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Occurrence and risk characterization of polycyclic aromatic hydrocarbons of edible oils by the Margin of Exposure (MOE) approach

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and genotoxic chemicals naturally derived from food during heat processing. Edible oil is one of the most frequently contaminated foods. Many researches were recently conducted to determine the contents of PAHs and to assess their risks, but there have been no studies characterising risks of PAHs by calculating Margin of Exposure (MOE) of total PAHs instead of toxic equivalency factors (TEFs) concept in Korea. To analyze the 4 PAHs including benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), and benzo(a)pyrene (BaP) simultaneously, gas chromatography with mass spectrometry was optimized. Total 303 edible oils were investigated and contaminated by 4 PAHs at ND–12.91 ng g^{-1}. The MOEs were estimated by PAHs contents, daily consumption, and were over 10,000. The risk of PAHs of edible oils in Korea was of low concern. Furthermore, the MOEs of the estimated equivalent BaP calculated by TEFs of other 3 PAHs were higher than those of mixed PAHs, which would be overestimated.

Keywords: Polycyclic aromatic hydrocarbons, Edible oil, Exposure assessment, Risk characterization, Toxic equivalency quotient

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of two or more fused benzene rings [1]. They are produced from the incomplete combustion of organic matter and geochemical process. Some PAHs have been proven to be carcinogenic and genotoxic compounds as they bind to DNA [1]. Sixteen PAHs are actually classified as priority pollutants by Environmental Protection Agency (EPA) on the basis of their occurrence and carcinogenicity [2]. The European Union had set maximum levels for benzo(a)pyrene (BaP) as an indicator for general PAHs in foods. However, European Food Safety Authority (EFSA) recently concluded that BaP is not suitable as marker for the PAHs, and PAH4 including benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), and benzo(a)pyrene (BaP) would be proper as indicators [3]. The European Union added new maximum levels for sum of PAH4 in foods [4].

The occurrence of PAHs in food is due to environmental contamination, manufacturing and cooking process, and occasionally PAHs appear in low amount from contaminated packaging material [5–7]. Some research has been conducted to investigate PAHs in food samples and much information of contamination to PAHs in various food stuffs have been published [3, 8]. Fats and oils are particularly prone to PAHs contamination because of their strong lipophilic characteristics [9]. Various routes of PAHs contamination in vegetable oils also have been suggested. The seed drying process using direct firing for production of hot air can be responsible for major PAHs contamination of some vegetable oils. Another possibility of PAHs contamination in vegetable oil may be carried over from contaminated soil, water, air or packaging materials [10]. The direct consumption or usage of fats and oils as an ingredient in foods is one of the most important reasons that PAHs in oil should be considered [11, 12].

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Furthermore, the strong intestinal absorption of PAHs in fats and oils is another important reason for the PAHs in fats and oils to be considered important concerns [13]. However, crude edible oil is refined and dewaxed through purification process. The PAHs levels can be drastically reduced by refining with the final level depending on the refining conditions [10]. Therefore, the control of pressed oil without refining process is more important than refined oils. Several researches estimated the exposure to PAHs by consuming edible oils, since US EPA adopted relevance of the toxic equivalency quotient (TEQ) concept to estimate of exposure to PAHs [15]. BaP equivalent concentrations (TEQ_{BaP}) were produced by multiplying each PAH concentration with its toxic equivalency factors (TEFs) [15–17]. However, EFSA recently concluded that the TEQ approach is only suitable for the compounds which have the same mechanism of toxicological effect such as polychlorinated dibenzo-*p*-dioxins and -dibenzofurans. Although a number of PAHs have the same effect showing the carcinogenic potency of PAHs by binding to DNA and inducing a mutation, PAHs also produce tumors in other mechanisms [3]. Therefore, a toxicological value calculated from mixture of PAHs should be used to assess the risk of PAHs. However, there have been no researches that assess the risk of PAHs using new toxicological value, not a TEQ approached-value. To assess a risk of PAHs to the public health by consuming edible oils, Margin of Exposures (MOEs) based on the benchmark dose lower confidence limit for a 10% increase in the number of tumour-bearing animals compared to control animals ($BMDL_{10}$) have been used [18, 19]. Substances which are genotoxic and carcinogenic may show the limit of detection in dose–response relationship of a bioassay, rather than an estimate of a possible threshold, and a health-based reference value could not be set [18]. Therefore, it has been recommended to reduce them to As Low As Reasonably Achievable (ALARA) amount [20]. The MOE has become the preferred option and has been used for providing a risk priority to risk managers [21]. The objectives of this study were to evaluate PAHs contaminations including BaA, CHR, BbF, and BaP in edible oils in the Korean market and to assess a risk to the public health by consuming edible oils with MOE. Furthermore, the researchers also compared the risks estimated from new toxicological values and traditional toxic equivalency factor (TEF) values.

