

## POLYCYCLIC AROMATIC HYDROCARBONS IN OILSEEDS, OILS AND DERIVED PROCESSED PRODUCTS- A REVIEW

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### Abstract

*This paper presents a review regarding the content of polycyclic aromatic hydrocarbons (PAHs) in oilseeds, oils and derived processed products and the factors that influence their presence.*

*PAHs are a large group of toxic environmental and food-processing contaminants with two or more fused aromatic rings which present mutagenic, genotoxic and carcinogenic effects and can contaminate food by many paths. Regulation (EU) No 835/2011 sets the maximum levels in oils and fats intended for direct human consumption or used as an ingredient in food at 2 µg/kg for benzo(a)pyrene and at 10 µg/kg for sum of 4 PAHs.*

*Different factors are correlated with the presence of PAHs in edible oils: environmental conditions and the seeds drying method, the stages of seeds processing to obtain the oil (crude oil extraction, refining and purification), storage conditions and how the oils are used (frying, roasting).*

*Vegetable oils and fats are widely used in human consumption, therefore the presence of these contaminants should be monitored as they represent a major source of dietary exposure to PAHs.*

**Keywords:** BaP, oilseeds, oils, PAH.

### 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of toxic environmental and food-processing contaminants with two or more fused aromatic rings (Singh et al., 2016; Wu et al., 2020). The number of condensed aromatic rings classifies them, generating the specific physical and chemical properties of these compounds. The light PAHs have one to four aromatic rings whereas the heavy PAHs have more than four benzene rings in their structure. Light PAHs are characterised by low toxicity and high volatility, whereas heavy PAHs has the opposite effect (low volatility and high toxicity) (Wang et al., 2022).

Regardless their origin, natural or anthropogenic, PAHs are formed through incomplete combustion of organic materials being omnipresent environmental pollutants (EFSA, 2008, Abdel-Shafy and Mansour, 2016).

PAHs are mutagenic, genotoxic and strongly carcinogenic compounds and can contaminate food by many paths (Wu et al., 2020; Sampaio et al., 2021).

IARC classified PAHs as possible carcinogens (Group 2B), probable carcinogens (Group 2A) and carcinogens for humans (Group 1) (IARC, 2010). The United States Environmental Protection Agency (US EPA, 2010) has listed 16 PAHs having carcinogenic effects: acenaphthene,

acenaphthylene, anthracene, benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene (ChR), dibenzo(a,h)anthracene, fluoranthene, fluorene, indene(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene.

Based on the carcinogenic effects, EFSA (2008) selected 4 PAHs to be indicators for the carcinogenicity: BaP, BaA, BbF and ChR. Of all, BaP is considered as the most carcinogenic compound, being classified as a carcinogen (Group 1) (Joint FAO/WHO, 2005). The other compounds from the class of the 4 PAHs were included in the group of possible carcinogens (Group 2B) (IARC, 2010).

In foodstuffs the Regulation (EU) No 835/2011 sets the maximum levels allowed for PAHs. For oils and fats intended for direct human consumption or use as an ingredient in food, these limits are 2 µg/kg for BaP and 10 µg/kg for sum of 4 PAHs.

The research on PAHs began in the field of environment, then the attention was focused on crops and food. Based on the studies made it was confirmed that the diet is the major source of human exposure to PAHs (Rojo Camargo et al., 2012), with oils and fats as the main category because they can easily accumulate in this type of matrices. BaP is considered a bioindicator of PAH exposure (SCF, 2002). It is necessary to detect the content and to assess health risk of PAHs in edible vegetable oils, since the PAHs contamination has been associated with lungs, bladder and skin cancer (Martorell et al., 2010).

The PAHs content in seeds, oils and derived products from oilseed is influenced by the raw material, region of cultivation and commercialization, the environmental conditions, the drying method used, the manufacturing process, the storage conditions, the way of using the oils and the composition of food.

This study is a literature review that analyses the content of PAHs in oilseeds, oils and derived processed products from oilseeds and evaluates the influence of different factors on the level of accumulation of these contaminants.

