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## HEALTH RISKS FROM TOXIC CONTAMINANTS FORMED DURING THE PROCESSING OF VEGETABLE OILS AND FATS

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**Abstract.** The purpose of this review was to summarize current research findings and unify ideas regarding methods to reduce the health risks to consumers posed by toxic contaminants, such as chloropropanols, glycidols, and their esters, which are formed during food processing, particularly during the refining of vegetable oils and fats, thereby critically impacting food safety. The review describes various aspects related to the occurrence of foodborne toxicants, it covers hazard characterization, their formation mechanisms, and control and regulatory strategies developed in recent years by the World Health Organization, the European Union Commission, and the Food and Agriculture Organization. Additionally, it concludes with an analysis of factors that favor the formation of toxic contaminants in food and discusses some methods for mitigating and monitoring the concentrations of precursors in raw materials. The material is also addressed to researchers, nutritionists and specialists in the domestic food industry, who should pay more attention to the health risk posed by oil and fat processing contaminants and methods of their removal from the raw material.

**Keywords:** *chlorinated propanols, glycidols, hazard characterization, mitigation strategy, oil refining.*

**Rezumat.** Scopul acestui studiu a fost de a trece în revistă rezultatele cercetărilor actuale și de a unifica tendințele concentrate asupra metodelor de diminuare a riscului pentru sănătatea consumatorului a contaminanților toxici, cloropropanolii, glicidolii și esterii acestora, care se formează în timpul procesării alimentelor, în special la rafinarea uleiurilor vegetale și a grăsimilor, afectând în mod critic siguranța alimentelor. Studiul descrie mai multe aspecte legate de răspândirea contaminanților de procesare, caracterizarea pericolelor de sănătate, modul de formare a contaminanților, strategia de control și reglementare, elaborată de Organizația Mondială a Sănătății, Organizația pentru Alimentație și Agricultură, de Comisiile Uniunii Europene în ultimii ani. Totodată, se concluzionează despre factorii care favorizează formarea contaminanților toxici în alimente, sunt discutate unele metodele de atenuare și monitorizare a concentrațiilor precursorilor în materia primă. Materialul se adresează și cercetătorilor, nutriționiștilor și specialiștilor din industria alimentară autohtonă, care ar trebui să acorde mai multă atenție riscului pentru sănătate pe care îl prezintă

contaminanții de prelucrare a uleiurilor și grăsimilor și metodelor de îndepărtare a acestora din materia primă.

**Cuvinte-cheie:** *caracterizarea pericolului, glicidoli, propanoli clorurați, rafinarea uleiului, strategii de atenuare.*

## 1. Introduction

Lipids, classified into triglycerides, phospholipids, phytosterols, and cholesterol, alongside carbohydrates and proteins, constitute the basic components of the human diet. Vegetable oils, fish oil, and animal fats, consumed daily, are important sources of macro- and micronutrients and provide the body with more energy (9 kcal/g) compared to carbohydrates and proteins. For this reason, the quality indicators and physico-chemical properties of edible fats and oils must comply with the requirements outlined in the regulations of the Codex Alimentarius Commission [1].

When discussing the quality of oils and fats, the following physico-chemical characteristics are targeted: color, specific gravity, refractive index, melting point, freezing point, smoke point, flash point, viscosity, acidity, acidity indices, iodine value, saponification value, fatty acid composition, trans isomer content, triacylglycerol composition, unsaponifiable matter content (sterols, tocopherols), and minor components (phospholipids, chlorophyll pigments, glycidyl esters of fatty acids, chloropropanols and their esters, metals, mycotoxins, pesticides, phthalates, etc.) [2].

Oils and fats have the property of becoming rancid. The deterioration (rancidity) of lipids is the consequence of chemical, photochemical, or biochemical decomposition processes. In the presence of air, light, moisture, microorganisms, enzymes, during the storage or processing of lipids, they undergo oxidation, cyclization, polymerization, hydrolysis reactions, leading to the formation of undesirable products that impart unpleasant taste and odor, and reduce the nutritional value of oils and fats. Usually, vegetable oils with high levels of polyunsaturated fatty acids rancidify more easily and are more susceptible to auto- and photo-oxidation [3]. To assess the degree of deterioration of oils and fats, peroxide, p-anisidine, carbonyl indices, polar compound content, and polymerized triacylglycerols are determined [4]. The consumption of rancid oils and fats may pose health risks including cancer and inflammation due to the formation of toxic and reactive oxidation products [5].

