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ORIGINAL PAPER

ESTIMATION OF THE INTAKE OF SELECTED FATTY ACIDS AND CHLORINATED HYDROCARBONS (PCB_s, γ-HCH, DDT AND ITS METABOLITES) FROM NUTS*

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Abstract

This study aimed to determine the fatty acid profile and content of chlorinated hydrocarbons (PCB, γ -HCH, DDT and its metabolites) as well as to estimate their mean daily intake with 30 g of nuts. It demonstrated that palmitic acid (C:16) was the saturated fatty acid occurring in the largest amount in all types of nuts studied. Its concentration in nuts was species-dependent and in the present study its highest mean concentration was determined in Brazil nuts (15.30%), whereas the lowest one was in walnuts (6.87%). Oleic acid (C18:1) and linoleic acid (C18:2) were predominating unsaturated fatty acids, and their concentrations were depended on nut species. The n-6/n-3 ratios was calculated. The best proportion of these acids was found in walnuts and the least favorable one in peanuts. The maximum permissible level (10 μ g 1000 g⁻¹) was exceeded in the case of one of the chlorinated hydrocarbons, i.e. γ -HCH – in hazel nuts $(1.894 \ \mu g \ 100 \ g^{-1})$ and in Brazil nuts $(1.058 \ \mu g \ 100 \ g^{-1})$. The maximum permissible level of Σ DDT in nuts was not exceeded. The highest content of DDT and its metabolites was determined in Brazil nuts and hazelnuts, with the mean amounts corresponding to 36 and 27% of the permissible level, respectively. The nuts tested were found to contain five PCB congeners (28, 101, 118, 138, 153), with the highest content determined for: 153, 28, and 138 congeners. The most toxic one appeared to be the 118 congener, and the highest value of its toxicity equivalents (TEQ) was found in almonds, although it still did not pose a risk to the consumer's health.

Keywords: nuts, saturated fatty acids, unsaturated fatty acids, quality, organic pollutants, daily intake.

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INTRODUCTION

Nuts and seeds represent important constituents of a well-balanced diet, including also the Mediterranean diet. The may contribute to the good health of consumers, at the same time making a positive contribution to food security (FAO 2010). Their fat content ranges from 45 to 75% (of weight). and is largely attributable to the presence of essential fatty acids (EFAs). Polyunsaturated fatty acids (PUFAs) exert beneficial effects on the human body, in particular they positively affect the circulatory system, reduce blood cholesterol level, and suppress synthesis of triacylglycerols (CARDOSO et al. 2017, TAS, GÖKMEN 2017). A human body is incapable of producing enzymes which synthesize polyunsaturated fatty acids (from n-3 and n-6 families), hence they need to be supplied with a diet. The major n-6 PUFA is linoleic acid, a precursor of arachidic acid, and the major n-3 PUFA is linolenic acid (JACKSON HU 2014, MOHAMMADIFARD et al. 2015). However, not only the content of PUFAs, but also the *n*-6/*n*-3 ratio matters for an everyday diet (LI HU 2011). The PUFAs are necessary to ensure appropriate bodily functions as they stimulate the immune system, exhibit anticarcinogenic, anti-atherosclerotic, and antidepressant properties, and have also been implicated to inhibit type II diabetes (KIRBASLAR et al. 2012). It is not only crucial to provide EFAs with a diet, but also to ensure their intake with an everyday diet in appropriate ratios, i.e. optimally at 2.5-5:1 (n-6:n-3). Previous research had shown that a diet including food products with a well-balanced n-3:n-6fatty acid ratio (optimal 1:5) reduced the risk of ischemic heart disease development, sudden death, and brain stroke (ADKINS, KELLEY 2010). According to dieticians, a recommended daily portion of nuts is *ca* 30 g.

According to dietary guidelines for healthy individuals, an everyday diet should provide no more than 30% energy from fats (as little as possible from SFAs and 4-8% of from n-6 PUFAs). The recommended intake of α -linolenic acid is set at 2 g per day, whereas other acids from n-3 family should be consumed at 200 mg per day. The remaining part of energy should be provided with monounsaturated fatty acids. For this reason, nuts are among food products indicated as a very good and commonly available source of MUFAs and PUFAs in a human diet (FAO 2010).

