

Study of organohalogenes in foodstuffs and environmental samples by neutron activation analysis and related techniques

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Abstract Pine needles and foodstuffs collected from Beijing, China, were analyzed by instrumental neutron activation analysis (INAA) combined with organic solvent extraction for total halogens, extractable organohalogenes (EOX) and extractable persistent organohalogenes (EPOX). The INAA detection limits are 50 ng, 8 ng and 3.5 ng for Cl, Br and I, respectively. The contents and distribution patterns of organohalogenes in these samples are reported. EOCl accounted for 0.013–0.016% and 1.6–2.7% of the total chlorine in yogurt and apples, respectively, which suggested that chlorine in foodstuffs mainly existed as inorganic species and non-extractable organochlorines. EOCl contents in pine needles and foodstuffs were noticeably higher than those of EOBr and EOI. For pine needles, yogurt and apples, 1.6–34%, 23–58% and 29–35% of EOCl remained as extractable persistent organochlorine (EPOCl), respectively. Pine needle containing higher EOCl contents in chemical industrial and traffic hub areas indicated that chemical industries and exhaust emission from vehicle were the main sources of organochlorines in the Beijing's air. The relative proportions of the known organochlorines (such as HCHs, DDTs, chlordanes, heptachlor, HCB and PCBs) to the total EOCl and EPOCl were 0.04–1.6% and 0.7–21.5%, respectively, which implied that the identity of species of a major portion of the EOCl and EPOCl measured in pine needles was unknown.

Key words instrumental neutron activation analysis (INAA) • pine needle • foodstuff • extractable organohalogen (EOX) • organochlorinated pesticides • Beijing

Introduction

Organohalogenes, especially organochlorinated compounds (OCs) such as polychlorinated biphenyls (PCBs), have long been recognized as a potential threat to human health and, therefore, these compounds have been widely investigated in foods [3, 27], vegetation [9, 14], and the atmosphere [1, 11]. Recently, interest in using extractable organohalogenes (EOX) as parameters for the quantification of total organohalogen content in sediment [7], biota [8], and water [20] has dramatically increased. However, there is ever-growing evidence that traditional analytical methods such as gas chromatography (GC) and GC-mass spectrometry (GC-MS) could only provide information about the known OCs, which contributed to less than 20% of total amount of extractable organochlorinated compounds (EOCl) in samples and, therefore, the results could not reflect the actual OCs contamination levels [13, 28]. INAA is a very convenient and quick method for halogen analysis, and is also the only analytical method currently available for simultaneously determining EOCl, extractable organobrominated (EOBr) and extractable organoiodinated compounds (EOI) in an extract [7, 8, 19].

Pine needles can accumulate organohalogenes from the ambient air and, therefore, can serve as a biomonitor to monitor the levels of atmospheric contamination of these compounds [4, 15]. Pine needle can integrate contaminants over a long time and is much easier to collect than air

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samples, especially in remote areas. Moreover, pine is widespread in Beijing area and its needle age is easy to determine.

Since OCs can be accumulated in organisms through the food chain as a result of their lipophilic property, the foodstuffs are considered to be the main source of human exposure to these compounds. The content of OCs in milk can be conveniently measured, therefore, the United Nations Environmental Programme recommend milk or dairy products as an indicator of OCs [26] and this type of foodstuff has been studied as an indicator of organochlorine pesticide exposure [21, 25].

Methods and materials

Sample collection

Pine needle

Samples of the *Pinus tabulaeformis* Carr. needles were collected at 22 sites of six functional areas in Beijing (Fig. 1) during March and April 2002. Pine needles were taken at least from three individual trees at heights of 1.5–3 m at each sampling site. Pine needles were reserved in polyethylene bags immediately after sampling, and then some samples were used to analyze water content, and the rest was dried and stored in polyethylene bags at room temperature in the dark until analysis. The water content of the pine needles was determined to be about 56–66% weight by drying (120°C) them to constant weight.