## **2. MATERIALS AND METHODS**

### **Data search and selection criteria**

The present literature review was performed in order to evaluate the PAHs contamination of oilseeds, edible oils and derived processed products from oilseeds. For this search articles indexed in Web of Science, the databases of Google Academic and Scopus published between 2010-2024 were studied. Original research articles and reviews published were gathered for this review using the following terms: "*PAH*", "*benzo(a)pyrene*", "*oilseeds*", "*oils*", "*margarine*" and "*derived processed products from oilseeds*". Based on the selection of the most relevant manuscripts, this review was synthesized and divided in the following categories: oilseeds, oils and derived processed products from oilseeds.

## **3. RESULTS AND DISCUSSIONS**

### **PAHs content in oilseeds**

Contamination of oilseeds with PAHs is influenced by the habitat conditions of the plants, pollution of the cultivation region, season of the year, capacity of crops to bioaccumulate PAHs, harvesting, transport, storage conditions, drying method (thermal treatment).

Bojanowska and Czerwinski (2010) studied the PAHs contamination of rapeseed from different regions in Poland and during post-harvest drying treatment. The authors determined a higher PAHs content in rapeseed pods than in seeds due to their direct exposure to atmospheric emissions. Also, a higher PAHs content was determined in the samples subjected to the drying heat treatment. Rapeseeds were subjected to natural drying and showed a lower level of 14 PAHs (9.54-27.64 µg/kg) than those subjected to additional drying (63.08-165.91 µg/kg). Following the drying treatment, Chr which was not present in naturally dried seeds was detected, and phenanthrene concentration increased.

In the study made by Rojo Camargo et al. (2012) it was shown that the harvest year (2007, 2008) and the harvest region (different areas of Brazil) of soybeans had influence on the PAH level in soybean oil. Analysing the sum of 13 PAHs, it was observed that crude soybean oils from 2007 had a lower contamination level (10–208 µg/kg) than those obtained in 2008 (26–316 µg/kg). This could be a result of to the climatic conditions of each year and to the geographical region (the southern area has higher humidity and a cooler climate, while the other areas have lower humidity due to the cooler temperature). As a consequence of the varied humidity, the seeds require different temperature regimes in the drying processes in order to obtain the oils. Soybeans from the southern regions need double drying, while soybeans from the other regions of Brazil require a moderate drying method. In general, in Brazil the combustion smoke is used for seeds drying, this way seeds being contaminated with PAHs on the surface as a result of direct contact with the smoke.

Another factor that affects the PAHs content of the final product is the time of harvesting. Sakin et al. (2023) studied the influence of ripening period and harvesting of olives on the PAHs content. By collecting olives between the beginning of the ripening and the end of the harvest period, it was shown that, in general, the PAHs content decreased over time. The BaP content decreased from 4.45 to 1.19 µg/kg, while the 16 PAHs content decreased from 339.76 to 38.10 µg/kg at the end of harvesting period.

### **PAHs content in oils**

The presence of PAHs in oils is usually correlated to environmental conditions- region of production, manufacturing processes (cold-pressed process, crude oil extraction, refining and purification), oil storage conditions and way of using the oils (frying, roasting) (Zhou, Jiang, Mao, Zhao, & Lu, 2016).

### ***Region of production and commercialization***

Several studies have been carried out in different countries to determine the level of PAHs in marketed oils. Table 1 is summarising the data shown by the literature of interest regarding the concentration of PAHs in different type of oils. These oils are either used as edible refined oils sold on the market or as unrefined crude oils.

Rascon et al. (2018) studied the level of contamination with 16 PAHs in various oils selected from supermarkets in European countries with different production regions (Spain, Italy, Morocco, Thailand, Sri Lanka). The content of 16 PAHs varied in the oils depending on the production area. In extra virgin olive oil, the highest mean content of 16 PAHs was determined in the oil produced in Italy (3.84 µg/kg), followed by the one from Morocco (3.34 µg/kg) and the one from Spain (1.81 µg/kg). Extra virgin olive oil from organic production (Spain) recorded the lowest mean content for 16 PAHs (0.15 µg/kg), possible as a result of lower exposure to contamination during olive

harvesting and processing. Also, refined olive oil produced in Spain had a low mean PAHs content (243 µg/kg).