Due to anthropogenic activity, many toxic substances are released into the natural environment, including lipophilic compounds that hardly degradable but well bioaccumulable, with long half-lives. They are synthesized in technological processes, also unintentionally (Stockholm Convention on Persistent Organic Pollutants (POPs) 2009). Food products made of high-fat raw materials may constitute a source of POPs in a man's diet, and thus pose health risks to consumers. Polychlorinated biphenyls and chlorinated hydrocarbons belong to a group of compounds whose levels in foodstuffs are regulated by law (Commission Regulation (EC) No 1881/2006, Commission Regulation (EC) No 149/2008). Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDD), and polychlorinated dibenzofurans (PCDF) are organic chemical substances produced during combustion or industrial processing. PCBs are representatives of highly toxic xenobiotics; in total, they constitute a group of 209 congeners which pose a threat to the health of people and animals by inducing adverse effects on the immune, nervous, endocrine, and reproductive systems. Their toxicity is reflected in their high carcinogenic potential (ESPOSITO et al. 2017, WEBER et al. 2017). This is due to the fact that within a group, these compounds differ in their toxicity, frequency of occurrence, and concentrations in environmental samples (BIFULCO 2015, ARREBOLA et al. 2017, ESPOSITO et al. 2017, LAMBIASE et al. 2017). The European Commission's Scientific Committee on Food has adopted a concept of the Toxic Equivalency Factor (TEF). Considering TEF values, the most toxic congeners are these with the following numbers: 126, 169, 77, 114, 156, and 157 (ESPOSITO et al. 2017).

This study aimed to determine the fatty acid profile and content of chlorinated hydrocarbons (PCB_s, γ -HCH, DDT and its metabolites) as well as to estimate their mean daily intake with 30 grams of nuts.

MATERIALS AND METHODS

Samples

Nuts were purchased in 2016-2018, in Poland, from supermarkets which belong large European retail chains. They originated from several countries: Italy, the USA, Poland, Vietnam, Turkey, Australia, Brazil, Iran, and Spain. The study material included walnuts almonds, cashew nut, peanuts, Brazil nuts, pistachios, and hazelnuts (each spices n=10).

Determination of fat content and fatty acid profile

Fat was extracted from nuts with an ether mixture [1:1] after earlier acidic hydrolysis. Fatty acids were esterified to methyl esters according to PEISKER (1964). Esters were separated using a 7890A gas chromatograph (Agilent Technologies) with a flame-ionization detector. The separation settings: capillary column (30 m x 0.32 mm); liquid phase: Supelcowax 10; film thickness: 0.25 μ m; temp.: detector 250°C, injector 230°C, column 190°C; carrier has: helium; flow rate: 1.5 ml min⁻¹, injection split ratio: 50:1.

Extraction and determination of organochlorine (OC) pesticides

A 5-g of sample was weighted and homogenized in 200 mL of *n*-hexane, filtered, and re-extracted with 100 mL of *n*-hexane. The extracts were washed with saturated sodium chloride solution. The concentrated hexane layer was treated with sulfuric acid and separated, then passed through an activated Florisil (Fluka) column (WIECZOREK et al. 2010). Separation and

388

determination of the other OCs were conducted with the method of capillary gas chromatography with electron capture detection (GC-ECD).

Determination of content of polychlorinated biphenyls

Content of the following congeners of individual polychlorinated biphenyls (PCBs) was determined in nut samples (IUPAC numbers): 6 non-dioxin-like polychlorobiphenyls (NDL-PCBs) 28, 52, 101, 138, 153, 180; and dioxin-like polychlorobiphenyl (DL-PCBs) congener 118. Individual PCB congeners were determined in samples with *n*-hexane extracts left after OC determination (WIECZOREK et al. 2010). Separation, identification and quantification of PCB congeners were carried out using a 6890 N gas chromatograph (Agilent Technologies) with an electron capture detector (ECD), under the following conditions: helium flow rate: 2.5 ml min⁻¹; capillary column (25 m x 0.32 mm); liquid phase: RTx-1701; film thickness: 0.25 μ m, temp.: detector 280°C, injector 250°C, column 200°C. Quantitative and qualitative results interpretation was conducted using Hewlett Packard software.

Total toxicity of PCB congeners was determined by computing their toxic equivalents (TEQ):

$$TEQ = \Sigma ([cPCBi] \cdot TEFi),$$

where:

TEQ – toxic equivalent,

cPCBi - concentration of *n*-th PCB congener,

TEFi – toxic equivalency factor of *n*-th PCB congener.

Statistical analysis

Quantitative and qualitative interpretation of results was conducted using software by Hewlett Packard. Differences between mean values were determined with one-way analysis of variance (ANOVA) at a significance level of $p \leq 0.05$. Results were presented in Table 1-6 and Figures 1-2.

RESULTS AND DISCUSSION

Results of determinations of the fat content, fatty acid profile and total content of SFA, MUFA and PUFA in nuts are presented in Table 1. The highest mean fat content was determined in Brazil nuts – 55.10%, and the lowest was in almonds – 27.46% (Table 1). Statistical analysis showed significant differences in the fat content among nut samples. BIERNAT et al. (2014) demonstrated the mean fat content to reach 67.01% in Brazil nuts, 48.33% in peanuts, and 35.71% in cashew nuts, and concluded that the fat content may be determined by the origin and cultivar of nuts, and climate conditions.