Foodstuffs

Yogurt and apple samples (10 each) were collected at random from several supermarkets of Beijing during the period between February and April of 2003. Five yogurt samples were from Shanghai and the other 5 from Inner Mongolia. The apples were from Shandong Province. The

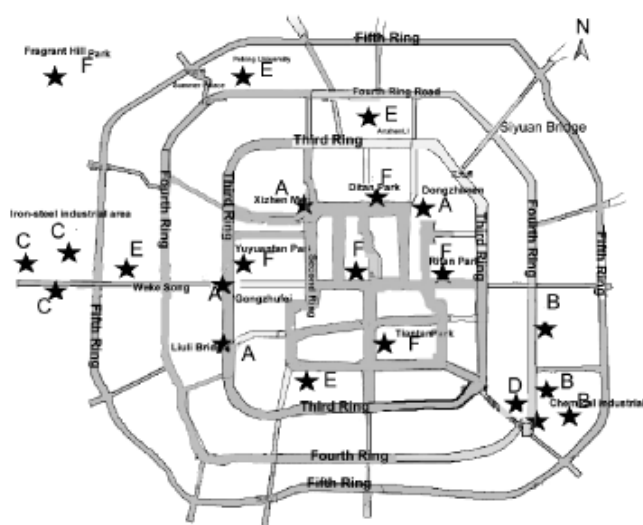


Fig. 1. Map of sampling sites in Beijing city. A – traffic hub area; B – chemical industrial area; C – iron-steel industrial area; D – residential area nearby chemical industries; E – common residential area; F – park.

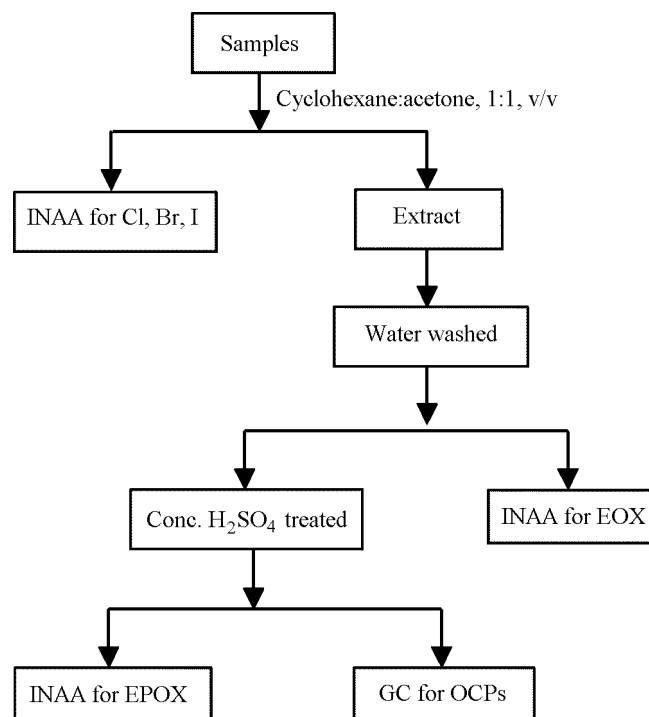


Fig. 2. Flow chart for analytical procedure.

samples were immediately lyophilized in freeze-dryer after collection. Their water contents were determined to be 80.3–80.6% and 85.5–86.2% weight, respectively, by lyophilizing until constant weight.

Extraction and cleanup

Methods of sample extraction and cleanup were described in [30]. The whole experimental procedure was outlined in Fig. 2.

Lipid analysis

The lipid contents in the yogurt and apple samples were determined by hydrochloric acid hydrolyzation according to the National Standard Method GB5009.6-85 [23].

Neutron activation analysis

The contents of total halogens, EOX and EPOX in pine needles and foodstuffs were measured by neutron activation analysis according to the method reported by Xu [30]. In summary, an aliquot of 1.2 mL of the extract for EOX or EPOX analysis was heat-sealed in a 1.5-mL acid-washed polyethylene vial. The vial was washed with distilled water and acetone after an acid rinse, stored in cyclohexane overnight, and dried in an oven at 50°C. Potassium chloride, potassium bromide, and potassium iodate of known concentrations, dissolved in distilled water, were used as standards. The concentrations of standards were 1.0, 1.0, and 0.7 µg/mL for Cl, Br, and I, respectively. INAA was carried out at a neutron flux of 8.0×10^{11} n/cm²·s for 15-min irradiation using a miniature neutron source reactor at the Institute of Atomic Energy (IAE), Beijing, China. To minimize the radioactivity background, the samples were transferred to a new counting vial after irradiation. The