**Table 1. Levels of PAHs in the most consumed edible oils**

Type of oil	Processing	PAHs (µg/kg)		References
		BaP	Total Sum	
Sunflower	Commercial	nd-5.29	6.96-24.3 (4)	Krajian and Odeh, 2016
			30.6-75.9 (16)	
	Commercial	0.71-1.56	2.38-4.07 (4)	Ma et al., 2021
			2.98-4.92 (8)	
			21.68-26.76 (15)	
	Commercial	<0.98	3.92 (8)	Martorell et al., 2010
	Commercial	0.65	0.65 (8)	Kang et al., 2014
	Commercial	nd-3.60	0.05-17.93 (8)	Alomirah et al., 2010
			0.42-41.3 (16)	
	Commercial	0.31-3.27	0.65-15.61 (4)	Molle et al., 2017
			0.65-17.88 (13)	
Soybean	Crude	0.73	5.78 (4)	Zachara et al., 2017
			8.06 (4)	
	Crude	1.24	13.19 (8)	Hua et al., 2016
			6.12 (4)	
	Refining	0.59	9.68 (8)	Zhao et al., 2018
			2.43 (4)	
	Commercial	nd-3.74	2.55 (8)	Zhao et al., 2018
			0.33-14.0 (4)	
	Commercial	<LOQ-9.25	1.83-51.1 (16)	Krajian and Odeh, 2016
			9.68-331.95 (15)	
	Commercial	0.48-0.94	1.42-1.47 (8)	Jiang et al., 2015
			3.04-7.30 (16)	
Rapeseed	Crude	0.31	318-7.95 (4)	Shi et al., 2015
			15.51-18.78 (16)	
	Crude	0.55	0.79 (8)	Kang et al., 2014
			3.84-9.10 (4)	
	Refining	0.03	3.84-9.10 (4)	Zachara et al., 2017
			2.08 (4)	
	Commercial	1.92	6.84 (8)	Hua et al., 2016
			2.82 (4)	
	Commercial	0.41-1.27	4.58 (8)	Zhao et al., 2018
			1.09 (4)	
Canola	Commercial	0.98-4.23	2.16 (8)	Zhao et al., 2018
			5.80 (4)	
			3.4-6.90 (4)	
	Commercial	0.48	3.97-7.50 (8)	Ma et al., 2021
			39.43-47.41 (15)	
			0.48 (8)	
	Commercial	nd-6.25	0.48 (8)	Kang et al., 2014
			nd-22.15 (4)	
Corn	Commercial	0.32-4.39	nd-31.70 (13)	Molle et al., 2017
			3.36-8.74 (8)	
	Commercial	0.74	10.29-12.23 (16)	Alomirah et al., 2010
			0.76-16.7 (4)	

Olive	Commercial	0.23-0.69	1.8-4.0 (4)	Ma et al., 2021
			2.65-4.81 (8)	
			12.41-20.64 (15)	
	Commercial	<LOQ-6.65	3.71-185.72 (15)	Jiang et al., 2015
	Commercial	0-1.97	0.01-5.63 (8)	Alomirah et al., 2010
			0.30-34.49 (16)	
	Commercial	0.27-7.46	2.61-30.98 (4)	Molle et al., 2017
			2.61-38.23 (13)	
	Commercial	<0.98	3.92 (8)	Martorell et al., 2010
	Commercial	0.48-1.21	0.82-1.7 (4)	Ma et al., 2021
			1.00-2.03 (8)	
			11.55-16.65 (15)	
	Commercial	0.26-0.62	1.82-3.46 (4)	Shi et al., 2015
			24.11-43.78 (16)	
	Commercial	0.67	0.67 (8)	Kang et al., 2014
	Commercial	nd	0.26-8.98 (8)	Alomirah et al., 2010
			3.63-192.54 (16)	
	Commercial-virgin	0.26-6.71	1.48-19.8 (4)	Krajian and Odeh, 2016
			39.4-96.7 (16)	
	Commercial-virgin	0-6.31	0.41-7.86 (8)	Alomirah et al., 2010
			7.43-124.07 (16)	
	Commercial-extra virgin	0.08-5.79	0.34-20.2 (4)	Krajian and Odeh, 2016
			33.4-82.4 (16)	

Nd- undetectable, LOQ- limit of quantification. The number in parentheses indicates the number of compounds included in the reported sum.

The content of 4 PAHs in refined rapeseed oils, sunflower oils, olive pomace oil, a mixture of rapeseed oil with olive oil and unrefined soybean oil sold on the Polish market was determined by Zachara et al. (2017). A BaP content higher than 1 µg/kg was found in two of the refined rapeseed oil samples and in one refined virgin rapeseed oil sample. The unrefined oils presented a higher content of PAHs than the other oils.

