

## 3-MCPD Occurrence in Vegetable Oils: Impact on Human Nutrition and Future Challenges

Tânia Gonçalves Albuquerque<sup>1,2</sup>, M Beatriz P P Oliveira<sup>2</sup> and Helena S Costa<sup>1,2\*</sup>

<sup>1</sup>Department of Food and Nutrition, National Institute of Health Dr. Ricardo Jorge, I.P., Portugal

<sup>2</sup>REQUIMTE-LAQV/Faculty of Pharmacy, University of Porto, Portugal

\*Corresponding Author: Helena S Costa, Department of Food and Nutrition, National Institute of Health Dr. Ricardo Jorge, I.P., Portugal.

Received: March 23, 2018; Published: June 21, 2018

### Abstract

Over the last years, the global production of vegetable oils increased, and palm oil is still the most produced vegetable oil, followed by soybean, rapeseed and sunflower oils. Processing of vegetable oils is essential to remove impurities from the oil and to assure their quality and safety. Nonetheless, some of the applied conditions, namely during deodorization, can lead to the formation of contaminants, such as chloropropanols. In this review, an overview of the occurrence of 3-monochloropropane-1,2-diol in vegetable oils, as well as its potential impact on human nutrition, based on exposure assessment to this contaminant, and future challenges are discussed. According to this literature review, notable differences are found for the occurrence of 3-monochloropropane-1,2-diol in the different vegetable oils, but also among the same type of oil, which is possibly due to the geographical origin of samples, their composition, but also due to the processing conditions applied. It has been observed that unprocessed oils/fats have non-detectable or very low amounts of 3-monochloropropane-1,2-diol, while the refined oils have high amounts. Amongst the reviewed data, the highest values reported were for rice bran oil (1449 - 2564 mg/kg) and edible blending oil (1367 mg/kg). For instance, for palm oil, which is the most widely consumed vegetable oil, the values for 3-monochloropropane-1,2-diol ranged from not detected to 540 mg/kg. With respect to mitigation strategies, the use of radical scavengers, such as phenolic compounds, is efficient, but there is still a lot of work to be done in this area of research. Regarding exposure assessment to this contaminant, few studies have focused on this subject, but the reported results indicate that the mean exposure value is lower than the tolerable daily intake (2 µg/kg of body weight/day). Nonetheless, among the different food groups evaluated for exposure assessment, vegetable oils/fats were identified as the major contributor for children. In the near future, it is crucial to evaluate other processing conditions, namely cooking methods (e.g. frying and baking), since it can have a significant impact on the occurrence of this hazardous compound. Also, it is necessary to monitor the occurrence of 3-monochloropropane-1,2-diol in other foodstuffs, to accurately estimate the exposure assessment.

**Keywords:** Chloropropanols; 3-MCPD; Edible Oils; Fats; Processing; Food Safety

### Abbreviation

3-MCPD: 3-monochloropropane-1,2-diol

### Introduction

Plant foods are the main sources of edible oils/fats, namely seeds (e.g. sunflower and rapeseed), legumes (e.g. soybean), nuts (e.g. walnut and almond) and fruits (e.g. palm and olive). In the last years, alternative sources of vegetable oils are being studied, namely food industry by-products, such as apricot kernel, grape seeds and melon seeds.

Over the last years, the global production of vegetable oils increased, but palm oil is still the most produced vegetable oil, followed by soybean, rapeseed and sunflower oils [1]. Generally, vegetable oils are distinguished by their fatty acids composition, although the presence of other minor compounds (tocopherols, phytosterols and carotenoids) is very important, especially for their oxidative stability. In

fact, this is one of the major concerns, since it decreases the shelf life of the oil itself, but also because it has a major impact on the quality and safety of foodstuffs.

From a nutrition and public health perspective, the inappropriate production and use of vegetable oils is linked to the pathogenesis of several diseases, namely cardiovascular diseases and cancer. Therefore, oils and fats are processed to improve their quality, stability and safety. Despite the removal of a large amount of impurities from the oil, processing can often originate new contaminants that can cause additional health hazards to those who consume these foods [2].

Besides industrial processing of vegetable oils, it is of utmost importance to consider the effect of cooking methods on the quality of vegetable oils, namely frying, because it is largely used. The most frequent chemical reactions taking place during frying are: hydrolysis, oxidation, isomerisation and polymerization, which lead to the formation of several degradation products, namely, free fatty acids, aldehydes, ketones, diglycerides and monoglycerides, *trans* isomers, hydrocarbons, triacylglycerols, conjugated fatty acids, and cyclic fatty acids [3-5].

3-monochloropropane-1,2-diol (3-MCPD) is a food processing contaminant included in the group of compounds known as chloropropanols [6]. In recent years, high quantities of 3-MCPD esters were reported in edible oils/fats and other foods. Therefore, in this manuscript an overview of the occurrence of 3-MCPD in vegetable oils, as well as its potential impact on human nutrition based on exposure assessment to 3-MCPD and future challenges are discussed.

### Methodology

In this literature review electronic databases were used, namely Science Direct, PubMed, and Google Scholar. Moreover, the following keywords were used: 'chloropropanols', 'edible oils and toxic compounds', 'vegetable oils and chloropropanols', '3-MCPD', 'chloropropanols precursors', '3-MCPD legislation', 'chloropropanols and mitigation', and 'analytical methods for chloropropanols determination'. One of the exclusion criterion was the language of the manuscripts, being only English papers considered.

Afterwards, a detailed review concerning sample preparation procedures, food matrices analysed, as well as geographical origin of samples, available data concerning the occurrence in edible oils and fats, mitigation strategies and impact on human nutrition, were compiled.

### 3-monochloropropane-1,2-diol

The 3-MCPD is a food contaminant, member of the chemical group of chloropropanols, which are a group of alcohols comprised of a 3-carbon backbone substituted with one or two chlorine atoms [7]. Chemically, 3-MCPD is a glycerol chlorohydrin, formed when one hydroxyl group is replaced by a chlorine atom [8]. Despite the structural similarity of 3-MCPD and 2-monochloropropane-1,3-diol (2-MCPD) compounds, they can have different and specific metabolic and toxicological profiles. Depending on the type of food, 3-MCPD may occur as a free substance, as ester with fatty acids or in both forms [9].