Table	1

	Walnuts	Almonds	Hazelnuts	Cashew nuts	Peanuts	Brazil nuts	Pistachios	Anova
Specifica-	x ±SD	F						
tion				Fat c	ontent			Ľ
	42.63±3.97	27.46±2.47	45.74±2.53	38.56±3.50	41.94±2.27	55.10±6.85	40.23±4.76	9.59 0.008
				fatty acids				
C14	0.04±0.01	-	0.07±0.01	0.04±0.01	0.07±0.06	0.07±0.01	0.12±0.02	54.87<0.001
C15	0.18±0.08	-	0.17±0.02	0.20±0.04	0.20±0.03	0.14±0.04	0.24±0.30	11.57<0.001
C16	6.87±0.59	6.96±0.31	5.85±0.26	10.37±0.74	13.66 ± 1.38	15.30 ± 0.52	10.45 ± 0.73	1.54 < 0.001
C16:1	0.09±0.01	0.56±0.07	0,17±0.03	0.42±0.09	0.22±0.31	0.37±0.07	0.70±0.10	7.39<0.001
C17	-	-	0,04±0.02	0.16±0.19	-	0.08±0.04	0.02±0.04	4.06<0.001
C18	2.28±0.22	2.02±0.35	2.46±0.23	9.46±0.99	3.95 ± 0.67	10.16 ± 0.87	2.15 ± 2.27	2.64<0.032
C18:1	18.53±0.80	65.28±3.14	82.04±3.07	63.18±3.09	45.34±2.17	35.16 ± 1.15	56.78±2.53	5.64<0.001
C18:2 (n6)	60.24±0.89	26.32±2.11	8.72±0.87	18.07±1.17	31.35 ± 1.74	39.13 ± 1.45	31.04 ± 2.20	2.79<0.026
C18:3 (n3)	12.21±1.03	-	0.10±0.01	0.24±0.08	-	0.11±0.03	0.33±0.08	17.17<0.001
C20:0	0.10±0.01	-	0.11±0.03	0.51±0,15	1.25±0.49	0.29±0.03	0.19±0.15	6.74<0.001
C20:1	0.21±0.02	-	0.19±0.04	0.28±0.11	0.98±0.31	0.09±0.01	0.47±0.08	20.15<0.001
C22:0	-	-	-	-	2.34±0.26	-	-	-
C24:0	-	-	-	-	1.21±0.17	-	-	-

Fat content and fatty acid compositions (% of total identified) of nuts (%)

Almonds contain the lowest amount of fatty acids. A predominating fatty acid was oleic acid (C18:1); its mean content reached 65.28% (Table 1). ČoLić et al. (2017) detected sixteen fatty acids in almond samples, with oleic and linoleic acids found in the highest concentrations. The most abundant saturated fatty acid in all nuts turned out to be palmitic acid (C:16). Its concentration in nuts is species-dependent, and its highest mean concentration was determined in Brazil nuts (15.30%) while the lowest one was in walnuts (6.87%). Regardless of a species, nuts were rich in MUFA and PUFA. In all the nut species studied, the highest concentrations were found for oleic acid (C18:1) and linoleic acid (C18:2), and their concentrations were determined by nut species. Samples contained only α -linolenic acid (C18:3) from the *n*-3 family. Its presence was detected in four nut species studied, with its highest mean concentration found in walnuts -12.21% (Table 1). The statistical analysis showed significant differences in content of individual fatty acids among the analyzed nut species.

KIRBASLAR et al. (2012) showed mean concentrations of oleic acid at 13.55% in walnuts, 67.18% in pistachios, and 71.98% in almonds; whereas concentrations of linoleic acid were 63.42%, 20.53%, and 20.37%, respec-

tively. Similar study results were reported by CARDOSO et al. (2017) and FERNANDES et al. (2017).