Analysing the concentration of 16 PAHs in corn, sunflower, soybean, extra virgin olive and virgin oils traded on the Syrian market, Krajian and Odeh (2016) found that the mean level of 16 PAHs was higher for virgin olive oil (63.7 µg/kg), extra virgin olive oil (54.8 µg/kg) and sunflower oil (51.6 µg/kg). The lowest PAH content was determined in corn oil (29.8 µg/kg). Of the 38 analysed samples, 11 samples (28.9%) did not meet the requirements of the European Regulation (EU) no. 835/2011. When it comes to BaP, 9 samples exceeded the limit of 2 µg/kg set in European legislation, and 2 samples exceeded the limit for sum of 4 PAHs (10 µg/kg).

In the study realized by Barzegar et al. (2023) it was studied the PAHs content of corn, canola, sunflower, blended and frying oils available on the market in Iran and determined a mean BaP content of 1.76, 6.99, 1.26, 1.45 and 1.97 µg/kg, while the 4 PAHs content was 51.4, 9.61, 14.3, 9.56 and 3.87 µg/kg, respectively. In more than 30% of the analysed oils, the BaP content exceeded 2 µg/kg. When Piravi-Vanak et al. (2024) analysed the PAHs content of olive, sesame, sunflower, blended and frying oils commercialized on the same market, the mean BaP content ranged between 0.16-0.30 µg/kg, while the 4 PAHs content varied between 1.08-1.78 µg/kg, much lower than the levels determined by Barzegar et al. (2023). None of the analysed sample exceeded the maximum established level for these compounds.



Additionally, Molle et al. (2017) determined the content of 13 PAHs in corn, canola and sunflower oils from the Brazilian market and obtained a level ranging between 2.61-38.23 µg/kg, undetectable-31.70 µg/kg and 0.65-17.88 µg/kg, respectively.

The mean content of BaP of vegetable oils marketed in China varied between 0.39-3.31 µg/kg, a content higher than 2 µg/kg being determined in peanut oil (3.31 µg/kg), rapeseed oil (2.40 µg/kg) and maize oils (2.21 µg/kg) (Liu et al., 2023). The mean content of 4 PAHs in vegetable oils ranged between 5.83-15.18 µg/kg, the highest content being obtained for peanut oil. Of the 91 samples, 32.4% exceeded the PAHs content established by the Regulation in force.

*Unconventional oils* such as those obtained from amaranth, linseed, safflower, sesame, poppy, walnut or borage, usually cold-pressed oils, contain various bioactive components, which can reduce the risk of different diseases (Czaplicki et al., 2011), but at the same time they can be sources of PAHs contamination.

Ciecierska and Obiedziński (2013) studied the degree of PAHs contamination of these cold-pressed non-conventional oils sold on the Polish market and detected BaP in amaranth, pumpkin, sesame, blackseed and borage oils. The content of BaP was about 8-fold higher than the maximum level established (2 µg/kg) in pumpkin seed oil. The content of 4 PAHs ranged from undetectable in linseed oil to 35.03 µg/kg in pumpkin seed oil. A high content of 4 PAHs was also determined in blackseed oil (15.85 µg/kg) and in amaranth oil (10.50 µg/kg).

When Alomirah et al. (2010) studied the PAHs content of unconventional sesame, mustard and peanut oils commercialized on the Kuwait market it was determined a mean concentration of BaP of 2.05, 2.53 µg/kg and undetectable, while the mean concentration of 8 PAHs was 7.30, 10.67 and 0.14 µg/kg, respectively for this type of oils. Kang et al. (2014) analysed the PAHs content of the sesame oil commercialized on the Korean market and determined a lower BaP (0.55 µg/kg) and 8 PAHs content (0.55 µg/kg) than the one reported by Alomirah et al. (2010).

Da Silva et al. (2017) evaluated the PAHs content in cold-pressed vegetable oils of safflower, evening primrose and linseed from food stores in Brazil. The BaP content in analysed samples ranged between undetectable-0.90 µg/kg in safflower oil, 0.61 µg/kg in evening primrose, and <LOQ (0.25 µg/kg) in linseed oil, respectively. The highest concentration of the sum of 4 PAHs was determined in evening primrose oil (9.0 µg/kg), followed by safflower oil (1.43-3.16 µg/kg) and linseed oil (<LOQ-2.44 µg/kg).