In 1978, chloropropanols were first described in acid-hydrolysed vegetable proteins, leading to intensive scientific research concerning this subject. Later, the presence of chloropropanols was also described in soy sauces. After some years, these compounds started to receive wider scientific and regulatory attention, since significant amounts were detected in several heat-processed foods, as well as in vegetable oils [9-11].

In 2001, the European Community has set a regulatory limit of 0.02 mg/kg for 3-MCPD in hydrolysed vegetable protein and soy sauce, with the maximum level given for the liquid product containing 40% of dry matter, corresponding to a maximum level of 0.05 mg/kg in the dry matter [12]. These levels of 3-MCPD in foods were established after the recommendation from the Scientific Committee on Food that has set a tolerable daily intake of 2 µg/kg of body weight and has concluded that 3-MCPD was a non-genotoxic carcinogen for humans [13].

According to the Joint FAO/WHO Expert Committee on Food Additives (JECFA), kidney is the main target organ for 3-MCPD toxicity, with chronic oral exposure resulting in nephropathy and tubular hyperplasia and adenomas [14]. The International Agency for Research on Cancer [15] has classified 3-MCPD as a possible human carcinogen (group 2B).

Therefore, the European Commission has established two first priorities: [1] to reduce the levels of 3-MCPD esters by mitigation measures to be applied by the food business operators; and [2] to consider possible maximum levels of 3-MCPD esters in foods once more information is available on the pathways of formation and on what levels are achievable [16].

In 2013, the European Food Safety Authority (EFSA) published a report that highlighted the food groups that mainly contribute to the exposure to these contaminants. Margarine and vegetable oils/fats were identified as the foods/ingredients with high quantities of these hazardous compounds [6].

Recently, EFSA published an update of the tolerable daily intake from 0.8 to 2 µg/kg of body weight/day for 3-MCPD and its fatty acid esters [17].

### 3-MCPD in oils/fats: precursors, occurrence and mitigation

It is assumed that 3-MCPD is formed when fat and salt containing foods are processed at high temperatures [16]. Moreover, other studies showed that these compounds are mainly formed during the high-temperature deodorization step of the refining process of oils, which is an essential step to reduce the amount of undesirable compounds that can negatively impact the taste, appearance, shelf life, safety and consumer acceptance [18]. Other studies appointed that 3-MCPD formation is linked with mono- and diacylglycerols.

Table 1 presents 3-MCPD content in oils and fats available in the literature. Large variations for 3-MCPD content have been observed between oils of different origin, but also amongst the oils of the same kind. Amongst the reviewed data, the highest values were reported by Zhou, *et al.* (2014) for rice bran oil (1449 - 2564 mg/kg) and edible blending oil (1367 mg/kg) [19].

Analytical method		Oils and fats	3-MCPD content (mg/kg)	Reference
Derivatization	Chromatographic conditions			
Acid cleavage	Gas chromatography Detector: MS  Column: Equity™-1 (30 m x 0.25 mm I.D., 1 µm film thickness) Injection mode: Splitless Injector temperature: 250°C Oven ramp: 80°C (1 min) to 300°C (37 min) at a rate of 10°C/min Carrier gas: Helium (0.8 mL/min) Injection volume: 1 µL	Virgin seed oils (n = 9)	< 0.1 - 0.34	[11]
		Almond	< 0.1	
		Soybean	< 0.1	
		Rapeseed	< 0.1	
		Sunflower	<0.1	
		Sesame (unroasted seed)	<0.3	
		Sesame (roasted seed)	0.34	
		Hazelnut	<0.1	
		Peanut	<0.1	
		Pumpkin	<0.1	
		Refined seed oils (n = 5)	<0.3 - 1.23	
		Soybean	1.23	
		Rapeseed (n = 2)	0.38 - 0.48	
		Sunflower	<0.3	
		Maize	0.37	
		Virgin olive oils (n = 4)	<0.1 - <0.3	
		Extra virgin olive oil (n = 2)	<0.1 - <0.3	
		Virgin olive oil (n = 2)	<0.1	
		Refined olive oils (n = 5)	<0.3 - 2.46	
		Olive oil (n = 3)	<0.3 - 2.46	
Olive pomace oil (n = 2)	1.05 - 2.33			

Acid cleavage	<p>Gas chromatography</p> <p>Detector: FID</p> <p>Column: SP-2560 (100m x 0.25 mm, I.D.; 0.2 µm film thickness)</p> <p>Injection mode: Split (75:1)</p> <p>Injector temperature: 240 °C</p> <p>Oven ramp: 175 °C to 240 °C at the rate of 4 °C/min or 90 °C to 200 °C at the rate of 6.9 °C/min, and from 200 °C to 240 °C at the rate of 2 °C/min</p> <p>Carrier gas: Helium (0.8 mL/min)</p> <p>Injection volume: 1 µL</p>	Virgin oils (n = 13)	0.06 – 0.08	[23]
		Virgin seed oil (n = 9)	0.06 <sup>a</sup>	
		Virgin olive oils (n = 4)	0.08 <sup>a</sup>	
		Refined oils (n = 19)	0.52 – 2.82	
		Refined seed oils (n = 5)	0.52 <sup>a</sup>	
		Refined palm kernel oils (n = 5)	1.17 <sup>a</sup>	
		Refined olive oils (n = 3)	1.46 <sup>a</sup>	
		Refined coconut oils (n = 2)	1.56 <sup>a</sup>	
		Refined palm oils (n = 4)	2.82 <sup>a</sup>	
Acid cleavage	<p>Gas chromatography</p> <p>Detector: MS</p> <p>Column: HP-1MS (60 m x 0.25 mm, I.D.; 0.25 µm film thickness)</p> <p>Injection mode: -</p> <p>Injector temperature: -</p> <p>Oven ramp: 80 °C (1.5 min), increase of 30 °C/min until 300 °C and held for 10 min</p> <p>Carrier gas: Helium (1.0 mL/min)</p> <p>Injection volume: -</p>	Fat mixes (n = 11)	0.90 – 2.44	[10]
		Fat (palm olein, 46%)	0.14	
		Fat (palm olein, 46%)	0.16	
		Fat (palm olein, 46%)	0.90	
		Fat (palm olein, 46%)	1.04	
		Fat (palm olein, 46%)	0.97	
		Fat (palm olein, 46%)	1.33	
		Fat (palm olein, 46%)	1.53	
		Fat (palm olein, 46%)	1.40	
		Fat (palm olein, 46%)	2.04	
		Fat (palm olein, 55%)	2.44	
		Fat (palm olein, 55%)	2.22	
		Salmon oil in dietary supplement capsules	0.7 – 13	
		Evening primrose oil	0.8 – 5.2	
		Borage oil	<0.1 – 0.2	
		Rose hip oil	0.8	
		Shea butter	0.2	
		Wheat germ oil	0.2	
		Palm kernel oil	0.2 – 0.9	
Palm oil degummed and bleached	1.0			