The highest total content of fatty acids was determined in Brazil nuts and peanuts, while the lowest one was in cashew nuts. Walnuts were characterized by the lowest total content of MUFA – 18.85%, but by the highest content of PUFA – 72.37% (Table 2). The *n*-6/*n*-3 ratios determined in all nut samples showed that the best proportion of these acids was in walnuts and the least favorable one appeared in peanuts. These results

Table 2

Fatty	Walnuts	Almonds	Hazelnuts	Cashew nuts	Peanuts	Brazil nuts	Pistachios
acids	$\overline{x}\pm SD$	x ±SD	x±SD	x ±SD	x ±SD	x ±SD	x±SD
∑SFA	9.45 ± 0.60	8.98±0.62	8.70±0.57	2.73±1.20	26.06 ± 0.82	22.89±2.17	13.17±2.19
∑MUFA	18.85±0.78	65.84±1.58	82.40±3.14	63.88±1.75	35.62±1.12	49.39±2.07	57,97±2.37
∑PUFA	72.37±1.70	26.33±1.34	8.82±0.88	18.40±0.72	39.25 ± 1.08	31.35±1.74	31.38±1.51
∑n6	60.16±0.82	26.33±1.34	8.72±0.87	18.07±0.64	39.14±1.05	31.35±1.74	31.05±1.45
∑n3	12.21±1.03	0	0.10±0.01	0.24±0.08	0.11±0.03	0	0.33±0.08
n6/n3	4.93	-	87.20	75.28	358.03	-	94.09

Sum of fatty acids in nuts (%)

 ${\rm SFA}$ – saturated fatty acids, ${\rm MUFA}$ – monounsaturated fatty acids, ${\rm PUFA}$ – polyunsaturated fatty acids

are similar to literature findings. For example, BIERNAT et al. (2014) showed the most favorable n-6/n-3 ratio in walnuts, where it equalled 5.26, whereas in the study conducted by KIRBASLAR et al. (2012) that ratio reached 5.01.

According to nutritional guidelines of dietitians and physicians, the recommended daily intake of nuts is ca 30g, and in line with the recommended intakes of individual fatty acids with a diet (2 g of *n*-3 fatty acids and up to 8% of energy from *n*-6 fatty acids), the most beneficial for a human body appeared to be walnuts. This conclusion is consistent with literature data (BEYHAN et al. 2017, COPOLOVICI et al. 2017). Table 3 provides information on the mean daily intake of fatty acids at the assumed recommended intake of nuts.

Man's interference into the natural environment, including the use of plant protection agents (pesticides and herbicides), influences the accumulation of lipophilic contaminants, which may pose a threat to consumers of food products rich in fat. Although perceived as highly valuable for a human body by dietitians, nuts may contain residues of plant protection agents owing to a high content of lipids. Table 4 shows data pertaining to the content of residues of organochlorine insecticides in nut samples. Pursuant to the *EC Commission Regulations (2008, 2017)* concerning the maximum permissible levels of pesticide residues in foods, Σ DDT should not exceed 0.05 mg kg⁻¹, whereas the content of γ -HCH should not be higher than 0.01 mg kg⁻¹. Results of the present study show that the highest total content

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0	0	-

Fatty acids	Walnuts	Almonds	Hazelnuts	Cashew nuts	Peanuts	Brazil nuts	Pistachios
C14	0.005	-	0.01	0.005	0.009	0.012	0.014
C15	0.023	-	0.023	0.023	0.025	0.023	0.029
C16	0.879	0.573	0.803	1.2	1.719	2.529	1.261
C16:1	0.012	0.046	0.023	0.049	0.028	0.061	0.084
C17	-	-	0.005	0.019	-	0.013	0.002
C18	0.292	0.166	0.338	1.094	0.497	1.679	0.259
C18:1	2.370	5.313	11.258	7.309	5.705	5.812	6.853
C18:2 (n6)	7.704	2.168	1.197	2.09	3.944	6.468	3.746
C18:3 (n3)	1.562	-	0.014	0.028	-	0.018	0.040
C20:0	0.013	-	0.015	0.059	0.157	0.047	0.023
C20:1	0.027	-	0.026	0.032	0.123	0.015	0.057
C22:0	-	-	-	-	0.294	-	-
C24:0	-	-	-	-	0.152	-	-
Σ SFA	1.212	0.166	1.194	2.4	2.848	4.303	1.588
∑MUFA	2.409	5.359	11.307	7.39	5.856	5.888	6.994
∑PUFA	9.266	2.168	1.21	2.118	3.944	6.486	3.786
<i>n6/n</i> 3	4.93	-	87.20	75.28	358.03	-	94.09

The average daily intake of fatty acids from nuts (g 30 g⁻¹)

of DDT was determined in Brazil nuts – 1.836 µg 100 g⁻¹ on average, and the lowest one was in pistachios – 0.311 µg 100 g⁻¹ on average. The statistical analysis of the results demonstrated no significant differences in either the total DDT content or the content of individual DDTs among the nut species tested (Table 4). High concentrations of γ -HCH were found in walnuts (1.894 µg 100 g⁻¹), followed by Brazil and cashew nuts (1.058 and 0.898 µg 100 g⁻¹), respectively), whereas the lowest one was in almonds (0.129 µg 100 g⁻¹) – Table 4. These results show that the permissible levels of γ -HCH residues were exceeded in samples of hazelnuts and Brazil nuts. The maximum permissible concentration set for hazelnuts in the EU Regulation, i.e. 10 µg 1000 g⁻¹, was exceeded almost twice, whereas the mean concentration of γ -HCH residues determined in cashew nuts approximated the upper permissible level.