Liu et al. (2024) studied the PAHs content of crude hazelnut oil and after exposure to different temperatures and times and for crude oil it determined a BaP content of 0.39 µg/kg, while the 4 PAHs content was 2.57 µg/kg. By exposing the oil to temperatures ranging between 30 and 210°C, in general the 4 PAHs content increased gradually.

### ***Manufacturing processes of oils***

In the stages of refining and purification for obtaining refined vegetable oils, there are changes in the content of PAHs that depend on the type of oil, the quality of raw material (purity, moisture content, fatty acid composition), the type of agent used for bleaching, the blending of oils and on certain phases within these stages.

Refining includes several technological phases: degumming, neutralization, bleaching and deodorization (Ma et al., 2024). By performing the first degumming stage, phospholipids and mucilaginous gums are removed (Jung et al., 1989). The neutralization and decolorization steps are performed to remove free fatty acids that promote lipid oxidation by forming soaps and pigments that can oxidize the fat and lead to undesirable colours in the final product. Through deodorization

or steam distillation, the quality (aroma) and stability of oils are improved by removing volatile compounds and decomposing peroxides (Ma et al., 2017). In this step PAHs with up to 4 aromatic rings are reduced. The resulting product is called refined oil and is ready for consumption or for making other products. Oil purification attempts to reduce possible oil impurities and minimize refining losses.

Studies done by Sun and Wu (2020) revealed that PAHs concentrations in refined vegetable oils are much lower than in crude oils. This was explained by the fact that the refining process can remove most of the PAHs during the decolouring and deodorization processes

Also, Rojo Camargo et al. (2012) showed that through the refining process up to 88% of the amount of 13 PAHs can be reduced in crude soybean oil, mainly due to the neutralization and deodorization process. Similarly, Ma et al. (2024) confirmed that through refining process of soybean oils the BaP, 4 PAH and 16 PAHs content decreased from 0.87, 5.85 and 21.03 µg/kg to 0.59, 3.11 and 8.22 µg/kg, respectively

Moreover, the effect of bleaching of soybean oil with bleaching earth and activated carbon on the reduction or elimination of BaP and 4 PAHs was studied by Aliyar-Zanjani et al. (2019). The bleaching process was carried out with different amounts of bleaching earth (1% w/w) and activated carbon (0.1% to 0.5% w/w), and the best results were obtained by applying 0.27% to 0.5% w/w activated carbon, thus eliminating PAHs content.

Additionally, Zhao et al. (2018) showed that by refining soybean and rapeseed oil the concentration of 8 PAHs decreased compared to crude oils. Refined soybean and rapeseed oil had a PAHs content about 2-fold lower than crude oils, as follows: refined oils had a content of 4.10 and 2.16 µg/kg, while crude oils presented a content of 9.68 and 4.58 µg/kg.

The role of neutralization and bleaching steps on the contamination of soybean and rapeseed oils with the 16 PAHs and oxygenated PAHs (OHAPs) were also evaluated by Hua et al. (2016). OHAPs are derivatives of PAHs that contain oxygen atoms in the form of hydroxyl and carbonyl functional groups, including quinone and hydroxy-PAHs. With the introduction of oxygen atoms into the molecule, OHAPs generally have higher activity than their precursors. These compounds have higher toxicities and may exceed those of the corresponding PAHs, causing adverse health effects. The concentration of 16 PAHs in crude soybean and rapeseed oil was 48.72 µg/kg and 38.02 µg/kg, while the concentration of 5 OHAPs was 20.04 µg/kg and 6.56 µg/kg, respectively. By refining the oils, there was a reduction in the concentration of the 16 PAHs by 59.5% and 55% for soybean and rapeseed oils, respectively, while the concentration of OHAPs was reduced by refining with 90% and 69%, respectively.

Shi et al. (2015) determined the content of 4 PAHs in refined soybean oil (3.18-7.95 µg/kg), crude peanut oil (8.78-35.16 µg/kg) and crude olive oil (1.82-3.46 µg/kg) from China. The 16 PAHs content of these oils ranged between 15.51-18.78 µg/kg for soybean oil, 65.70-161.12 µg/kg for peanut oil, and between 24.11-43.78 µg/kg for olive oil, respectively. This study also confirms that crude oils present higher level of PAHs. The higher PAHs content in peanut oil could be explained by the process of roasting the peanuts at high temperatures and also it can be caused by the incomplete refining method used in China to produce flavoured oils.