DGF C-III 18(09)	Gas chromatography	Refined olive oil (n = 9)	0.14 – 0.16	[33]
	Detector: FID	Cold-pressed safflower oil (n = 8)	<0.1 – 2.46	
	Column: DB-5MS (30 m x 0.25 mm, I.D.; 0.25 µm film thickness) Injection mode: splitless Injector temperature: 250 °C Oven ramp: 60 °C (5 min) raised to 280 °C, with a heating rate of 10 °C/min, held by 20 min Carrier gas: Helium (1.2 mL/min) Injection volume: 1 µL	Refined safflower oil (n = 3)	2.34 – 3.22	
DGF C-III 18(09)	Gas chromatography	Refined vegetable oils (n = 57)	0.4 – 1.7	[34]
	Detector: FID	Palm kernel oil (n = 3)	1.7 <sup>a</sup>	
	Column: DB-5MS (30 m x 0.25 mm, I.D.; 0.25 µm film thickness)	Coconut oil (n = 4)	0.6 <sup>a</sup>	
	Injection mode: splitless	Olive oil (n = 6)	1.2 <sup>a</sup>	
	Injector temperature: 250 °C	Sunflower oil (n = 15)	1.0 <sup>a</sup>	
	Oven ramp: 60 °C (5 min) raised to 280 °C, with a heating rate of 10 °C/min, held by 20 min	Rapeseed oil (n = 10)	0.4 <sup>a</sup>	
	Carrier gas: Helium (1.2 mL/min)	Soybean oil (n = 6)	0.9 <sup>a</sup>	
	Injection volume: 1 µL	Safflower oil (n = 8)	1.4 <sup>a</sup>	
		Corn oil (n = 5)	1.7 <sup>a</sup>	
-	Liquid chromatography	Cocoa butter (n = 2)	<0.5	[35]
	Detector: TOF/MS	Palm shortening/olein (n = 6)	0.4 – 0.6	
	Column: Phenomenex Luna C18 (50 mm x 3 mm, I.D.; 3 µm film thickness)	Vegetable oils (n = 10)	<0.5	
	Mobile phase: A (methanol/ acetonitrile/methanol-sodium acetate solution (0.26 mM), 8:1:1, v/v/v) and B (methanol-sodium acetate solution (0.26 mM)/ methylene chloride/acetonitrile, 1:8:1, v/v/v)	Corn oil	<0.5	
		Canola oil	<0.5	
		Soybean oil	<0.5	
		Sesame oil	<0.5	
		Walnut oil	<0.5	

Alkali/Br	<p>Gas chromatography</p> <p>Detector: MS</p> <p>Column: Resteck Rxi®-17 GC column (30 m x 0.25 mm, I.D., 0.25 µm film thickness); HP-5MS (30 m x 0.25 mm, I.D.; 0.25 µm film thickness)</p> <p>Injection mode: Split/Splitless</p> <p>Injector temperature: -</p> <p>Oven ramp: 90 °C, isothermal 0.1 min, with 78 °C/min to 175 °C, isothermal 1.0 min with 20 °C/min to 290 °C, isothermal 8.3 min</p> <p>Carrier gas: Helium (1.2 mL/min)</p> <p>Injection volume: 2 µL</p>	Refined seed oils (n = 8)	0.2 – 19	[20]
		Apricot kernel oil	0.4	
		Coconut oil	0.2 – 0.4	
		Corn oil	0.2	
		Hazelnut oil	19	
		Grape seed oil	0.8 – 4.2	
		Peanut oil	0.1 – 0.9	
		Safflower oil	0.6 – 1.0	
		Walnut oil	1.2 – 19	
Olive oil	0.3 – 1.2			
DGF C-III 18(09)	<p>Gas chromatography</p> <p>Detector: FID</p> <p>Column: DB-5MS (30 m x 0.25 mm, I.D.; 0.25 µm film thickness)</p> <p>Injection mode: splitless</p> <p>Injector temperature: 250 °C</p> <p>Oven ramp: 60 °C (5 min) raised to 280 °C, with a heating rate of 10 °C/min, held by 20 min</p> <p>Carrier gas: Helium (1.2 mL/min)</p> <p>Injection volume: 1 µL</p>	Native or cold-pressed vegetable oils (n = 57)	<0.1 – 0.4	[36]
		Refined vegetable oils (n = 144)	0.2 – 14.7	
		Margarine (n = 37)	0.4 – 4.5	
		Frying fat, used and unused (n = 38)	0.5 – 5.2	