γ -energy spectra were detected with a germanium detector of high purity with associated electronics interfaced to a computer-controlled EG&G Ortec multichannel analyzer for peak area calculations. The analyses were based on γ -peaks from ^{38}Cl ($t_{1/2} = 37.24$ min, $E_{\gamma} = 1642$ keV), ^{80}Br ($t_{1/2} = 17.68$ min, $E_{\gamma} = 617$ keV), and ^{128}I ($t_{1/2} = 24.99$ min, $E_{\gamma} = 443$ keV). The counting time was 15 min. The detection limits were 50, 8 and 3.5 ng for Cl, Br and I, respectively. Cellulose extraction thimble was extracted and processed in the same manner as the samples to obtain the blank values, once each 6 samples. The blank values of Cl, Br and I were subtracted to correct the experimental values. ^{24}Na ($t_{1/2} = 15.0$ h, $E_{\gamma} = 2754$ keV) was simultaneously determined as a check for contamination caused by inorganic halogens [5]. In our practice, ^{24}Na was not found in the sample and blank extracts. The relative standard deviations of the five replicate analyses were 8% for EOCl, 8% for EOBr and 12% for EOI. In order to check the accuracy of INAA results, 6 known-concentration organochlorinated pesticide standards at two levels 9.34 and 1.17 $\mu\text{g/mL}$ Cl were analyzed by INAA in the same manner as the samples and the relative error were $\pm 1.7\%$ and $\pm 0.2\%$, respectively. So, the accuracy of INAA was unquestionable.

GC and GC/MS analyses

The GC analyses were carried out by a Varian 3800 gas chromatograph equipped with a ^{63}Ni electron capture detector, using a fused silica capillary column (CP-Sil 8 CB 30 m \times 0.25 mm i.d., with 0.25 μm film thickness). The temperature of injection and the detector was 250 and 300°C, respectively. An initial column temperature of 90°C was hold for 3 min, and then programmed at 5°C/min to 120°C, 14°C/min to 250°C and 15°C/min to 280°C, and hold at 280°C for 5 min. High pure He was used as carrier gas.

The gas chromatographic condition of GC-MS was the same as GC. Effluents from the GC column were fed into a 70 eV electron impact source held at 150°C. The mass spectrometry was operated in a full-scan acquisition mode with mass range 50–650. A 250 mL aliquot of cyclohexane:acetone (1:1) was concentrated to 0.2 mL and used

to check the contamination from the reagent used. No significant peaks overlapping OCs standards appeared in the chromatogram of the blank. GC peak identification was conducted by comparing the gas chromatographic retention time (in GC chromatogram) and mass spectra (in GC-MS) with those of authentic standards. Each analysis was performed in duplicate or triplicate, and the chemical recoveries of the experimental procedure were estimated by spiking the pine needle samples with 10 OCs standards at three levels: 100, 400, and 800 ng/mL, respectively. The average recoveries ($n = 3$) were $92 \pm 4\%$ for HCHs, $85 \pm 5\%$ for DDTs, $84 \pm 5\%$ for chlordanes, and $89 \pm 12\%$ for PCBs. The detection limits were calculated on the basis of a signal/noise ratio of 3, which ranged from 0.003 to 0.075 ng/g for 10 OCs and 0.0004–0.09 ng/g for PCBs, low enough to determine pesticide and PCBs residues at the required levels in this study.

Results and discussion

Distribution of EOX and EPOX in pine needles

Extractable organohalogens

The contents of organohalogens were in the order of EOCl \gg EOBr $>$ EOI (see Table 1). EOCl accounted for more than 96% of EOX in all the pine needle samples, which showed that EOCl was the major fraction of the organohalogens. Similar results have been gained in our previous study for needles from remote areas in China [30], and reported by Bottaro and co-workers [2] and Kannan *et al.* [12] for aqueous biota. The reason for the high content of EOCl is likely attributed to two factors: (1) Most organohalogenated pollutants in the atmosphere are present as OCs that can be taken up by pine needles. Laniewski and co-workers [16] found that most absorbable organohalogens in rain and snow were OCs. Yokouchi [31] provided further evidence that chlorinated methane originated from both natural and anthropogenic sources was the most abundant organohalogen in the atmosphere

Table 1. Contents of EOX and EPOX in pine needles in Beijing ($\mu\text{g/g}$, dry weight)^a.