Experimental procedures

Chemicals and materials

The standards of PAH4; BaA, CHR, BbF, BaP and 2 deuterated internal standards; and CHR-d12 and BaP-d12 were obtained from Supelco (Bellefonte, PA, USA). The 4 standards and 2 internal standards were separately dissolved in dichloromethane to make stocking standard of 100 μg mL^{-1} and stored in ambient storage at −25 °C. Working standards (1–500 μg L^{-1}) were prepared by diluting stocking standard with dichloromethane, and stored at 4 °C. HPLC grade of *N,N*-dimethylformamide(DMF), ethylacetate, and *n*-hexane from Merck (Darmstadt, Germany), and HPLC grade of dichloromethane from Burdick & Jackson (Muskegon, MI, USA) were prepared. Distilled Water (DW) was made by purifying tap water with a Milli-Q System (Millipore, Bedford, MA, USA). Sodium sulfate was obtained from Wako (Osaka, Japan). Sep-pak® Vac (1 g/6 cc) with silica resin of Waters Corporation (Milford, MA, USA) and SupelMIP® SPE—PAHs (50 mg/3 cc) of Supelco (Bellefonte, PA, USA) were purchased as SPE cartridge.

Sample preperation

We chose edible oils to analyse and assess the risk according to the consumption data from the Korea National Health and Nutrition Examination Survey (KNHANES) and the procedure to extract oils. Sesame oils, perilla oils and olive oils were selected because they are the most consumed oils in Korea by the KNHANES. There are no consuming data for other edible oils in the KNHANES. And red pepper oils and red pepper seasoning oils were also selected because they were extracted followed by frying seeds with high temperature, which can produce PAHs easily [22–24]. In total, 303 edible oils including 129 sesame oils, 71 perilla oils, 16 pepper seeds oils, 53 olive oils and 34 red pepper seasoning oils were purchased at Korean offline markets relative to population by region and online markets in 2013. All sesame oils and perilla oils are extracted on markets by ourselves with Korean sesame seeds and perilla seeds. Others are purchased on markets which were already extracted by stores. Samples were stored in the darkness in near-full bottles at blow of 20 °C.

Pretreatment of sample

A sample of 10 g was weighed and moved into a separatory funnel, and then it was shaken with *N,N*-DMF-DW (9:1, v/v) of 50 mL and *n*-hexane of 100 mL in the presence of the 2 deuterated internal standards (4 ng g^{-1}). The *N,N*-DMF-DW (9:1, v/v) was moved to an another separatory funnel and hexane layer solution extracted twice with 25 mL of *N,N*-DMF-DW (9:1, v/v) by shaking and equilibrating it. A sodium sulfate solution (1%) of 100 mL aliquot and *n*-hexane of 50 mL were added to the *N,N*-DMF-DW layer and shaken, and the *n*-hexane layer was transferred to another separatory funnel. The extraction with *n*-hexane was repeated twice. The extracted hexane were washed with 40 mL of DW 3 times, and then, anhydrous Na_2SO_4 (15 g) was added to the hexane extract to remove DW remained. The extract was evaporated to approximately 2 mL by a rotary evaporator (Eyela, Tokyo Rikakikai Co. Ltd., Japan) to be purified with SPE catrideges [25]. The condensed extract was firstly purified with the silica cartridge activated with dichloromethane (10 mL) and *n*-hexane (20 mL), and then the cartridge was washed with *n*-hexane (5 mL) and eluted with *n*-hexane-dichloromethane (3:1, v/v) (15 mL). The eluate was concentrated to approximately 2 mL using a rotary evaporator. The concentrate was purified by passing through a SPE-PAHs cartridge previously activated with *n*-hexane (1 mL), and the cartridge was eluted with 0.5 mL and 1 mL of *n*-hexane followed by 3 mL of ethylacetate. The eluate was dried with a nitrogen evaporator (Oa-SYS Heating Device 5085, Organomation Associates. Inc., USA) at 20 psi stream of nitrogen (40 °C). The analyte was finally prepared by dissolving the dryness in 200 μL of dichloromethane for GC–MS analysis.

GC–MS analysis of PAHs

Determination of PAHs was conducted using a GC apparatus (Agilent Technology 7890A, USA) with a mass spectrometer (Agilent Technology 5975C, USA). GC was equipped with a DB-5 ms Column (30 m length × 0.25 mm inner diameter × 0.25 μm film thickness, Agilent Technology, USA), and the oven initially prepared at 80 °C for 1 min was heated to 245 °C at a rate of 4 °C min^{-1}. And then, the temperature of oven was ramped up to 270 °C at a rate of 30 °C min^{-1} and finally held for 10 min. Helium was flown at 1.5 mL min^{-1} as carrier gas. The injector temperature and injection volume were 320 °C and 1 μL, respectively. The analyte was injected to GC–MS with a splitless mode. Temperature of MS source was 250 °C and spectrometry of MS was obtained by using selective ion monitoring (SIM) modes with the electron ionization (EI) at 70 eV. The BaA and CHR ions were m/z 228, m/z 229, m/z 226, and the quantitative analysis target ion was m/z 228. BbF and BaP were m/z 252, m/z 253, m/z 250, and the quantitative analysis target ion was m/z 252. CHR-d12 was m/z 240, m/z 241, m/z 236, and the quantitative analysis target ion was m/z 240. BaP-d12 was m/z 264, m/z 265, m/z 260, and the quantitative analysis target ion was m/z 264. When the difference of the ratios of other two qualifying ions in sample and standard were within 10%, the peaks of PAHs in sample were accepted [25].