-	Liquid chromatography Detector: MS/MS Column: Pursuit XRs C18 (150 mm x 2 mm i.d., 3 µm particle size) Injection volume: 5 µL Flow: 0.2 - 0.25 mL/min Mobile phase: (A) 2 mM ammonium formate/0.05% formic acid in methanol/water (92:8, v/v); (B) 2 mM ammonium formate/0.05% formic acid in isopropanol/water (98:2, v/v)	Almond oil, unrefined (n = 1)	<LOQ	[24]
		Almond oil (n = 1)	2.11	
		Butter unrefined (n = 4)	<LOQ - 0.045	
		Canola oil (n = 7)	<LOQ - 0.33	
		Coconut oil, unrefined (n = 2)	<LOQ	
		Coconut oil (n = 7)	0.025 - 0.38	
		Corn oil (n = 9)	0.06 - 0.42	
		Cottonseed oil (n = 2)	0.14 - 0.72	
		Extra virgin olive oils, unrefined (n = 5)	<LOQ - 0.025	
		Flaxseed oil (n = 1)	<LOQ	
		Grape seed oil (n = 3)	0.24 - 3.91	
		Hemp oil, unrefined (n = 2)	<LOQ - 0.039	
		Macadamia nut oil (n = 1)	<LOQ	
		Mixed oils (n = 5)	0.035 - 1.88	
		Olive oil (n = 5)	0.15 - 0.73	
		Palm oil, unrefined (n = 1)	<LOQ	
		Palm oil (n = 14)	1.51 - 7.23	
		Palm kernel oil (n = 2)	0.038 - 0.20	
		Palm olein (n = 5)	1.40 - 8.43	
		Palm stearin (n = 1)	3.24	
		Peanut oil, unrefined (n = 2)	<LOQ	
		Peanut oil (n = 3)	0.14 - 0.69	
		Pumpkin seed oil (n = 1)	<LOQ	
		Safflower oil (n = 5)	0.28 - 1.77	
		Sesame oil, unrefined (n = 3)	0.16 - 0.45	
Shortening oil (n = 5)	0.35 - 0.46			
Soybean oil (n = 6)	0.041 - 0.24			
Sunflower oil, unrefined (n = 1)	<LOQ			
Sunflower oil (n = 4)	0.19 - 0.93			
Vegetable edible fats (n = 6)	0.009 - 1.10			
Walnut oil (n = 1)	0.63			
-	Liquid chromatography Detector: MS/MS Column: Luna-3u C18 (50 mm x 2.1 mm i.d., 1.7 µm particle size) Flow: 0.2 mL/min Injection volume: 10 µL Mobile phase: (A) water; (B) 0.01 mol/L ammonium acetate in methanol; (C) methanol; (D) 2-propanol	Soybean oil	0.58	[25]
		Rapeseed oil	0.50	
		Rice oil	1.78	
		Safflower oil	0.83	
		Sesame oil	0.58	
		Olive oil	4.34	
		Grape seed oil	25.35	
		Perilla oil	1.43	
		Palm oil	14.4	
		Lard, refined	0.76	

-	<p>Gas chromatography</p> <p>Detector: MS</p> <p>Column: VF-1MS (30 m x 0.25 mm, I.D.; 0.25 µm film thickness)</p> <p>Injection mode: -</p> <p>Injector temperature: -</p> <p>Oven ramp: 60 °C (1 min), 6 °C/min to 190 °C, 20 °C/min to 280 °C (held for 30 min)</p> <p>Carrier gas: Helium (1.2 mL/min)</p> <p>Injection volume: -</p>	Soybean oil (A)	0.19 ± 0.02 – 1.19 ± 0.01	[26]
		Soybean oil (B)	nd – < 0.10	
		Soybean oil (C)	< 0.10 – 0.16 ± 0.04	
		Soybean oil (D)	0.34 ± 0.01 – 0.37 ± 0.04	
		Soybean oil (E)	1.11 ± 0.03	
		Soybean oil (F)	0.21 ± 0.05 – 0.23 ± 0.00	
		Corn oil (A)	< 0.10 – 0.12 ± 0.01	
		Corn oil (B)	< 0.10	
		Corn oil (C)	nd	
		Corn oil (D)	0.20 ± 0.00	
		Corn oil (E)	< 0.10	
		Corn oil (F)	1.04 ± 0.01 – 1.12 ± 0.05	
		Sunflower oil (A)	0.14 ± 0.02 – 0.16 ± 0.01	
		Sunflower oil (B)	0.13 ± 0.01 – 0.15 ± 0.02	
		Sunflower oil (C)	0.10 ± 0.00 – 0.20 ± 0.02	
		Sunflower oil (D)	0.22 ± 0.00 – 0.21 ± 0.03	
		Sunflower oil (E)	0.25 ± 0.01 – 0.27 ± 0.06	
		Sunflower oil (F)	0.25 ± 0.07	
		Canola oil (A)	0.13 ± 0.00 – 0.16 ± 0.02	
		Canola oil (B)	< 0.10 – 0.10 ± 0.02	
		Canola oil (C)	0.11 ± 0.02 – 0.30 ± 0.04	
		Canola oil (D)	< 0.10 – 0.14 ± 0.03	
		Canola oil (E)	0.14 ± 0.00 – 0.25 ± 0.07	
		Canola oil (F)	0.14 ± 0.03 – 0.24 ± 0.03	
		Canola oil (G)	0.23 ± 0.03	
		Maize, sunflower, canola oils (A)	< 0.10 – 0.12 ± 0.02	
		Maize, sunflower, canola oils (B)	0.39 ± 0.02	
		Olive extra virgin oil (A)	nd	
		Olive extra virgin oil (B)	0.10 ± 0.03 – 1.29 ± 0.01	
		Olive oil (virgin + refined)	0.14 ± 0.03 – 0.33 ± 0.08	
		Olive + pomace oil (A)	1.46 ± 0.03	
		Olive + pomace oil (B)	5.09 ± 0.02	
		Palm oil (A)	0.25 ± 0.01 – 0.32 ± 0.02	
		Palm oil (B)	0.30 ± 0.05 – 0.33 ± 0.02	
		Palm oil (C)	nd	
		Palm kernel oil	0.17 ± 0.05	
		Palm fat (A)	1.64 ± 0.01 – 3.31 ± 0.03	
		Palm fat (B)	2.20 ± 0.02 – 2.56 ± 0.03	
		Palm fat (C)	2.29 ± 0.05 – 2.60 ± 0.02	
		Palm fat (D)	1.47 ± 0.03 – 2.45 ± 0.08	
Peanut oil (A)	0.13 ± 0.00 – 0.29 ± 0.03			
Sesame oil (A)	0.48 ± 0.00 – 0.58 ± 0.05			
Hydrogenated vegetable fat (A)	0.29 ± 0.06 – 0.45 ± 0.08			
Mix of fats	0.40 ± 0.00 – 0.66 ± 0.04			
Shortening	3.14 ± 0.02 – 3.87 ± 0.03			
-	<p>Liquid chromatography</p> <p>Detector: TOF/MS</p> <p>Column: Acquity C18 (50 mm x 2.1 mm, 1.7 µm particle size)</p> <p>Flow: 0.3 mL/min</p> <p>Injection volume: 1 µL</p> <p>Mobile phase: (A) Methanol; (B) 10 mM aqueous sodium acetate solution containing 0.1% formic acid</p>	Edible vegetable blending oil	nd	[19]
		Natura cereal blending oil	81 ± 3.0	
		Edible blending oil	1367 ± 0.03	
		Sunflower oil	nd	
		Rice bran oil	65 ± 3.7	
		Rice bran oil	122 ± 1.1	
		Camellia seed oil	nd	
		Rice oil	1449 ± 6.2 – 2564 ± 4.4	
		Camellia blending oil	nd	
		Peanut oil	738 ± 1.4	
		Soybean oil	58 ± 2.7	
		Palm oil	336 ± 3.6 – 540 ± 1.9	
		Corn oil	132 ± 1.5 – 143 ± 3.1	
		Canola oil	685 ± 1.0	
		Corn oil (n = 1)	0.019	
		Crude palm oil (n = 1)	nd	
		Edible blend oil (n = 5)	0.026 – 0.301	
		Extra virgin olive oil (n = 1)	nd	
		Maize germ oil (n = 1)	0.102	
		Peanut oil (n = 7)	0.080 – 1.046	
		Peanut sesame blend oil (n = 1)	0.164	
		Rapeseed oil (n = 1)	0.427	
		Sesame blend oil (n = 1)	0.227	
		Soybean crude oil (n = 1)	nd	
		Soybean oil (n = 6)	0.322 – 1.167	
		Sunflower oil (n = 2)	0.164 – 0.313	
		Virgin rapeseed oil (n = 1)	0.007	
		Tea seed oil (n = 1)	0.052	