Compound	A	B	C	D	E	F
EOCl	36 ^b 23–48 ^c	40 23–65	12 9–16	30 9–44	14 4.6–23	10 2.7–18
EOBr	0.25 0.11–0.39	0.45 0.17–0.78	0.19 0.13–0.24	0.35 0.30–0.38	0.3 0.1–0.5	0.21 0.06–0.49
EOI	0.13 0.044–0.22	0.15 0.03–0.27	0.12 0.05–0.17	0.11 0.09–0.14	0.17 0.052–0.28	0.07 0.04–0.09
EPOCl	4.7 3.4–5.9	2.0 0.6–2.9	0.6 0.3–1.1	2.0 0.4–4.8	0.95 0.7–1.2	1.6 0.5–3.1
EPOBr	0.12 0.043–0.18	0.06 0.04–0.13	0.04 0.03–0.05	0.06 0.02–0.11	0.045 0.03–0.06	0.032 0.007–0.09
EPOI	0.04 0.018–0.0	0.03 0.01–0.05	0.02 0.01–0.04	0.02 0.02–0.03	0.01 0.01–0.01	0.015 0.004–0.036
EOBr/EOCl(%)	0.7	1.1	1.6	1.2	2.2	2.1
EPOBr/EPOCl(%)	2.6	3.0	6.7	3.0	4.7	2.0

^a EOX expressed as Cl, Br, I. ^b Average content ($\mu\text{g/g}$, dry weight). ^c Content range ($\mu\text{g/g}$ d.w.).

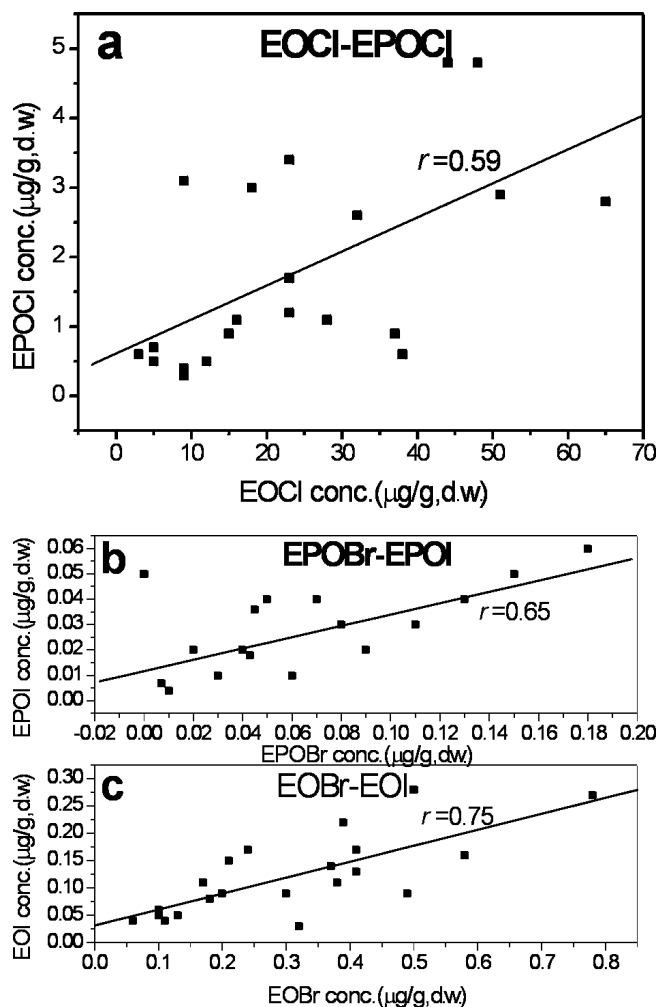


Fig. 3. Relationships of EOC_i to EPOC_i (a), EPOBr to EPOI (b) and EOBr to EOI (c) in pine needles.

and was continuously released in large quantities into the atmosphere from coastal land. Rhew *et al.* [24] also found that a huge amount of natural brominated methane and chlorinated methane was released into the atmosphere from coastal salt marsh with an average molar flux ratio of rough 1:20. (2) OCs may be more difficult to be transformed and degraded than organobrominated and iodinated compounds in the environment.

The highest content of EOC_i in Beijing was in the chemical industrial area (40 µg/g, dry weight), followed by the traffic hub area (36 µg/g) and residential area nearby chemical industries (30 µg/g), which were about 3–4-fold higher than the lowest content (10 µg/g) in park. The content of EOC_i in six functional areas decreased as follows: chemical industrial area > traffic hub area > residential area nearby chemical industries > common residential area > iron-steel industrial area > park. The EOC_i content in the residential area nearby chemical industries was twice higher than the common residential area. The pine needles in chemical industrial area contained the highest EOC_i content, which indicated that the chemical industry was one of main sources of OCs in the Beijing's air. The considerably high content of EOC_i in the traffic hub area showed that the exhaust emission from vehicle was another severe source of OCs in the Beijing's air.