Analytical quality control

The method was validated to ensure the quality of analytical results. Performance parameters: specificity, limit of detection (LOD), limit of quantification (LOQ), linearity, recovery, and precision were obtained to validate the method based on guidelines recommended by the International research group [26]. Specificity was obtained by checking the isolation of PAHs peaks from noise peaks in samples fortified with PAHs. LOD was statistically estimated by multiplying 3 to a standard deviation obtained in repeated analysis of the lowest control 7 samples of 1.0 ng g^{-1}. LOQ was calculated by multiplying 9 to the same standard deviation. Linearity of calibration curve was evaluated by calculating the correlation coefficient (R^2). Six working standards of 1.0, 5.0, 10.0, 50.0, 100.0 and 500.0 μg L^{-1} were plotted and calibration curve was obtained by regressing an equation of 6 plots. The relative recovery of accuracy was obtained by analyzing five samples fortified with standards of 2.0 ng g^{-1} and 10 ng g^{-1} and deuterated internal standards of 4.0 ng g^{-1} and calculating the average percentage of determined concentration via fortified amount. The repeatability of accuracy was evaluated by calculating the relative standard deviation (RSD^r) obtained in the recovery experiments. The reproducibility of accuracy was evaluated by calculating the relative standard deviation (RSD^R) in experiments conducted by 4 different labs.

Exposure estimation and risk characterisation

Exposure to PAHs was estimated by combining PAHs contamination levels and edible oil consuming amounts. PAHs concentration and edible oil consuming data were obtained by this study and KNHANES, respectively. Consumption data of edible oils for total population and consumers were originated from KNHANES IV and V. KNHANES IV was conducted from 2007 to 2009 and KNHANES V was carried out from 2010 to 2012. The second and third programmes of KNHANES IV in 2008 and 2009 and the first programme of KNHANES V in 2010 were selected to assess exposure to edible oils. The numbers of samples in 2008, 2009 and 2010 were 9308, 10,078 and 8473, respectively [22–24]. The KNHANES is composed of three surveys: health interview, health examination and nutrition survey and food consumption data is collected by nutrition survey. Nutrition survey is conducted by face to face interview in sample person's home using the 24 h recall method [27].

The values below LOD were statistically assumed based on the recommendation of GEMS/Food. When the proportion of data below LOD was zero, the concentration of PAHs was not statistically modified. Meanwhile, when the proportion was between 60 and 80% and more than 25 samples were detected, or when the proportion of not-detected samples was higher than 80%, the PAHs concentration was assumed to zero for lower-bound (LB) and to value of LOD for upper-bound (UB). When not-detected sample was between 0% and 60%, the concentration of PAHs was replaced to half of LOD value [28]. To calculate total PAHs concentration, the concentrations of each PAH were combined to use new toxicological

Table 1 Performance parameters of the method in optimum condition

Oil type	PAHs	LOD (ng g^{-1})	LOQ (ng g^{-1})	Recovery		RSD^r (%)		RSD^R (%)	
				2 ng g^{-1}	10 ng g^{-1}	2 ng g^{-1}	10 ng g^{-1}	2 ng g^{-1}	10 ng g^{-1}
Sesame oil	BaA	0.04	0.14	87.0	112..6	5.4	4.9	9.8	6.9
	CHR	0.05	0.18	93.1	103.6	3.3	5.8	17.2	5.5
	BbF	0.04	0.14	79.0	96.9	3.1	2.6	9.6	9.8
	BaP	0.02	0.08	78.3	99.5	0.3	2.0	5.5	8.9
Perilla oil	BaA	0.08	0.26	106.6	94.5	5.3	5.9	4.9	3.9
	CHR	0.05	0.16	99.1	96.5	3.0	7.1	7.7	0.9
	BbF	0.08	0.25	70.7	95.9	1.1	3.0	12.0	9.8
	BaP	0.07	0.23	83.4	100.5	0.3	6.1	7.4	8.1
Pepper seeds oil	BaA	0.09	0.30	107.7	112.1	3.2	1.7	9.7	8.9
	CHR	0.13	0.44	100.5	112.6	2.4	3.0	2.1	9.4
	BbF	0.02	0.06	73.5	99.7	2.2	2.6	11.5	8.4
	BaP	0.02	0.06	87.6	111.6	1.3	5.4	4.7	12.5
Olive oil	BaA	0.04	0.12	110.4	79.9	5.0	8.0	6.9	10.3
	CHR	0.10	0.32	97.0	94.5	6.9	1.4	7.7	6.7
	BbF	0.03	0.11	71.4	90.2	1.3	8.8	14.4	12.7
	BaP	0.02	0.08	83.0	84.9	1.3	1.9	6.2	5.3

LOD limit of detection, *LOQ* limit of quantification, *RSD^r* relative standard deviation of repeatability in single-lab, *RSD^R* relative standard deviation of reproducibility in multi-lab

values. Meanwhile, to use TEQ concept, BaA, CHR and BbF were estimated as BaP equivalent concentrations (TEQ_{BaP}) by multiplying each PAH concentration with its TEF. TEFs of BaA, CHR and BbF were 0.1, 0.01, and 0.1, respectively [11].