-	-	Edible oils and fats sampled in 2011 (n = 43)	nd - 8.340	[22]
		Extra virgin olive oil (n = 6)	nd	
		Light olive oil (n = 2)	0.584 - 1.560	
		Vegetable oil spray (n = 5)	nd - 0.481	
		Mix vegetable oil (n = 3)	nd - 1.220	
		Coconut oil (n = 1)	0.315	
		Coconut oil, unrefined (n = 1)	nd	
		Canola oil, unrefined (n = 1)	nd	
		Canola oil (n = 2)	0.191 - 0.218	
		Canola and extra virgin olive oil (n = 1)	0.299	
		Canola and sunflower oil (n = 1)	0.165	
		Rice bran oil (n = 1)	8.340	
		Corn oil (n = 1)	0.239	
		Sunflower oil, unrefined (n = 1)	nd	
		Sunflower oil (n = 2)	0.150 - 0.245	
		Grapeseed oil (n = 2)	1.380 - 3.190	
		Walnut oil (n = 1)	11.6	
		Almond oil (n = 1)	0.515	
		Peanut oil, unrefined (n = 1)	nd	
		Avocado oil, unrefined (n = 1)	nd	
		Avocado oil (n = 1)	0.912	
		Toasted sesame oil (n = 1)	0.757	
		Toasted sesame oil, unrefined (n = 1)	0.700	
		Margarine (n = 4)	0.092 - 0.434	
		Vegetable shortening (n = 1)	0.502	
		Lard (n = 1)	0.432	
		Edible oils and fats sampled in 2013 (n = 44)	nd - 8.420	
		Extra virgin olive oil (n = 6)	nd	
		Light olive oil (n = 2)	0.739 - 0.921	
		Vegetable oil spray (n = 2)	nd - 0.130	
		Mix vegetable oil (n = 2)	nd - <0.1	
		Coconut oil (n = 1)	0.333	
		Coconut oil, unrefined (n = 1)	nd	
		Canola oil, unrefined (n = 1)	nd	
		Canola oil (n = 2)	0.210 - 0.304	
		Canola and extra virgin olive oil (n = 1)	0.235	
		Canola and sunflower oil (n = 1)	0.077	
		Rice bran oil (n = 1)	0.368	
		Corn oil (n = 1)	0.121	
		Sunflower oil, unrefined (n = 1)	nd	
		Sunflower oil (n = 2)	0.090 - 2.54	
		Grapeseed oil (n = 2)	2.14 - 3.60	
		Walnut oil (n = 1)	2.87	
		Almond oil (n = 1)	1.04	
		Peanut oil, unrefined (n = 1)	nd	
		Avocado oil, unrefined (n = 1)	0.062	
		Avocado oil (n = 1)	0.435	
		Sesame oil (n = 1)	1.290	
		Toasted sesame oil, unrefined (n = 1)	0.588	
		Margarine (n = 4)	0.164 - 0.441	
		Vegetable shortening (n = 1)	0.551	
		Lard (n = 1)	0.412	
		Peanut oil (n = 1)	0.384	
		Palm oil shortening (n = 1)	8.420	
		Palm oil unrefined (n = 3)	0.087 - 0.558	