The maximum permissible level of Σ DDT in nuts was not exceeded. The highest content of DDT and its metabolites was determined in Brazil nuts and hazelnuts, where it accounted for 36 and 27% of the permissible level, respectively.

Although the use of DDT and γ -HCH has been forbidden (eliminated) or minimized in many European countries including Poland, residues of these plant protection agents may still be detected in both soil and food products.

Speci- fica-	Walnuts	Almonds	Hazelnuts	Cashew nuts	Peanuts	Brazil nuts	Pistachios	Anova
tion	$\overline{x}\pm SD$	F p						
γHCH	0.55 ± 0.5	1.894 ± 0.314	0.453 ± 0.622	1.058 ± 0.437	0.898 ± 0.188	0.176 ± 0.091	0.129 ± 0.076	2.94 0.008
DDE	0.012±0.018	0.049 ± 0.018	0.012±0.009	0.007 ± 0.003	0.006 ± 0.002	0.002 ± 0.001	0.050 ± 0.022	$1.12\ 0.364$
DDD	0.216±0.291	0.188±0.036	0.061±0.037	0.365±0.240	0.076±0.025	0.063±0.024	0.121 ± 0.058	2.06 0.056
DDT	0.718 ± 1.065	1.114 ± 0.341	0.324±0.257	1.464 ± 0.283	0.398 ± 0.214	0.246 ± 0.042	0.698 ± 0.204	$1.53\ 0.169$
ΣDDT	0.892±1.335	1.35 ± 0.359	0.398±0.303	1.836 ± 0.526	0.480±0.241	0.311±0.067	0.868 ± 0.284	1.54 0.166

The average content of chloroorganic insecticide residues in nuts (µg 100 g⁻¹)

SZYMONA (2010) demonstrated residues of DDT, withdrawn from use in Poland over 50 years ago, in soil from arable lands intended for organic farming. The presence of these insecticides in nuts has been confirmed by many authors. ÖZKAN (2015) demonstrated that in two out of six analyzed samples of pistachios from Turkey the content of organochlorine insecticides reached 0.13 and 0.296 mg kg⁻¹. In their study, LIU et al. (2015) also detected DDT and γ -HCH in nuts. The predominating DDT isomer was DDE, whereas of HCS – it was γ -HCH. The presence of pesticide residues: DDT and γ -HCH, in nuts was also reported by AIKPOKPODION et al. (2013), and EMAMI et al. (2017). The present study and literature data indicate that despite the ban on use or reduced use of organochlorine insecticides in agriculture, these substances are still detected in food products in concentrations exceeding the maximum permissible level of residues stipulated in *EC Regulations* from 2008 and 2017.

Considering their high fat content, nuts may also be one of the sources of PCBs. According to the EC Commission Regulations No. 1259/2011 of 2 Dec. 2011, the total content of 6 indicatory congeners from the NDL-PCBs group (28, 52, 101, 138, 153 and 180) in vegetable oils and plant lipids should not exceed 40 μ g kg⁻¹. This is due to the fact that NDL-PCBs are very stable in the natural environment and meet criteria set for POPs (Stockholm Convention 2009).

In Figure 1 there are results of our determination of the total concentration of 6 congeners classified as NDL-PCBs. The permissible maximum total concentration of these compounds was not exceed in any nut species studied. Their highest concentration was determined in Brazil nuts – 0.067 µg 100 g⁻¹, and the lowest one occurred in cashew nuts – 0.027 µg 100 g⁻¹ on average (Figure 1). After considering the lipid content in samples of nuts, the total content of these 6 PCB congeners accounted for 5.6% of the maximum permissible level in almonds (i.e. 40 µg 100 g⁻¹ lipids), 3.5% in peanuts, 3.0% in Brazil nuts, 2.8% in walnuts, 2.2% in pistachios, 2.1% in hazelnuts, and 1.8% in cashew nuts. The statistical analysis of our results showed significant differences in the content of PCB congeners among the nut samples.