The daily intakes of 4 PAHs and TEQ_{BaP} were calculated by using Eq. (1) [29].

In Eq. (2), MOE is calculated by dividing $BMDL_{10}$ value by the estimated daily exposure, and $BMDL_{10}$ value was set by the dose–response analysis for tumor type. $BMDL_{10}$ for BaP and the sum of 4 PAHs ranged from 0.07 to 0.20 mg kg^{-1} b.w. day^{-1} and from 0.34 to 0.93 mg kg^{-1} b.w. day^{-1} based on total tumour-bearing animals, respectively. Therefore, 0.07 and 0.34 mg kg^{-1} b.w. day^{-1} were conservatively adopted for $BMDL_{10}$ of the BaP and the 4 PAHs [3].

$$\text{Daily exposure}\left(\frac{\text{ng}}{\text{kg b.w.day}}\right) = \frac{\text{concentration of PAHs }\left(\text{or }TEQ_{BaP}\right)\left(\frac{\text{ng}}{\text{g}}\right) \times \text{daily edible oil intake }\left(\frac{\text{g}}{\text{day}}\right)}{\text{body weight }(\text{kg})} \tag{1}$$

To characterize a risk of PAHs, MOE was estimated by using Eq. (2). The MOE is used for assessing the risk of substances which does not show a threshold in the dose–response curve because of their genotoxic and carcinogenic properties. Exposure of it should be minimized according to "As Low As Reasonably Achievable (ALARA)" principle. However, Risk manager cannot get any information from ALARA which degree they should reduce which substances. The MOE could be one of the suitable approaches for the risk managers to set a priority list by comparing an appropriate reference point with human intake. The MOE of 10,000 or high in general would be interpreted as low concern to public health [3].

Results and discussion

Quality control

The specificity of the method was guaranteed by comparing retention times with reference materials in blank samples and monitoring fragment ions for each target compound. The calibration plots based on the linear regression analysis revealed good linear relationships between peak area and concentrations over the ranges 1–500 μg L^{-1} with correlation coefficients over 0.99. The LOD and LOQ ranged from 0.02 to 0.13 ng g^{-1} and

$$\text{Margin of Exposure} = \frac{BMDL_{10}\left(\frac{\text{ng}}{\text{kg b.w.day}}\right)}{\text{The estimated daily exposure }\left(\frac{\text{ng}}{\text{kg b.w.day}}\right)} \tag{2}$$

Table 2 PAHs concentrations in edible oils

Country	Sample type	No.	BaA ($ng\ g^{-1}$)		CHR ($ng\ g^{-1}$)		BbF ($ng\ g^{-1}$)		BaP ($ng\ g^{-1}$)		Total ($ng\ g^{-1}$)		Reference (origins)
			Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	
(This study)	Sesame oil	129	0.41	ND–3.91	0.41	ND–2.52	0.35	ND–2.07	0.18	ND–1.11	1.35	ND–7.46	(Korea)
	Perilla oil	71	0.54	ND–2.78	0.97	ND–8.64	0.61	ND–3.66	0.20	ND–1.60	2.33	ND–12.91	(Korea)
	Red pepper seeds oil	16	0.88	ND–1.93	1.08	ND–2.68	0.75	ND–1.53	0.47	ND–1.19	3.18	ND–6.26	(Unknown)
	Olive oil	53	0.51	0.17–1.00	0.95	ND–1.77	0.37	ND–1.05	0.22	ND–0.48	2.05	0.42–4.07	(Unknown)
	Red pepper seasoning oil	34	0.61	ND–2.52	0.95	ND–2.92	0.64	0.12–1.89	0.32	ND–1.15	2.53	0.12–6.88	(Unknown)
Germany	Sesame oil	1	< 0.1		0.6[a]		0.1[b]		ND				[7]
	Olive oil	7	1.6	1.0–1.9	4.6[a]	3.7–6.9[a]	2.4[b]	1.0–2.8[b]	0.7	0.2–1.2			
Spain	Virgin olive oil	6							0.6	0.3–1.2			[33]
	Olive–pomace oil	10							19.2	0.5–49.3			
Denmark	Sesame oil	1							0.2				[34]
	Extra virgin olive oil	46							0.15	< 0.2–0.4			
	Olive oil	6							0.12	< 0.2–0.2			
Australia	Extra virgin olive oil	2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ[b]	<LOQ[b]	<LOQ	<LOQ	<LOQ	<LOQ	[35]
	Olive oil	3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ[b]	<LOQ[b]	<LOQ	<LOQ	<LOQ	<LOQ	
Italy	Olive–pomace oil	3	12.4	6.0–25.0	60.9	18.6–133.2	11.3[b]	1.1–31.4[b]	5.9	0.9–15.4	90.5	26.8–205.0	
Portugal	Virgin olive oil	2	0.7	0.5–0.9	0.3	0.1–0.6	0.4	0.3–0.4	0.2	0.1–0.3	1.6	1.0–2.2	[12]
Kuwait[c]	Sesame oil	9							2.05	0.28–11.05			[14]
	Extra virgin olive oil	21							0.53	0–6.77			
	Virgin olive oil	7							0.90	0–6.31			
	Olive oil	7							ND				
	Pomace olive oil	6							2.06	0–3.62			