DGF method C-VI 18 (10)	Gas chromatography  Detector: MS  Column: HP-5MS (30 m x 0.25 mm, I.D.; 0.25 µm film thickness)  Injection mode: Splitless  Injector temperature: 280 °C  Oven ramp: 85 °C (0.5 min), 6 °C/min to 150 °C, 12 °C/min to 180 °C, 25 °C/min to 280 °C (held for 7.16 min)  Carrier gas: Helium (1.0 mL/min)  Injection volume: -	Refined edible oils (n = 102)	0.219 – 2.586	[21]
		Sunflower seed oil (n = 6)	0.504 – 1.044	
		Peanut oil (n = 15)	0.450 – 1.187	
		Rapeseed oil (n = 18)	0.226 – 1.069	
		Sesame oil (n = 4)	0.651 – 1.344	
		Soybean oil (n = 18)	0.224 – 1.090	
		Corn germ oil (n = 12)	0.219 – 1.826	
		Blend oil (n = 11)	0.246 – 0.806	
		Palm oil (n = 3)	1.294 – 1.646	
		Lard (n = 5)	0.225 – 0.310	
		Camellia oil (n = 5)	0.988 – 2.586	
		Margarine (n = 5)	0.789 – 1.602	
		Crude edible oils (n = 41)	0.025 – 0.555	
		Sunflower seed oil (n = 8)	0.025 – 0.098	
		Peanut oil (n = 6)	0.025 – 0.083	
		Rapeseed oil (n = 9)	0.025 – 0.438	
		Sesame oil (n = 6)	0.025 – 0.356	
Soybean oil (n = 7)	0.025 – 0.109			
Camellia oil (n = 5)	0.025 – 0.555			
DGF method C-VI 18 (10)	Gas chromatography  Detector: MS  Column: HP-5MS (30 m x 0.25 mm, I.D.; 0.25 µm film thickness)  Injection mode: Splitless  Injector temperature: 280 °C  Oven ramp: 85 °C (0.5 min), 6 °C/min to 150 °C, 12 °C/min to 180 °C, 25 °C/min to 280 °C (held for 7.16 min)  Carrier gas: Helium (1.0 mL/min)  Injection volume: -	Sunflower oil	0.765 ± 0.033	[37]
		Soybean oil	0.479 ± 0.036	
		Lard	0.302 ± 0.021	
		Rapeseed oil	0.622 ± 0.026	
		Sesame oil	0.734 ± 0.028	
		Camellia oil	1.156 ± 0.048	
		Peanut oil	0.699 ± 0.039	
		Blend oil	0.566 ± 0.030	
		Peanut oil (crude, hot squeezed)	0.101 ± 0.023	
		Rapeseed oil (crude, hot squeezed)	0.112 ± 0.020	
		Sesame oil (crude, cold squeezed)	nd	
		Rapeseed oil (crude, cold squeezed)	nd	

AOCS Cd 29b-13	Gas chromatography	Refined sunflower seed oils (n = 11)	0.08 – 0.96	[27]
	Detector: MS	Refined palm oils, palm stearin, palm mid fraction (n = 6)	0.18 – 2.48	
	Column: J&W (60 m x 0.25 mm, I.D.; 1 µm film thickness)	Refined rapeseed oils (n = 5)	0.03 – 0.51	
	Injection mode: Split	Crude and refined oils and fats (n = 13)	<0.005 – 7.55	
	Injector temperature: 150 °C			
	Oven ramp: 40 °C (6 min), 5 °C/min to 140 °C, 20 °C/min to 230 °C (held for 3 min)			
	Carrier gas: Helium (0.9 mL/min)			
	Injection volume: 25 µL			

**Table 1:** 3-MCPD content (mg/kg) for oils and fats.

<sup>a</sup>: Results are expressed as mean value; LOQ: Limit of Quantification; nd: Not Detected

For refined seed oils, Zelinková, *et al.* (2006) have reported values for 3-MCPD ranging from <0.3 to 1.23 mg/kg, while Kuhlmann (2011) has presented results varying between 0.2 and 19 mg/kg [11,20]. With respect to olive oil, the content of 3-MCPD in refined olive oils was approximately eight times higher than for virgin olive oils [11]. Recently, Li, *et al.* (2015) have evaluated 102 refined edible oils and 41 crude edible oils. It was possible to observe that for sunflower, peanut, rapeseed, sesame, soybean and camellia oils, the reported values for 3-MCPD content were significantly higher for refined (1.044 - 2.586 mg/kg) than for crude oils (0.083 - 0.555 mg/kg) [21].

Around forty vegetable oils from the Canadian market were analysed in 2011 and 2013, but it was not possible to establish a trend concerning the decrease of 3-MCPD amounts, because for some types of oil, the values were lower in 2011 than in 2013, but the opposite was also observed [22]. Nonetheless, the high amount of 3-MCPD in 2011 was determined for rice bran oil (8.340 mg/kg), while in 2013 it was for palm oil shortening (8.420 mg/kg). Also, authors reported that for unprocessed oils, 3-MCPD was only detected in trace amounts or not detected [22].

As mentioned before, palm oil is the most used vegetable oil. Therefore, several authors have reported 3-MCPD values for palm oil, varying between not detected and 540 mg/kg [10,19,22-27].

Regarding the mitigation of 3-MCPD, different strategies have been already evaluated, such as: (a) removal of potential precursors; (b) modifications of processing parameters; and (c) degradation or removal of the compounds in the final product [28]. Concerning the first one, washing the crude oil before refining to remove water-soluble chloride is appointed as feasible and effective [29]. Concerning the modifications of processing parameters, one of the main difficulties to decrease the formation of these compounds is the fact that MCPD esters begin forming at 180 - 200 °C, which are the temperatures applied in deodorisation step [24]. Nonetheless, for the last strategy, the use of radical scavengers is efficient, namely phenolic compounds from other foods (like lipophilic tea polyphenols and rosemary extract) [30].