Fig. 1. Sum of PCB congeners in nuts – mean \pm SD (µg 100 g⁻¹ product) with a percentage of the permission threshold (*A*, *B*, *C* – statistically significant differences $p \leq 0.05$)

Figure 2 there shows the content of 7 individual PCB congeners in the analyzed nuts. Among the 7 congeners studied, five were detected in the analyzed nut samples, i.e.: 28, 101, 118, 138, and 153, and the highest concentrations were found for congeners 153, 28, and 138. The most toxic of the PCB congeners examined turned out to be congener 118 belonging to dioxin-like PCBs (WHO-TE =0.0001, BAARS et al. 2004). When investigating oils produced from various oleaginous plants, Roszko et al. (2012) demonstrated that among the dioxin-like PCB congeners, the 118 congener was detected in vegetable oils in the highest concentrations. Its mean concentrations in oils produced from various seeds ranged from 0.0005 to 0.0054 μ g 100 g⁻¹, whereas in nut lipids (lipid content at *ca* 40%) its concentrations were higher and ranged from 0.0075 to 0.0225 μ g 100 g⁻¹.

When comparing results of our study (Figure 2) with these reported by Roszko et al. (2012), similar observations were made as for the high concentrations of congener 28. In nuts, its mean concentrations ranged from 0.009 to 0.03 μ g 100 g⁻¹ (i.e. from about 0.0225 to 0.075 μ g 100 g⁻¹ fat), whereas in most of the oil samples analyzed by Roszko et al. (2012) they ranged from 0.006 to 0.079 μ g 100 g⁻¹. In contrast, very high concentrations of congeners 153 and 138 were determined in nuts only.

After considering the TEF value set for congener 118, in Table 5 we collated values of toxic equivalents (TEQ) as an outcome of the risk assessment of consumer exposure to PCB compounds present in the analyzed nuts (Table 5). The highest TEQ value was determined for almonds. ESPOSITO



Nuts	TEQ (µg 100 g ⁻¹)	TEQ (µg 30 g ⁻¹)
Pistachios	$9 \cdot 10^{-8}(a)$	$2.7\cdot10^{-8}$
Cashew nuts	$12 \cdot 10^{-8}(a)$	$3.6\cdot10^{-8}$
Peanuts	$21 \cdot 10^{-8}(b)$	$6.3\cdot10^{-8}$
Brazil nuts	$12 \cdot 10^{-8}(a)$	$3.6\cdot10^{-8}$
Almonds	$27 \cdot 10^{-8}(c)$	$8.1 \cdot 10^{-8}$
Walnuts	$9 \cdot 10^{-8}(a)$	$2.7\cdot10^{-8}$
Hazelnuts	$18 \cdot 10^{-8}(b)$	$5.4\cdot10^{-8}$

Equivalent of toxicity PCB congeners in nuts

 $a,\,b,\,c-$ statistically significant differences $p{\leq}0.05$

Specifica- tion	Walnuts	Hazel- nuts	Peanuts	Brazil nuts	Cashew nuts	Pista- chios	Almonds
γHCH	0.165	0.568	0.136	0.317	0.269	0.053	0.039
DDE	0.004	0.015	0.004	0.002	0.002	0.001	0.015
DDD	0.065	0.056	0.018	0.110	0.023	0.019	0.036
DDT	0.215	0.334	0.097	0.439	0.119	0.074	0.209
ΣDDT	0.268	0.405	0.119	0.551	0.144	0.093	0.260
∑PCB	0.012	0.017	0.020	0.021	0.009	0.009	0.011

The average daily intake of PCB γ -HCH, DDT and its metabolites from nuts ($\mu g \ 30 \ g^{-1}$)

et al. (2017) demonstrated mean TEQ values in walnuts and cashew nuts at 0.071 and 0.034 pg g^{-1} product, respectively, whereas the sum of congeners expressed per 1 g was 0.444 pg g^{-1} in the case of walnuts and 0.004 pg g^{-1} in the case of cashew nuts.

Considering nutritional recommendations of dietitians, analyses were conducted to estimate a daily intake of organochlorine insecticides and the total content of 7 PCB congeners with an everyday diet containing 30 g of nuts. The estimated daily intake of these compounds was presented in Table 6.

Hazelnuts turned out to be the largest source of γ -HCH, but such low concentration levels are not an important source of this compound for consumers.

CONCLUSIONS

The high fat content of nuts makes them high-energy snacks. Moreover, the fat they contain is a very good source of unsaturated fatty acids indispensable to a human body. The major saturated fatty acid of nuts turned out to be palmitic acid, and the major unsaturated fatty acids included oleic and linoleic acids. Walnuts were found to be a rich source of α -linolenic acid (C18:3); in addition, they had the most favorable *n*-6/*n*-3 ratio, from the nutritional point of view.