TR, Turkey; SY, Syria; IT, Italy; ES, Spain; PS, Palestine; TN, Tunisia; LB, Lebanon; CA, Canada; SA, Saudi Arabia; SG, Singapore; KW, Kuwait; IN, India; TH, Thailand

[a] Sum of chrysene and triphenylene

[b] Sum of benzo[b]fluoranthene, benzo[j]fluoranthene and benzo[k]fluoranthene

[c] Samples purchased from Kuwait markets originated from various countries. The original countries of sesame oils were SA, KW, IN, TH and SG, and those of extra virgin olive oils were from TR, SY, IT, ES, PS, TN, LB, CA and SA. The Virgin olive oils were made from TR, SY, PS and IT, and the pomace olive oils were from ES

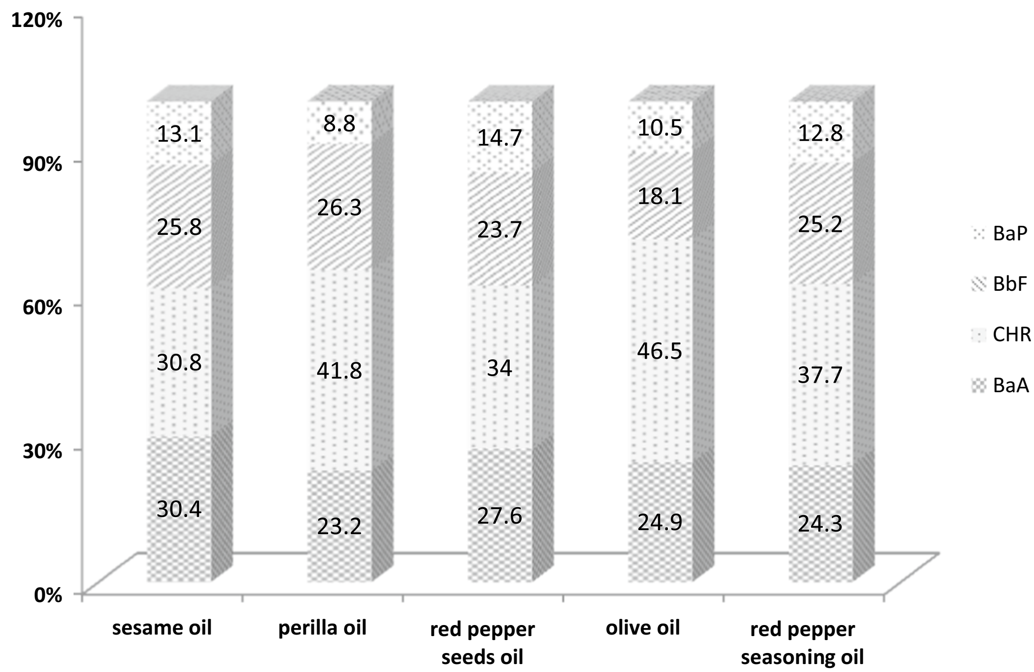

Fig. 1 Relative contribution of 4 PAHs in 5 edible oil categories

from 0.06 to 0.44 ng g^{-1} at four types of oil samples, respectively. The relative recoveries of 4 PAHs were from 70.7 to 110.4% at 2 ng g^{-1} and from 79.9 to 112.6% at 10 ng g^{-1}. The RSD^r for repeatability at a level of 2 ng g^{-1} were from 0.3 to 6.9%, and from 1.4 to 8.8% at a level of 10 ng g^{-1}. The RSD^R for reproducibility was from 2.1 to 17.2% at a level of 2 ng g^{-1} and from 0.9 to 12.7% at a level of 10 ng g^{-1}. All values of performances are shown in Table 1, and they are satisfying the criteria proposed by Association of Official Agricultural Chemists (AOAC) (Table 1) [30].