### Exposure assessment to 3-MCPD

Food processing induces changes in foods and these modifications can result in harmful, as well as beneficial effects on the food quality, and therefore on human nutrition. As previously described, 3-MCPD is a processing food contaminant, but its mitigation is not always easy to achieve. Furthermore, literature data shows (Table 1) that some vegetable oils contain high amounts of this cytotoxic and mutagenic compound. On the other hand, vegetable oils are largely used in different procedures, for example for frying, but are also ingredients of several foodstuffs, which enlarges the probability of exposure to these hazardous compounds. Nonetheless, few studies have focused on risk assessment of these compounds [21,26,31]. Another difficulty in this assessment, is the fact that most of the times it is not possible to accurately evaluate the effect of vegetable oils, because they are ingredients of the other foods, and the food itself can also contain 3-MCPD. Arisseto, *et al.* (2014) evaluated the exposure assessment to 3-MCPD for 17 food groups, but did not include edible oils and fats, while Arisseto, *et al.* (2017) evaluated the exposure assessment to this hazardous compound only of infant formulas [26,31]. Therefore, as far as we know, only Li, *et al.* (2015) have specifically evaluated the exposure assessment to 3-MCPD of edible oils and fats [21].

Li, *et al.* (2015) evaluated the exposure assessment of Chinese population to 3-MCPD esters, using the determined values for the concentrations of 3-MCPD of 143 edible oils and fats from Chinese market. The mean exposure values for children aged between 7 and 10 years old was 1.29 and 1.31  $\mu\text{g}/\text{kg}$  body weight/day for males and females, respectively. For adolescents (14 - 17 years old) it was 0.72  $\mu\text{g}/\text{kg}$  body weight/day (males) and 0.82  $\mu\text{g}/\text{kg}$  body weight/day (females), which is very similar to the values obtained for adults (0.71  $\mu\text{g}/\text{kg}$  body weight/day). Also, it is notable that the mean exposure values decreased when age increased, being almost the double for children than for adults (>50 years old) [21]. Nonetheless, these values are lower than the recently revised tolerable daily intake (2  $\mu\text{g}/\text{kg}$  of body weight/day) [17].

In 2016, EFSA published a report on "Risks for human health related to the presence of 3- and 2-MCPD, and their fatty acid esters, and glycidyl fatty acid esters in food" [32]. In this report, 7175 occurrence data were used, and these were distributed in three groups: soy sauce, hydrolysed vegetable protein and related products; oils and fats; and other food groups. According to the reported results, the mean exposure to 3-MCPD was 0.5-1.5  $\mu\text{g}/\text{kg}$  body weight/day for infants, toddlers and other children; while for adolescents and adult population it ranged from 0.2 to 0.7  $\mu\text{g}/\text{kg}$  body weight/day [32].

Also, the major food groups that contribute to 3-MCPD exposure by age groups were evaluated. It was concluded that vegetable fats and oils were one of the major contributors for infants and other children, while for adults and elderly, it was the group of margarines and similar products [32].

### Summary Points and Future Challenges

- In general, there is a great variation of 3-MCPD content between the different vegetable oils, but also in the same type of oils, which makes it difficult to establish a relationship between the source of the oil and the occurrence of this contaminant;
- Higher levels of 3-MCPD are reported for refined vegetable oils/fats than for unprocessed oils, which strongly supports that processing conditions are related to the increase of these compounds. Nonetheless, it is of utmost importance to consider that processing is essential to assure the quality and safety of vegetable oils. Therefore, more studies should accurately evaluate realistic processing conditions that mitigate the formation of 3-MCPD, but do not compromise the safety of these oils;
- Concerning exposure assessment, it is urgent to monitor the occurrence of 3-MCPD in edible oils, but also in other food matrices, to increase the number of studies regarding this subject. Nonetheless, it is possible to conclude that children are the most vulnerable group, and among the different food groups studied, vegetable oils and fats were described as the major contributors;
- In the near future, it is necessary to involve academy, researchers, industry to obtain more analytical data, as well as health professionals to perform dietary surveys to accurately estimate exposure assessment and potential impact for public health. Also, sharing knowledge from different research areas and from experts with different skills, will certainly contribute to efficiently diminish the presence of this cytotoxic and mutagenic compound in vegetable oils.

#### Acknowledgements

This work has been funded by National Institute of Health Dr. Ricardo Jorge, I.P., under the project PTranSALT (Reference number 2012DAN828) and by the project UID/QUI/50006/2013 - POCI/01/0145/FEDER/007265 with financial support from FCT/MEC through national funds and co-financed by FEDER, under the Partnership Agreement PT2020. Tânia Gonçalves Albuquerque acknowledges the PhD fellowship (SFRH/BD/99718/2014) funded by the FCT, FSE and MEC.

#### Conflict of Interest

Authors declare that any conflict of interest exists.

#### Bibliography

1. Foster R., *et al.* "Culinary oils and their health effects". *Nutrition Bulletin* 34 (2009): 4-47.
2. Albuquerque TG., *et al.* "4-Hydroxynonenal: A parameter of quality and safety of vegetable oils". *EC Nutrition* ECO.01 (2017): 27-29.
3. Choe E and Min DB. "Chemistry of Deep-Fat Frying Oils". *Journal of Food Science* 72 (2007): 77-86.
4. Zhang Q., *et al.* "Chemical alterations taken place during deep-fat frying based on certain reaction products: a review". *Chemistry and Physics of Lipids* 165 (2012): 662-681.
5. Brühl L. "Fatty acid alterations in oils and fats during heating and frying". *European Journal of Lipid Science and Technology* 116.6 (2014): 707-715.
6. EFSA, European Food Safety Authority. "Analysis of occurrence of 3-monochloropropane-1,2-diol (3-MCPD) in food in Europe in the years 2009-2011 and preliminary exposure assessment". *EFSA Journal* 11 (2013): 3381.
7. Stadler RH. "Monochloropropane-1,2-diol esters (MCPDEs) and glycidyl esters (GEs): and update". *Current Opinion in Food Science* 6 (2015): 12-18.
8. Jędrkiewicz R., *et al.* "3-MCPD: A Worldwide Problem of Food Chemistry". *Critical Reviews in Food Science and Nutrition* 56.14 (2016): 2268-2277.
9. Svejsovská B., *et al.* "Esters of 3-chloropropane-1,2-diol in foodstuffs". *Czech Journal of Food Sciences* 22.5 (2004): 190-196.
10. Seefelder W., *et al.* "Esters of 3-chloro-1,2-propanediol (3-MCPD) in vegetable oils: significance in the formation of 3-MCPD". *Food Additives and Contaminants: Part A* 25.4 (2008) 391-400.
11. Zelinková, Z., *et al.* "Fatty acid esters of 3-chloropropane-1,2-diol in edible oils". *Food Additives and Contaminants* 23.12 (2006): 1290-1298.
12. European Commission. "Commission Regulation (EC) No. 466/2001 of 8 March 2001 setting maximum levels for certain contaminants in foodstuffs". *Official Journal of the European Communities* L77 (2001): 1-13.
13. SCF (Scientific Committee on Food). "Opinion of the scientific committee on food on 3- monochloro-propane-1,2-diol (3-MCPD)". Updating the SCF opinion of 1994. Brussels, Belgium: European Commission (2001).
14. JECFA (Joint FAO/WHO Expert Committee on Food Additives). "3-Chloro-1,2- propanediol. Safety evaluation of certain food additives and contaminants". Prepared by the fifty-seventh meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA), Geneva WHO Food Additives Series, 48 (2002).