Despite the ban imposed on the use of the DDT insecticide in farming (apart from permissible exceptions – Appendix B of the Stockholm Convention), its residues were still detected in the analyzed nut samples, whereas the maximum permissible level of another organochlorine insecticide – γ -HCH – was exceeded in hazelnuts and Brazil nuts. In contrast, the maximum permissible level of Σ DDT was not exceeded in any of the samples. Similar observations were made for individual PCB congeners, pollutants whose sources include technological processes and technical facilities.

Their concentrations determined in nut lipids were low and posed no risk to the health of consumers.

REFERENCES

- ADKINS Y., KELLEY DS. 2010. Mechanisms underlying the cardioprotective effects of omega-3 polyunsaturated fatty acids. J Nutr Biochem., 21: 781-792 DOI: 10.1016/j.jnutbio.2009.12.004
- AIKPOKPODION P., ODUWOLE O., ADEBIYI S. 2013. Appraisal of Pesticide Residues in Kola Nuts obtained from Selected Markets in South Western, Nigeria. J Sci. Res Rep, 2(2): 582-597.
- ARREBOLA J.P., CASTAÑO M., ESTEBAN A., BARTOLOMÉ M., PÉREZ-GÓMEZ B., JOSÉRAMOS J. 2017. Differential contribution of animal and vegetable food items on persistent organic pollutant serum concentrations in Spanish adults. Toxics, 5: 33. DOI: 10.3390/toxics5040033
- BAARS A.J., BAKKER M.I., BAUMANN R.A., BOON P.E., FREIJER J.I., HOOGENBOOM L.A.P., HOOGERBRUGGE R., VAN KLAVEREN J.D., LIEM A.K.D., TRAAG W.A., DE VRIES J. 2004. Dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs: occurrence and dietary intake in the Netherlands, Toxicol Lett, 151: 51-61. DOI: 10.1016/j.toxlet.2004.01.028
- BEYHAN O., OZCAN A., HATICE OZCAN H., KAFKAS E., KAFKAS S., SUTYEMEZ M., ERCISLI S. 2017. Fat, fatty acids and tocopherol content of several walnut genotypes. Not Bot Horti Agrobo, 45(2): 437-441. DOI: 10.15835/nbha45210932
- BIERNAT J., DRZEWICKA M., ŁOŻNA K., HYLA J., BRONKOWSKA M., GRAJETA H. 2014. Content of fatty acids in commercially available nuts and seeds in the context of healthy dietary guidelines. Bromat. Chem. Toksykol., 47(2): 121-129. (in Polish)
- BIFULCO M. 2015. Comments on Triassi et al. Environmental Pollution from Illegal Waste Disposal and Health Effects: A Review on the "Triangle of Death". Int. J. Environ. Res. Public Health, 12: 3358-3359. DOI: 10.3390/ijerph120303358
- CARDOSO B.R., GRAZIELA B., SILVA DUARTE B., REIS Z., COZZOLINO MF. 2017. Review of Brazil nuts: Nutritional composition, health benefits and safety aspects. Food Res Int, 100(2): 9-18. DOI: org/10.1016/j.foodres.2017.08.036
- ČOLIĆ S.D., FOTIRIĆ-AKŠIĆ M.M., LAZAREVIĆ K.B., ZEC G.N., GAŠIĆ U.M., DABIĆ D.C., NATIĆ M.M. 2017. Fatty acid and phenolic profiles of almond grown in Serbia. Food Chem., 234(1): 455-463. DOI: org/10.1016/j.foodchem.2017.05.006
- Commission Regulation (EC) No 149/2008 of 29 January 2008 amending Regulation (EC) No 396/2005 of the European Parliament and of the Council by establishing Annexes II, III and IV setting maximum residue levels for products covered by Annex I thereto.
- Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.
- Commission Regulation (EU) 2017/978 of 9 June 2017 amending Annexes II, III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for fluopyram; hexachlorocyclohexane (HCH), alpha-isomer; hexachlorocyclohexane (HCH), beta-isomer; hexachlorocyclohexane (HCH), sum of isomers, except the gamma isomer; lindane (hexachlorocyclohexane (HCH), gamma-isomer); nicotine and profenofos in or on certain products.
- Commission Regulation (EU) No 1259/2011 of 2 December 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non dioxin-like PCBs in foodstuffs.
- COPOLOVICI D., BUNGAU S., BOSCENCU R., MIRELA D., COPOLOVICI L. 2017. The fatty acids composition and antioxidant activity of walnut cold press oil. Rev. Chim., 68(3): 507-509.
- EMAMI A., MOUSAVI Z., RAMEZANI V., SHOEIBI S., RASTEGAR H., AMIRAHMADI M., EMAMI I. 2017. Residue levels and risk assessment of Pesticides in Pistachio Nuts in Iran. IJT, 11(2): 1-6. DOI: 10.29252/arakmu.11.2.1