Furthermore, Ma et al. (2017) determined the concentration of 4 PAHs and 16 PAHs in crude and refined peanut oil, and showed that a higher content was obtained in crude oil. The content of 4 PAHs (129.20 µg/kg) and 16 PAHs (736.94 µg/kg) determined in the crude oil was higher than that obtained in the study realized by Shi et al. (2015). According to the authors, neutralised, decolorized and deodorized peanut oil showed a 4 PAHs/16 PAHs contamination level of

73.39/338.41  $\mu\text{g/kg}$ , 1.74/95.80  $\mu\text{g/kg}$ , and 74.64/399.8  $\mu\text{g/kg}$ . The content of 4 PAHs decreased by refining the oil with 43% through neutralization, with 99% through decolorization and with 42% through deodorization. Regarding the content of 16 PAHs, the concentration decreased with 56% through neutralization, with 87% through decolorization and with 48% through deodorization. Several absorbents were tested for the bleaching process: activated clay and two types of activated charcoal (Notit-8015 and WT). Activated charcoal was the most effective in reducing PAHs. Using 0.2% Notit-8015 activated charcoal resulted in a 98.5% and 81.5% reduction in 4 PAHs and 16 PAHs concentration, respectively, reducing almost all 4-6 ring analytes. Comparable results were obtained using 1% WT activated carbon. By using a higher percentage (2%) of WT charcoal, light PAHs can also be reduced by 93%, and 16 PAHs by 94%. Due to the high rate of PAHs reduction, the use of activated charcoal is recommended for PAHs removal during the refining process. Even though Notit charcoal has the best efficiency for PAHs reduction by using a small amount of adsorbent, due to its high price, its use is limited.

Among edible oils contaminated with PAHs, olive pomace oil can accumulate a high content of PAHs. Based on the quality, olive oils can be divided from high quality extra virgin olive oil to low-quality olive pomace oil. Extra virgin olive oil is produced in specific regions and is extracted from the olive fruit only by mechanical and physical methods, without any exposure to thermal processes and refining. In general, extra virgin olive oil contains very small amounts of PAHs, which come from the tree. Olive pomace oil is produced by drying the olive pomace with smoke and hot air, the solvent extraction being done after. By these processes, a higher PAHs content is produced in olive pomace oil. Thus, olive oil can be frauded or adulterated by mixing extra virgin olive oil with olive pomace oil (Sun et al., 2019). In the study realized by Alomirah et al. (2010) it was determined a mean content of BaP of 2.06  $\mu\text{g/kg}$ , while the mean 8 PAHs content was 4.35  $\mu\text{g/kg}$  for olive pomace oil. The content of BaP and 8 PAHs was much higher than the one determined for extra virgin olive oil (0.53/1.81  $\mu\text{g/kg}$ ), virgin olive oil (0.90/1.88  $\mu\text{g/kg}$ ), while for olive oil BaP was not detected and the 8 PAHs content was 2.09  $\mu\text{g/kg}$ .

In order to reduce the PAHs content, Kiralan et al. (2017) studied the influence of applying microwave pre-treatment to olive pomace before drying at 200°C (moisture < 5%) compared to drying at 200°C and vacuum drying on the PAH content of pomace olive oil. By applying the drying process at 200°C to olive pomace, the content of 15 PAH in oil was 3471  $\mu\text{g/kg}$ , while by using the vacuum drying process, the content decreased at 815  $\mu\text{g/kg}$ . By using microwaves, the PAHs content was reduced by 34-75%, depending on the applied parameters. By decreasing the power from 270 to 60 W and increasing the microwave application time from 90 to 270 s, the effectiveness of microwave pre-treatment on PAHs concentration reduction increased.