15. IARC (International Agency for Research on Cancer). "3-Monochloro-1,2-propanediol". In: IARC Monographs Volume 101. Some Chemicals Present in Industrial and Consumer Products, Food and Drinking-water. Lyon, France (2012): 349-374.
16. Larsen JC. "3-MCPD esters in food products". ILSI Europe (2009).
17. EFSA, European Food Safety Authority. "Update of the risk assessment on 3-monochloropropane diol and its fatty acid esters". *EFSA Journal* 16.1 (2018): 1-48.
18. Hori K., *et al.* "Simultaneous determination of 3-MCPD fatty acid esters and glycidol fatty acid esters in edible oils using liquid chromatography time-of-flight mass spectrometry". *LWT - Food Science and Technology* 48.2 (2012): 204-208.
19. Zhou H., *et al.* "Direct measurement of 3-chloropropane-1,2-diol fatty acid esters in oils and fats by HPLC method". *Food Control* 36.1 (2014): 111-118.
20. Kuhlmann J. "Determination of bound 2,3-epoxy-1-propanol (glycidol) and bound monochloropropanediol (MCPD) in refined oils". *European Journal of Lipid Science and Technology* 113.3 (2011): 335-344.
21. Li C., *et al.* "Exposure assessment of 3-monochloropropane-1, 2-diol esters from edible oils and fats in China". *Food and Chemical Toxicology* 75 (2015): 8-13.
22. Becalski A., *et al.* "A pilot survey of 2- and 3-monochloropropanediol and glycidol fatty acid esters in foods on the Canadian market 2011-2013". *Journal of Food Composition and Analysis* 37 (2015) 58-66.
23. Karšulinová L., *et al.* "Analysis of the lipid fractions of coffee creamers, cream aerosols, and bouillon cubes for their health risk associated constituents". *Czech Journal of Food Sciences* 25.5 (2007): 257-264.
24. MacMahon S., *et al.* "Occurrence of 3-MCPD and glycidyl esters in edible oils in the United States". *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment* 30.12 (2013) 2081-2092.
25. Yamazaki K., *et al.* "A new, direct analytical method using LC-MS/MS for fatty acid esters of 3-chloro-1,2-propanediol (3-MCPD esters) in edible oils". *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment* 30.1 (2013): 52-68.
26. Ariseto AP., *et al.* "Determination of 3-monochloropropane-1,2-diol fatty acid esters in Brazilian vegetable oils and fats by an in-house validated method". *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment* 31.8 (2014): 1385-1392.
27. Kuhlmann J. "Analysis and occurrence of dichloropropanol fatty acid esters and related process-induced contaminants in edible oils and fats". *European Journal of Lipid Science and Technology* 118.3 (2016): 382-395.
28. Ariseto A., *et al.* "Ésteres de cloropropanóis e de glicidol em alimentos". *Química Nova* 36.9 (2013): 1406-1415.
29. Matthäus B., *et al.* "Strategies for the reduction of 3-MCPD esters and related compounds in vegetable oils". *European Journal of Lipid Science and Technology* 113.3 (2011): 380-386.
30. Zhang H., *et al.* "Mitigation of 3-Monochloro-1,2-propanediol ester formation by radical scavengers". *Journal of Agricultural and Food Chemistry* 64.29 (2016): 2-7.
31. Ariseto AP., *et al.* "3-MCPD and glycidyl esters in infant formulas from the Brazilian market: Occurrence and risk assessment". *Food Control* 77 (2017): 76-81.
32. EFSA, European Food Safety Authority. "Risks for human health related to the presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food". *EFSA Journal* 14.5 (2016): e04426.

33. Weißhaar R. "Determination of total 3-chloropropane-1,2-diol (3-MCPD) in edible oils by cleavage of MCPD esters with sodium methoxide". *European Journal of Lipid Science and Technology* 110.2 (2008): 183-186.
34. Weißhaar R and Perz R. "Fatty acid esters of glycidol in refined fats and oils". *European Journal of Lipid Science and Technology* 112.2 (2010): 158-165.
35. Haines TD., *et al.* "Direct determination of MCPD fatty acid esters and glycidyl fatty acid esters in vegetable oils by LC-TOFMS". *Journal of the American Oil Chemists' Society* 88.1 (2011): 1-14.
36. Weißhaar R. "Fatty acid esters of 3-MCPD: Overview of occurrence and exposure estimates". *European Journal of Lipid Science and Technology* 113.3 (2011): 304-308.
37. Li C., *et al.* "Formation and reduction of 3-monochloropropane-1,2-diol esters in peanut oil during physical refining". *Food Chemistry* 199 (2016): 605-611.

**Volume 13 Issue 7 July 2018**

**©All rights reserved by Helena S Costa., *et al.***