- ESPOSITO M., DE ROMA A., CAVALLO S., DILETTI G., BALDI L., SCORTICHINI G. 2017. Occurrence of polychlorinated dibenzo-p-dioxins and dibenzofurans and polychlorinated biphenyls in fruit and vegetables from the "Land of Fires" area of Southern Italy. Toxics, 5(4): 33. DOI:org/10.3390/toxics5040033
- FERNANDES G.D., GÓMEZ-COCA R.B., PÉREZ-CAMINO M.C., MOREDA W., BARRERA-ARELLANO D. 2017. Chemical characterization of major and minor compounds of nut oils: almond, hazelnut, and pecan nut. J Chem., 549-559. DOI:org/10.1155/2017/2609549
- FAO 2010. Int. Scientific Symp. *Biodiversity and sustainable diets-united against hunger*. Rome, Italy. FAO headquarters, 2010.
- JACKSON C.L., HU F.B., 2014. Long-term associations of nut consumption with body weight and obesity. Am. J. Clin. Nutr., 100: 408-411. DOI: 10.3945/ajcn.113.071332
- KIRBASLAR F.G., TÜRKER G., ÖZSOY-GÜNEŞ Z., UNAL M., DÜLGER B., ERTAŞ E., KIZILKAYA B. 2012. Evaluation of fatty acid composition, antioxidant and antimicrobial activity, mineral composition and calorie values of some nuts and seeds from Turkey. Rec. Nat. Prod., 6(4): 339-349.
- LAMBIASE S., SERPE F.P., CAVALLO S., ROSATO G., BALDI L., NERI B., ESPOSITO M. 2017. Occurrence of polychlorinateddibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in eggs from free-range hens in Campania (southern Italy) and risk evaluation. Food Addit. Contam. Part A. Chem. Anal. Control Expo. Risk Assess, 34: 56-64. DOI: org/10.1080/19440049.2016.1260167
- LI D., HU X. 2011. Fatty acid content of commonly available nuts and seeds. In: Nuts and Seeds in Health and Disease Prevention. PREEDY V.R., WATSON R.R., PATEL V.B. (Eds). ELSEVIER, 35-42.
- LIU Y., SHEN D., LI S., NI Z., DING M., YE C., TANG F. 2016. Residue levels and risk assessment of pesticides in nuts of China. Chemosphere, 146: 645-651. DOI:org./10/1016/j.chemosphere. 2015.09.008
- MOHAMMADIFARD N., SALEHI-ABARGOUEI A., SALAS-SALVAD J., GUASCH-FERRÉ M., HUMPHRIES K. 2015. The effect of tree nut, peanut, and soy nut consumption on blood pressure: A Systematic review and meta-analysis of randomized controlled clinical trials 1-3. Am. J. Clin. Nutr., 101: 966-982. DOI: 10.3945/ajcn.114.091595
- OZKAN A. 2015. Determination of pesticide residues in some oilseeds and nuts using lc-ms/ms analysis. Fresen. Environ. Bull., 24(2a): 615-620.
- PEISKER K. 1964. A rapid semi-micro method for preparation of methyl esters from triglycerides using chloroform, methanol, sulphuric acid. J Am Oil Chem Soc, 41: 87-88.
- ROSZKO M., SZTERK A., SZYMCZYK K., WASZKIEWICZ-ROBAK B. 2012. PAHs, PCBs, PBDEs and pesticides in cold-pressed vegetable oils. J Am Oil Chem Soc., 89: 389-400. DOI: 10.1007/s11746--011-1926-5
- Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009. Text and Annexes.
- SZYMONA J. 2010. Problem of chemical plant protection products' residues in organic raw material. J. Res. Appl. Agric Eng, 55(4): 146-149.
- TAŞ N., GÖKMEN V. 2017. Phenolic compounds in natural and roasted nuts and their skins: A brief review. Curr. Opin. Food Sci., 14: 103-109. DOI: 10.1016/j.cofs.2017.03.001
- WEBER R., HEROLD C., HOLLERT H., KAMPHUES J., UNGEMACH L., BLEPP M., BALLSCHMITER K. 2017. Life cycle of PCBs and contamination of the environment and of food products from animal origin. Environ. Sci. Pollution Res., 25(17): 16325-16343. DOI:org/10.1007/s11356-018-1811-y
- WIECZOREK J., PIETRZAK M., OSOWSKI A., WIECZOREK Z. 2010. Determination of lead, cadmium, and persistent organic pollutants in wild and orchard-farm-grown fruit in northeastern Poland. J. Toxic. Environ. Health, Part A, 73: 1236-1243. DOI: 10.1080/15287394.2010.492009