The influence of seeds roasting on the PAHs content of peanut, sesame, sunflower, rapeseed and flaxseed oil was studied by Ji et al. (2020). By exposure of the seeds to six temperatures ranging between 160 to 260°C for 10 to 60 min at each temperature, the PAHs content increased, especially when the temperature was higher than 200°C, roasting time having a greater effect on the PAHs content than temperature. When seeds were exposed to 260°C for 60 min, the BaP content was 12.9-fold higher for peanut oil than the one obtained from unroasted seeds, and 0.6-fold higher in the case of flaxseed oil. For sesame, sunflower and rapeseed oils, the BaP content was 0.4-, 1.1- and 0.8-fold higher than the permitted level.

When pumpkin seeds were roasted at temperature ranging between 90 and 200°C for 60 min, only after seeds were roasted at 150°C, BaP was detected, at 180 and at 200°C a content of 0.02  $\mu\text{g/kg}$  being determined (Potočnik and Košir, 2017).



### ***Oils storage conditions***

PAHs and PAHs derivatives (OHAPs) can be formed during edible oil storage (Zhao et al., 2018). The formation depends not only on the nature and composition of the oils, but also on the degree of processing and storage conditions. However, the exact mechanism of PAHs formation during storage remains unclear. Many undesirable reactions can occur during storage, such as lipid oxidation, volatilization, polymerization and degradation (Mocek and Ciemniak, 2016; Zhao et al., 2018). During edible oils storage, the toxic substances formed by the lipid degradation and other undesirable compounds present, undergo changes.

In the study realized by Zhao et al. (2018) it was shown that time (270 days) and storage temperature (4°C, 25°C) influenced the PAHs concentration of crude and refined soybean and rapeseed oils stored in the dark. It was observed that the content of 8 PAHs in crude and refined soybean oil increased by 81% and 117%, respectively, by storage at 25°C (270 days). However, an increase of only 15% and 27%, respectively, was observed at 4°C. In crude and refined rapeseed oil the concentration of 8 PAHs increased by 88% and 198% after storage at 25°C and by 61% and 55%, respectively, when it was stored at 4°C. The content of OHAP was higher in both crude soybean and rapeseed oils and it increased after storage, the increase being more obvious at 25°C than at 4°C.

In general, the main PAHs determined in the analysed oils were those containing 3 or 4 aromatic rings, summing 57.11–78.38% of PAHs. During storage, the percentage of heavy PAHs decreased. It could be concluded that the content of PAHs during storage is influenced by the unstable light PAHs (Zhao et al., 2018).

Additionally, Mocek and Ciemniak (2016) studied the stability of PAHs at different temperatures (40°C, 100°C, 200°C) and times and it was shown that at a higher temperature, the reduction of PAHs in oils is greater. Even though the content of PAHs is reduced by exposure to temperature, it cannot be said that their toxicity is reduced, as OPAHs can be formed.

Another factor that affects the PAHs content of stored oils is the exposure to UV radiation. By direct exposure to UV, the 16 PAHs content of rapeseed and sunflower oils was reduced from 354.44 µg/L to 154.71 µg/L, while a lower PAHs reduction (234.36 µg/L) occurred with the indirect application of UV (plate-based), the degree of reduction being strongly correlated with the duration of exposure (Mocek and Ciemniak, 2016). Similarly with the study conducted by Zhao et al. (2018), Mocek and Ciemniak (2016) showed that heavy PAHs were more stable than light ones. However, the process of using UV radiation is still at an early stage and faces challenges such as the oxidation of fatty acids present in the oils and the possibility of formation of new compounds from PAHs that can produce toxicity. The study thus concluded that there is a need to explore this broad-spectrum application.

### ***Way of using the oils***

The concentration of PAHs in oils can vary depending on their use as a cooking medium, the type of food being fried or the repetitive use of oils.

Hao et al. (2016) analysed the PAHs content in fresh rapeseed, soybean, peanut and olive oils and after the oils were used for deep-frying potatoes and chicken nuggets for 15, 30 and 45 min. In fresh oils, none of the 4 PAHs regulated were detected. After deep-frying potatoes and chicken nuggets, none of the 4 PAHs were detected in rapeseed oil, and in soybean oil the 4 PAHs were detected only in oil used for deep frying potatoes for 45 min (29.66 µg/kg). In the case of peanut and olive

oil, the 4 PAHs content increased gradually by increasing the frying time, exceeding the maximum permitted limit.