Extractable persistent organohalogens

About 1.6–34% of EOC_i survived as the species of EPOC_i (sulfuric acid-resistant) after treatment with concentrated sulfuric acid, which suggested that >66% of EOC_i in pine needles were an acid-labile or acid-soluble fraction. Most compounds with heteroatoms (oxygen or nitrogen atom) or an unsaturated bond, such as most known naturally occurring organochlorinated compounds, could be protonated or decomposed and removed from the extracts after treatment with concentrated sulfuric acid [6, 19]. Thus, a conclusion could be drawn that the natural EPOC_i could not be neglected, but its contribution was probably limited in comparison with that from the ambient air. A weak correlation ($r = 0.59$) was observed between the concentrations of EOC_i and EPOC_i (Fig. 3a), which further indicated that major fractions of EOC_i and EPOC_i in pine needles were not of natural origin, but of the ambient atmospheric source. However, there was a correlation between the contents of EOBr and EOI ($r = 0.75$) and a similar pattern for EPOBr and EPOI ($r = 0.65$) (Figs. 3b and 3c), which demonstrated that EOBr and EOI in pine needles mainly came from the natural source. The plots of EOC_i to EOBr and EOC_i to EOI showed the segregated feature. No correlation between the contents of EOC_i and EOBr or EOI implied that their sources were different.

The contents of EPOX were also in the order of EPOC_i >> EPOBr > EPOI. Major fraction (88%) of EPOX was EPOC_i. The ratios of EOBr/EOC_i ranged from 0.7–2.2%, whereas 2.0–6.7% for EPOBr/EPOC_i, which implied the relative stable proportion of EOBr was higher than EOC_i. Our previous study on pine needle from the remote areas gained the similar results [30]. A study on terrestrial oils found that EOBr was quite stable, and the major portion of EOBr existed in fatty acid after saponification [18].

The contents of the known (identified) organochlorines, such as HCHs, DDTs, heptachlor, HCB, PCBs and chlordanes, in pine needles are listed in Table 2. The known organochlorines accounted for 0.7–21.5% of EPOC_i and below 2% of EOC_i in pine needles, which implied that the relative proportions of the known to unknown organochlorine were very low. The known compounds were reported to account for 5–25% of EOC_i in fish from the United States [12] and 2–18% in marine organisms from the Osaka Bay [28]. About 45% of EOC_i reported in blubber lipid of beluga whales were attributed to the known compounds [13]. About 25–50% of EOC_i in herring gull eggs from the Lake Ontario can be explained by the known compounds [22]. The identified compounds in birds from Georgia (USA) accounted for 1–14% of EOC_i [12]. In Japanese human adipose, about 59% of EOC_i can be accounted by PCBs, DDTs, PCTs, and HCHs [28]. In contrast with the above results, the relative proportions of the unknown EOC_i in pine needles are higher than those found in aqueous and terrestrial biota.

Distribution of EOX and EPOX in foodstuffs

Total halogens

The concentrations of the total halogens, EOX and EPOX in yogurt and apple determined by INAA are given in

Table 2. Contents of the known organochlorine in pine needles in Beijing.

Compound	A	B	C	D	E	F
OCPs-Cl (ng/g)	22.4 ^a	82.4	26.0	97.9	23.0	33.3
Range (ng/g)	22.4 ^{b,*}	16.1–276	16.4–37.4	29.2–232.5	13.4–32.6	23.1–45.5
PCBs-Cl (ng/g)	147.8	50.5	33.5	155.5	25.5	34.2
Range (ng/g)	70.7–224.8	12.1–88.9	5.1–58.2	155.5 [*]	25.5 [*]	18–54.8
Known Cl (ng)	170.2	132.9	29.5	253.4	48.5	41.1
Known Cl/EOCl(%)	0.5	0.34	0.5	0.8	0.35	0.6
Range	0.1–0.5	0.04–1.6	0.33–0.62	0.08–0.9	0.17–0.71	0.27–1.6
Known Cl/EPOCl(%)	3.7	6.8	9.4	12.5	5.1	3.6
Range	0.7–4.7	1.3–21.5	6.8–14.9	3.2–8.1	3.2–4.7	1.4–16

^a Average content of the known organochlorine (ng/g). ^b Content range of the known organochlorine. ^{*} One sample.

Table 3. Their concentrations were in the order of Cl >> Br > I, being in agreement with their elemental abundances in nature. EOCl and EPOCl accounted for 0.013–0.016% and 0.003–0.009% of the total chlorine in yogurt, which suggested that chlorine in yogurt mainly existed as inorganic species and non-extractable organochlorines. For apples, 1.6–2.7% and 0.56–0.77% of total chlorine were EOCl and EPOCl, while EOBr and EPOBr were 4.5–36.4% and 2.0–10.9% of total bromine, and 10.4–50.0% of total iodine were EOI, which indicated that the relative proportions of EOBr and EOI were much higher than those of EOCl.