Concentrations of PAHs in edible oil samples

Table 2 shows means and ranges for BaA, CHR, BbF, BaP and the sum of PAHs from edible oils analyzed in this study. A value below the LOQ was assigned to ND (not detected). The perilla oils and sesame oils were highly contaminated with PAHs. A maximum limit value of 2 ng g^{-1} for BaP was established in edible oils in Korea and EU [4]. The mean concentration of PAHs in 129 sesame oil samples analyzed was 0.41 ng g^{-1} for BaA, 0.41 ng g^{-1} for CHR, 0.35 ng g^{-1} for BbF, 0.18 ng g^{-1} for BaP and 1.35 ng g^{-1} for the sum of 4 PAHs, respectively. The contents of BaP in sesame oils were lower than maximum limit. The mean concentration of BaA (0.54 ng ng^{-1}), CHR (0.97 ng ng^{-1}), BbF (0.61 ng ng^{-1}) and BaP (0.20 ng ng^{-1}) for 71 perilla oil samples were analyzed and BaP were contaminated lower than the established maximum limit. Table 2 shows PAHs content of edible oils in other countries. Red pepper seeds oil contained the highest 4 PAHs content in edible oils in Korea. However, there were no researches to determine PAHs content in red pepper seed oils in other countries. Meanwhile, PAHs contents in sesame oil and olive oil in Korea were similar with or lower than those in other countries. The relative contributions of each of the 4 PAHs to the total content of 4 PAHs in five edible oil categories were shown in Fig. 1. CHR had the highest average contributions of 30.8–46.5% in edible oils, and BaA, BbF and BaP had the average contributions of 23.2–30.4%, 18.1–26.3% and 8.8–14.7%, respectively. Figure 2 shows the correlation of BaP and 4 PAHs in 5 edible oils. BaP has strong correlations with 4 PAHs in sesame oil, red pepper seasoning oil and red pepper seeds oil with correlation coefficients higher than 0.8. BaP has also correlations with 4 PAHs in other edible oils. However, some sesame oils and perilla oils contain 4 PAHs when BaP is not detected. Therefore, BaP is not good to represent 4 PAHs, even though BaP has correlations with 4 PAHs. Alomirah also figured out that Bap was not detected in some olive oils while eight genetoxic PAHs were detected and BaP is not good as the indicator for PAHs [14].

Consumptions of edible oils

The consumption of sesame oils, perilla oils and olive oils were reported in KNHANES, whereas the consumptions

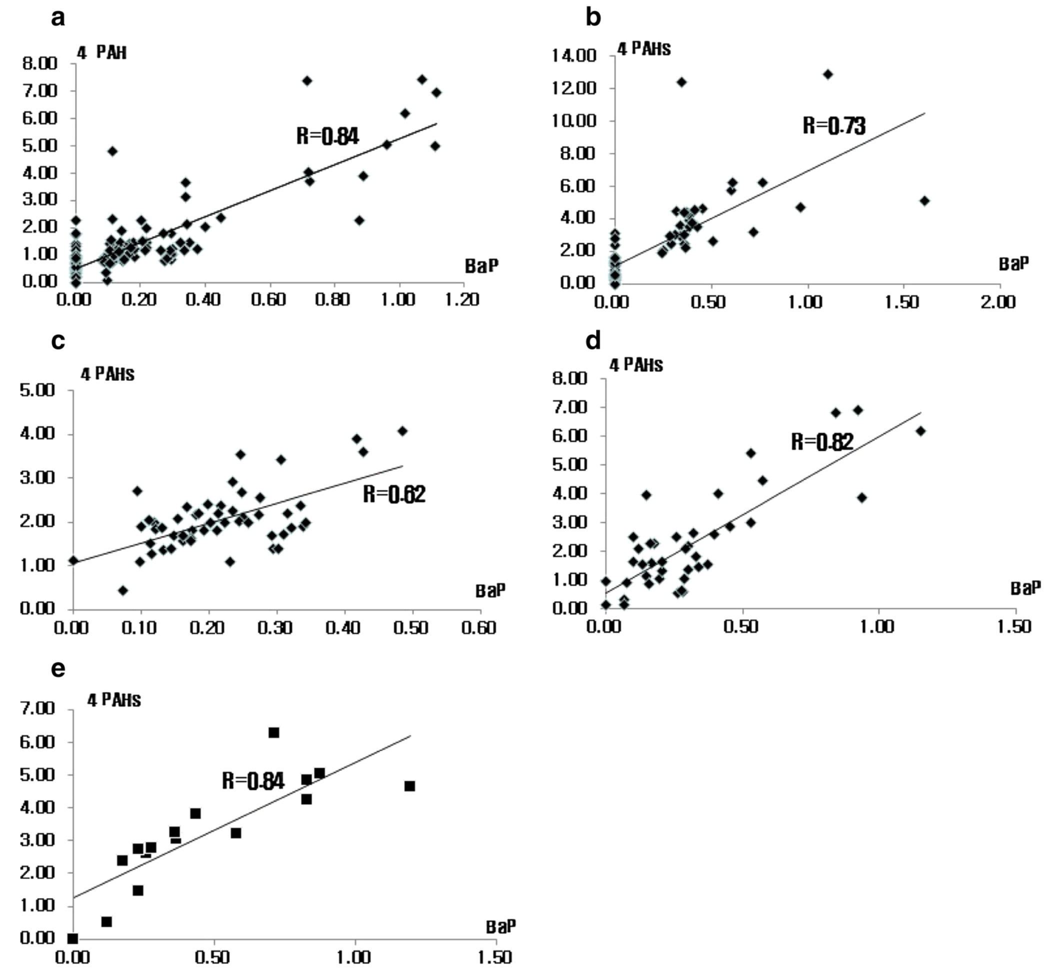

Fig. 2 Correlations between 4 PAHs and BaP in 5 edible oil categories; **a** sesame oil, **b** perilla oil, **c** olive oil, **d** red pepper seasoning oil, and **e** red pepper seeds oil

Table 3 Consumption amounts of edible oils and estimated concentrations of each 4 PAH according to the proportion of not-detected samples