It was observed that the formation of BaP is influenced by the food type fried and by the frying time. In rapeseed oil, the presence of BaP occurred only after potatoes were fried for 15 min, and in soybean oil the formation of BaP was achieved after 45 min of frying. On the contrary, frying potatoes and chicken nuggets for different time durations (15–45 min) in peanut and olive oils resulted in the formation and accumulation of BaP at a concentration ranging between 15.1–99 µg/kg in oils. The study concluded that olive oil should not be used for frying and repetitive use of oil in cooking should be avoided. The cooking time in the same edible oil should not be very long to ensure health safety and minimize the food risk associated with PAHs formed in oil. By increasing the frying time, a higher amount of heavy PAHs was determined in oils with the exception of rapeseed oil used for frying nuggets in which these compounds were not found (Hao et al., 2016).

Rascon et al. (2018) studied the influence of frying meat and fish at 175°C for 5 times on the PAHs content of virgin olive oils and obtained a content of 16 PAHs of 14.46 and 15.02 µg/kg, respectively. By applying frying mainly increased the concentration of naphthalene and ChR and new PAHs appeared compared to oils not subjected to heat treatment.

In the study made by Sun and Wu (2020), PAHs content was determined in waste frying oils (soybean oil, shortening and canola blend oil) after frying pumpkin pie or chicken meat. The 16 PAHs content determined in waste oils ranged between 39.21-197.44 µg/kg. When shortening was used for frying chicken chops, the highest 16 PAHs content was determined in this waste oil (197.44 µg/kg). A higher BaP content (2.30 µg/kg) than the one established in regulation was registered when soybean oil was used for obtaining pumpkin pie. In canola blend oils used for frying chicken meat, the content of BaP and 4 PAHs exceeded the established limits from regulation, ranging between 2.95-6.60 µg/kg, and 12.01-18.82 µg/kg, respectively.

Additionally, Sun and Wu (2020) determined the PAHs content in vegetable oil deodorized distillates obtained from soybean and rapeseed oils and the content of BaP was very high, the values ranging between 64.70-83.58 µg/kg, while the 4 PAHs content varied between 364.10-536.41 µg/kg.

Wu and Yu (2012) studied the PAHs content of oil collected from a kitchen range hood and from a fried food stall and determined a BaP content of 1.18 and 1.71 µg/kg, respectively, oils containing a higher proportion of light PAHs than heavy PAHs.

A higher BaP content (3.37 µg/kg) of frying oils collected from restaurants from China was determined in the study realized by Liu et al. (2023). The 4 PAHs content determined was 10.9 µg/kg. By frying the oils, the mean content of each of the 4 PAHs increased significantly.

### **PAHs in derived processed products**

Besides the factors that influence the PAHs content in oilseeds and oils, in derived processed products the concentration is dependent by the home cooking practices (heating, baking) used to incorporate ingredients in the processing of certain food commodities to make new foodstuffs, such as margarine.

Alomirah et al. (2010) studied the content of PAHs in table margarine samples collected from retail stores in Kuwait. The BaP content found ranged between 0-3.67 µg/kg and 8 PAHs concentration varied between 0.24-5.02 µg/kg. The authors reported that from the 4 samples analysed, one table margarine had a content of BaP higher (3.67 µg/kg) than the level set by Regulation in force.

Martorell et al. (2010) analysed some samples of margarine commercialized on the market in Spain and determined a BaP content lower than 1 µg/kg. The 16 PAHs concentration found was 19.25 µg/kg.

In a study conducted in France, Veyrand et. al. (2013) determined a mean content of BaP of 0.151 µg/kg, while the sum of 4 PAHs was 1.34 µg/kg. A higher content of BaP and 4 PAHs was determined in the study realized by Lan and Wu (2023) who investigated the contamination with 24 PAHs of 5 samples of margarine purchased online. The concentrations of BaP varied between 0.44-1.16 µg/kg with a mean content of 0.8 µg/kg, while the mean content of 4 PAHs was 3.0 µg/kg.

#### 4. CONCLUSIONS

Different factors are correlated with the presence of PAHs in oleaginous seeds, edible oils and derived products from oilseeds: environmental conditions, harvesting period, the seeds drying method, the stages of seeds processing to obtain the oil (crude oil extraction, refining and purification), storage conditions, cooking practice (frying, baking), type of food cooked in oil.

Vegetable oils are an important source of dietary human exposure to PAHs, their presence being a concern to human health. The content of PAHs should be reduced, improved processing practices should be developed to decrease the content of these contaminants.

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