Extractable organohalogenes

EOCl in yogurt was noticeably higher than EOBr and EOI (see Table 3), whose average concentration was 3.0 µg/g on fat weight basis and accounted for ≥91% of the total EOX, indicating that EOCl was the main pollutant in the environment. Similar results have been reported by Xu *et al.* [30] for terrestrial vegetation and by Kannan *et al.* [12] for aqueous biota. And a similar trend was found in apples. EOCl concentrations in apples were 30–46 µg/g lipid weight, which were 10–15-fold higher than those in yogurt. The direct use of Cl-containing pesticides and low lipid contents partially contributed to higher concentration of

EOCl in apples. Since no data on the concentration of EOCl in yogurt and apples are available, other biological samples are used for comparison. On the lipid weight basis, the concentrations of EOCl in yogurt (3.0 µg/g) and apples (38 µg/g) were much lower than those of fish (595–2170 µg/g, lipid weight), birds (560–3080 µg/g, lipid weight) at estuarine marsh near a former chloralkali plant [12]. The average concentrations of EOBr and EOI in yogurt and apples were 0.099 µg/g and 0.23 µg/g, 0.69 µg/g and 0.34 µg/g lipid weight basis, respectively, also much lower than in marine biota or biological samples near the chloralkali plant [12]. The high concentration of EOX in the latter is likely attributed to the biosynthesized organic halogenated compounds and the disposal of wastes from the chloralkali process, which enriches EOX through the food chains [12, 29]. In contrast the terrestrial biota and feed contain relatively less biosynthesized organic halogenated compounds.

Extractable persistent organohalogenes

About 23–58% and 29–35% of EOCl survived as the species of EPOCl after treatment with concentrated sulfuric acid for yogurt and apple, respectively, which suggested that the considerable proportion of EOCl in them was an acid-

Table 3. Concentrations of halogens, EOX and EPOX in foodstuffs (µg/g, wet weight).

Sample	Yogurt 1 ^a	Yogurt 2 ^b	Apple 1 ^c	Apple 2
Lipid (%)	3.3	3.5	0.33	0.35
EOCl	0.12 ^d (3.6) ^c	0.088(2.4)	0.099(30)	0.16(46)
EOBr	0.0033(0.099)	ND	0.00058(0.17)	0.004(1.2)
EOI	0.0075(0.23)	0.0084(0.23)	0.00057(0.17)	0.0018(0.51)
EPOCl	0.069(2.1)	0.02(0.55)	0.035(10)	0.046(13)
EPOBr	ND	ND	0.00026(0.078)	0.0012(0.34)
EPOI	0.0036(0.11)	0.0034(0.093)	ND	0.00018(0.051)
Total Cl	740	670	6.2	6.0
Total Br	0.99	0.84	0.013	0.011
Total I	0.099	0.11	0.0055	0.0036

^a Yogurt 1 from South China. ^b Yogurt 2 from North China. ^c Apple sample from Shandong province. ^d Values on a wet weight. ^e Values on a lipid weight. ND – not detected.

liable or acid-soluble fraction. In comparison with pine needle, the EPOCl proportion in foodstuffs was higher. The concentrations of EPOX were also in the order of EPOCl >> EPOBr > EPOI in apple, while EPOCl >> EPOI and EPOBr in yogurt. More than 85% and 97% of EPOX were accounted for as EPOCl in yogurt and apple, respectively, which showed that the major fraction of EPOX was EPOCl. The concentration of EPOCl in yogurt (2.1 µg/g, lipid weight) from South China (Shanghai) was higher than that from North China (Inner Mongolia, 0.55 µg/g lipid weight), which was in agreement with the consumed amount of pesticides in China (Shanghai, 9.85 kg/ha; Inner Mongolia, 0.36 kg/ha) [17]. Similar results have been found in our milk studies [32]. This tendency also corresponded to the level of economic development in China. In South China, a number of chemical plants release more waste into the environment. In addition, a higher temperature and wet climate in South China avail of the reproduction and breeding of insects. Thus, more pesticides are needed to kill them. This might explain the relatively high concentration of EOCl in South China (3.6 µg/g, lipid weight). A similar trend was reported for organochlorinated pesticides in soil and foodstuffs [10].

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