Type	Daily intake (g day^{-1})				Estimated concentration (ng g^{-1})					
	Total population		Consumer only		BaA	CHR	BbF	BaP	4 PAHs[b] (sum)	TEQ_{BaP} [c] (TEFs)
	Mean	P95[a]	Mean	P95						
Sesame oil	1.60	6.52	2.30	7.60	0.43	0.43	0.36	0.19	1.41	0.27
Perilla oil	0.14	0.51	1.70	6.10	0.58	0.99	0.64	0.26	2.47	0.39
Red pepper seeds oil	0.01	0	2.00	5.00	0.90	1.12	0.76	0.47	3.23	0.30
Olive oil	0.10	0	2.50	9.80	0.51	0.96	0.37	0.22	2.05	0.11
Red pepper seasoning oil	0.01	0	2.00	5.00	0.65	0.98	0.64	0.33	2.59	0.46

[a] Daily intake of edible oils at the 95th percentile

[b] The Sum of BaA, CHR, BbF and BaP contents

[c] The estimated equivalent concentrations of BaP calculated by TEFs of BaA, CHR and BbF

Table 4 Dietary exposures to each PAH and total 4 PAHs by consuming edible oils

Type	Population	Dietary exposure (ng kg^{-1} b.w. day^{-1})											
		BaA		CHR		BbF		BaP		4 PAHs[a]		TEQ_{BaP} [b]	
		MEAN	P95[c]	Mean	P95	Mean	P95	Mean	P95	Mean	P95	Mean	P95
Sesame oil	Total	1.17×10^{-2}	4.76×10^{-2}	1.19×10^{-2}	4.83×10^{-2}	9.88×10^{-3}	4.03×10^{-2}	5.22×10^{-3}	2.13×10^{-2}	3.87×10^{-2}	1.58×10^{-1}	7.50×10^{-3}	3.06×10^{-2}
	Consumer only	1.68×10^{-2}	5.55×10^{-2}	1.71×10^{-2}	5.63×10^{-2}	1.42×10^{-2}	4.69×10^{-2}	7.50×10^{-3}	2.48×10^{-2}	5.56×10^{-2}	1.84×10^{-1}	1.08×10^{-2}	3.56×10^{-2}
Perilla oil	Total	1.39×10^{-3}	5.07×10^{-3}	2.38×10^{-3}	8.66×10^{-3}	1.54×10^{-3}	5.60×10^{-3}	6.18×10^{-4}	2.25×10^{-3}	5.92×10^{-3}	2.16×10^{-2}	9.34×10^{-4}	3.40×10^{-3}
	Consumer only	1.69×10^{-2}	6.06×10^{-2}	2.89×10^{-2}	1.04×10^{-1}	1.87×10^{-2}	6.70×10^{-2}	7.51×10^{-3}	2.69×10^{-2}	7.19×10^{-2}	2.58×10^{-1}	1.13×10^{-2}	4.07×10^{-2}
Red pepper seeds oil	Total	1.54×10^{-4}	–	1.91×10^{-4}	–	1.30×10^{-4}	–	0.80×10^{-4}	–	5.55×10^{-4}		5.17×10^{-5}	
	Consumer only	3.07×10^{-2}	7.68×10^{-2}	3.83×10^{-2}	9.57×10^{-2}	2.59×10^{-2}	6.48×10^{-2}	1.60×10^{-2}	4.00×10^{-2}	1.11×10^{-1}	2.77×10^{-1}	1.03×10^{-2}	2.58×10^{-2}
Olive oil	Total	8.74×10^{-4}	–	1.64×10^{-3}	–	6.40×10^{-4}	–	3.71×10^{-4}	–	3.52×10^{-3}		1.83×10^{-4}	
	Consumer only	2.19×10^{-2}	8.57×10^{-2}	4.10×10^{-2}	1.61×10^{-1}	1.60×10^{-2}	6.27×10^{-2}	9.28×10^{-3}	3.64×10^{-2}	8.81×10^{-2}	3.45×10^{-1}	4.58×10^{-3}	1.80×10^{-2}
Red pepper seasoning oil	Total	1.12×10^{-4}	–	1.68×10^{-4}	–	1.09×10^{-4}	–	0.56×10^{-4}	–	4.45×10^{-4}		8.00×10^{-5}	
	Consumer only	2.25×10^{-2}	5.61×10^{-2}	3.35×10^{-2}	8.38×10^{-2}	2.18×10^{-2}	5.45×10^{-2}	1.11×10^{-2}	2.79×10^{-2}	8.89×10^{-2}	2.22×10^{-1}	1.59×10^{-2}	3.98×10^{-2}

[a] The sum of BaA, CHR, BbF and BaP contents

[b] The estimated equivalent concentrations of BaP calculated by TEFs of BaA, CHR and BbF

[c] Dietary exposure to PAHs at the 95th percentile

Table 5 MOEs of total 4PAHs by sum of each PAH and TEQ_{BaP} as BaP concentration estimated by TEFs

