 1.0–3.2	5.6 3.8–7.3	ND	ND	ND	ND	ND	1.3 1.0–1.6	ND	ND	ND
15	ND	8.2 7.1–9.3	ND	ND	ND	ND	ND	2.5 1.6–3.4	ND	ND	0.03 ND–0.06
16	ND	3.6 3.3–3.8	0.7 0.6–0.8	ND	ND	ND	ND	0.9 0.7–1.2	ND	ND	0.07 0.04–0.1
17	ND	3.0 2.9–3.1	ND	ND	ND	ND	ND	0.9 0.7–1.1	ND	ND	ND
18	ND	4.6 4.5–4.7	ND	ND	ND	ND	ND	1.1 1.0–1.2	ND	ND	ND

¹ND = Not detected.

does not mean zero risk. For endocrine-disrupting chemicals, including HCH, DDT, heptachlor epoxide, chlordans, and aldrin, there may be no safe doses, just as there are no safe doses of carcinogens (ENDS, 1997).

PCB in 18 Chinese Commercial Yogurt Samples

The mean concentrations of the PCB in 18 retail yogurts are listed in Table 2. The results indicated that about 44 to 81% of total PCB was attributed to PCB103; PCB202, detected in 78% of yogurt specimens, was the most frequently detected congener among the target PCB. Figure 2 also shows that the contamination pattern of the selected PCB in yogurt was in the order of 4–6CB >> 7–10CB. The higher proportions of 4–6CB congeners reflected the historical use of PCB₅ in China. It was reported that approximately 10,000 tons of PCB were produced in China from 1965 to 1974 (Qin et al., 2003). The Chinese technical PCB₅, with similar composition to Aroclor 1,254 (a commercial European mix-

ture, containing approximately 21% 4-CB, 48% 5-CB, 23% 6-CB, and 6% 7-CB; Jiang et al., 1997) have been widely used in industry as heat-transfer fluids, hydraulic lubricants, dielectric fluids, and transformer oil. The variable compositions of PCB in yogurt implied that there were different sources of PCB inputs in the different areas such as PCB₃ (similar to Aroclor 1,242) or other commercial mixtures of PCB.

It has been found that the metabolism of PCB in mammals occurs by hydroxylation at the 2- and 4-positions through the hepatic cytochrome P-448 and P-450 enzyme systems, respectively (Matthews and Dedrick, 1984). McLachlan (1993) further demonstrated that 4-hydroxy-PCB were the primary metabolites of several congeners in cows and indicated that the presence of a chlorine atom at the 4-position, or the presence of chlorine atoms at both the adjacent 3- and 5-positions, would inhibit the formation of the intermediate arene oxide at the 4-position. This is in agreement with our observations; that is, the substitution patterns of the

Figure 2. Concentration and composition of polychlorinated biphenyls (PCB) in 18 Chinese commercial yogurt samples; 4-6 chlorinated biphenyls (CB): $\Sigma(4\text{CB} + 5\text{CB} + 6\text{CB})$; 7-10CB: $\Sigma(7\text{CB} + 8\text{CB} + 9\text{CB} + 10\text{CB})$; 4CB = PCB60; 5CB = PCB103+105; 6CB = PCB128+143+154; 7CB = PCB173; 8CB = PCB202+205; 9CB = PCB208; 10CB = PCB209.

detected PCB in the yogurt samples, such as PCB60 (2,3,4,4'-), 103 (2,2',4,5',6'-), 105 (2,3,3',4,4'-), 128 (2,2',3,3',4,4'-), 143 (2,2',3,4,5,6'-), 154 (2,2',4,4',5,6'-), 173 (2,2',3,3',4,5,6'-), 202 (2,2',3,3',5,5',6,6'-), 205 (2,3,3',4,4',5,5',6'-), 208 (2,2',3,3',4,4',5,6,6'-), and 209 (2,2',3,3',4,4',5,5',6,6'-) were almost all in accordance with the rule, suggesting that the 4,4'- and 2,3,5-substitution patterns were characteristic of the PCB residues in yogurt.

PCB105. PCB105, one of dioxin-like PCB with a toxicity equivalency factor of 0.0001, was detected in 4 yogurt samples, whose concentrations and toxic equivalent (TEQ) ranged from 0.7 to 2.2 µg/kg of lipid and 0.07 to 0.2 ng/kg of lipid, respectively. King et al. (1999) reported that TEQ of PCB contributed to 37% of total TEQ in British milk and a higher proportion (52%) was observed in Dutch milk, which implied that PCB contamination in dairy products was a major concern.

EPOCl in 18 Chinese Commercial Yogurt Samples

The concentrations of EPOCl and the identified organochlorine compounds; that is, the sum of OCP and PCB determined by GC-electron capture detector expressed as chlorine, in 18 commercial brands of yogurt samples are listed in Table 3. The results indicated that 0.7 to 13.1% of total EPOCl were accounted for in the yogurt samples, which suggested that a major portion of EPOCl measured in yogurt remained uncharacterized. Because few reports on EPOCl in dairy products are available in literature, only a comparison with other

Table 3. The average concentration of identified OC¹ and EPOCl¹ in 18 Chinese commercial yogurt samples

Yogurt no.	Identified OC, ² µg/kg lipid	EPOCl, µg/kg lipid	Unidentified OC in EPOCl, %
1	45.2	1,400	97.0
2	112.4	750	86.9
3	19.7	950	98.0
4	53.6	630	92.1
5	15.2	180	92.4
6	9.2	1,400	99.3
7	52.7	950	94.7
8	42.6	2,000	97.9
9	38.1	1,100	96.5
10	79.3	2,100	96.4
11	10.4	640	98.4
12	16.3	640	97.5
13	24.5	1,300	98.1
14	33.5	1,600	97.9
15	40.8	1,200	96.6
16	22.1	740	97.1
17	19.6	980	98.0
18	28.1	1,800	98.4

¹OC = organochlorine compounds; EPOCl = extractable persistent organochlorine.

²Identified OC: the sum of detected target organochlorine pesticides and polychlorinated biphenyls expressed as chlorine.

biological or environmental samples could be made. Similar to our results, Gustavson and Mar (1999) reported that PCB contributed to less than 1.3 to 21% of EPOCl in surface sediment, and that PCB, HCH, and DDT contributed to less than 0.2 to 19% of EPOCl in blue mussels from the Baltic Sea. Other reports showed that 74 to 99% of extractable organochlorines in several species of fish (Newsome et al., 1993) and 80.6 to 98.6% of EPOCl in pine needles from China (Xu et al., 2003) could not be accounted for by PCB and OCP.

CONCLUSIONS

The contamination patterns of the selected OCP in yogurt samples were in the order of DDT $\approx$ HCH $\gg$ aldrin $\geq$ chlordanes $\geq$ heptachlor epoxide. The main contributors to OCP residues in yogurt were HCH and DDT, despite the long-time restrictions or bans of their use. Also, β -HCH and p,p'-DDE were the predominant isomers of HCH and DDT in yogurt, respectively. The contamination patterns of the selected PCB in yogurt samples were in the order of 4-6CB $\gg$ 7-CB, and PCB, with 4,4'- and 2,3,5-substituted residues being the predominant congeners of PCB. Less than 4% of EPOCl can be explained by OCP and PCB in the studied yogurt samples. Our results indicate that an exposure risk of these pollutants to humans through dairy products and their impact on human health should not be neglected.

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