Type	MOEs							
	Total population				Consumer only			
	4 PAHs[a]		TEQ_{BaP} [b]		4 PAHs		TEQ_{BaP}	
	Mean	P95[c]	Mean	P95	Mean	P95	Mean	P95
Sesame oil	8,785,530	2,151,899	9,333,333	2,287,582	6,115,108	1,847,826	6,481,481	1,966,292
Perilla oil	57,432,432	15,740,741	74,916,474	20,588,235	4,728,790	1,317,829	6,194,690	1,719,902
Red pepper seeds oil	613,076,828	–	1,346,153,846	–	3,063,063	1,227,437	6,796,117	2,713,178
Olive oil	96,590,909	–	381,758,653	–	3,859,251	985,507	15,283,843	3,888,889
Red pepper seasoning oil	764,501,697	–	879,715,456	–	3,824,522	1,531,532	4,402,516	1,758,794
Total	6,919,104	1,893,096	8,000,634	2,058,824	818,291	264,386	1,323,752	437,774

[a] The sum of BaA, CHR, BbF and BaP contents

[b] The estimated equivalent concentrations of BaP calculated by TEFs of BaA, CHR and BbF

[c] Dietary exposure to PAHs at the 95th percentile

of red pepper seeds oils and red pepper seasoning oils did not appear in KNHANES. Therefore, the amounts of red pepper seeds oils and red pepper seasoning oils intake were substituted by the consumption data of hot sauces. The mean daily intake and the consumption at the 95th percentile of edible oils for total population and consumers are shown in Table 3. The zero consumption data at 95th percentile means that the Korean consumer intake edible oils a lot whenever they eat, but not too frequently.

Exposure assessment

The proportions of samples contaminated with PAHs below the LOD were below 60% and the values below the LOD was replaced to half of LOD. The estimated mean concentrations of 4 PAHs in edible oils were from 0.19 to 1.12 ng g^{-1} (Table 2). The total contents of 4 PAHs and the total BaP equivalent values were from 1.41 to 3.23 and from 0.11 to 0.46 (Table 3). The average bodyweight of Korean was 58.3 kg [22–24]. Table 4 shows the average and 95th percentile daily intakes of 4 PAHs for total populations and consumers. The daily exposures to high consumers in the 95th percentile were from three times to five times greater than that of mean daily consumers. Furthermore, the mean and high exposures to total 4 PAHs for total populations and consumers only were shown in Table 4, and they were compared with the exposures to estimated equivalent BaP. Korean people were the most highly exposed to PAHs from sesame oils among edible oils according to the estimations by both sum of each PAH and TEQ_{BaP}. This highest intake of PAHs by consumption of sesame oils arises because Korean people consume sesame oil over 10 times more than other edible oils although the sesame oils are not highly contaminated with PAHs compared to others. Meanwhile, Korean consuming edible oils was exposed to PAHs mostly by olive oil due to the highest contamination of PAHs. In Brazil, people exposure to 4 PAHs of 7.3 ng kg^{-1} b.w. day^{-1} via edible oils (soybean oils) [31], and in Australia, People consume canola oil of 0.3 g day^{-1} and it contains BaA of below 0.06 ng g^{-1}, Chr of below 0.1 ng g^{-1}, BaP of below 0.08 ng g^{-1}. People in Australia exposure to BaA of 0.018 ng kg^{-1} day^{-1}, Chr of 0.03 ng kg^{-1} day^{-1} and BaP of 0.024 ng kg^{-1} day^{-1} at most [32]. In Europe, the exposure to BaP and 4 PAHs via fats (vegetable and animal) are 26 ng day^{-1} and 177 ng day^{-1} [3]. Korean is not highly exposed to PAHs by eating edible oils comparing to other countries' people.

Risk characterisation

The risk of PAHs by dietary intake of edible oils was characterised by calculating MOEs (Table 5). With regard to average consumption, the MOE of 4 PAHs for total population was 6,919,104 and that of consumers only was 818,291. In the case of high consumption in the 95th percentile, the MOEs were 1,893,096 and 264,386 for total population and consumers, respectively. All MOEs were over 1.0×10^4 and it was found that the risk of 4 PAHs in edible oils is "low concern from a public health point of view" [3]. According to the French total diet study, edible oils are the main contributors (16.2%) to PAHs exposure via foods [33]. If Korean people are exposed to PAHs by edible oils with contribution of about 20%, MOEs will be between 66,096 and 1,729776. Therefore, exposure to PAHs by consuming food does not still represent a food safety issue to Korean people.

Furthermore, the MOEs of the estimated equivalent BaP calculated by TEFs of other 3 PAHs were from 2,058,824 to 8,000,634 for total population and 437,774 to 1,323,752 for consumers only. These MOEs are from 1.1 to 1.7 times higher than those of total of 4 PAHs.

Therefore the risk of 4 PAHs estimated by the TEFs can be over-estimated comparing to the risk of total 4 PAHs. Many studies assessing the risk of PAHs by TEFs need to be re-assess the risk of PAHs by using total PAHs concentration and toxicological value from mixture of PAHs.

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Authors' contributions
JG validated analytical method and analysed samples and JH statistically analysed data. HJ interpreted effects of food processing on contents of PAHs. All authors read and approved the final manuscript.

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