Currently, alongside the products of fat rancidity and other undesirable substances, a number of toxic contaminants, known as processing contaminants or foodborne toxicants, are under the scrutiny of researchers.

Some processing contaminants, as minor components in oils and fats, raise greater health concerns due to their advanced toxicity [6].

Processing contaminants are chemical substances that have not been intentionally added to edible oils or foods but are formed at various stages of production and processing, especially at high temperatures. Foodborne toxicants can be formed either in the food product itself or in the raw materials used for food manufacturing [7].

The first pathway of formation of toxic contaminants in the food product is termed endogenous formation, while the second is exogenous intake [6].

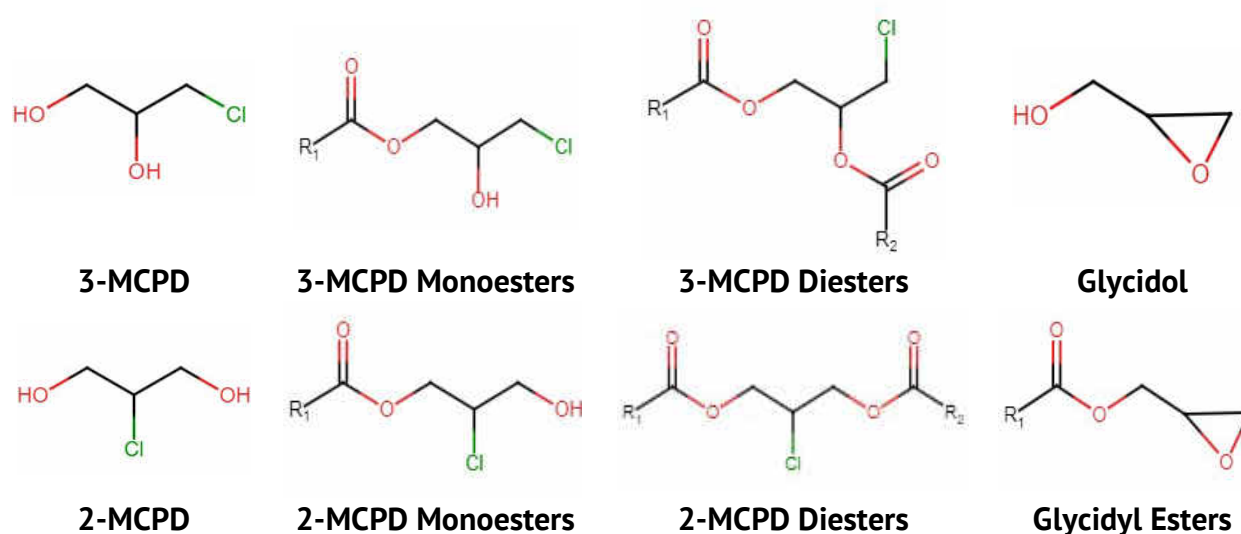
From a food safety perspective, the presence of processing contaminants in food products must be carefully monitored to avoid negative impacts on consumer health [8].

## 2. Toxic processing contaminants and their occurrence in oils and fats

As noted, the toxic processing contaminants, most commonly found in refined vegetable oils and refined fats, include chloropropanols and glycidols. Chlorinated propanols were discovered in 1978 in soy sauces, seasonings, and broths as contaminants of acid-hydrolyzed vegetable protein processed under high-temperature conditions [9]. Davídek J. et al., 1980, demonstrated that chloropropanols can form as a result of the reaction between hydrochloric acid and residual lipids [10].

Chlorinated propanols are compounds formed by replacing the hydroxyl groups of glycerol with one or two chlorine atoms [11]. Depending on the number of chlorine atoms and their positions, they can be divided into monochloropropanediols (MCPD) and dichloropropanols (DCP), with systematic names: 3-chloropropane-1,2-diol (3-MCPD), 2-chloropropane-1,3-diol (2-MCPD), 1,3-dichloropropane-2-ol (1,3-DCP), and 2,3-dichloropropane-1-ol (2,3-DCP), Figure 1. Typically, the amount of MCPD in foods is 100 to 10,000 times higher than that of DCP [12].

In refined vegetable oils, animal fats, and processed fatty foods, only a small amount of chloropropanols exists in free form [13]. Most chloropropanols are found as esters with fatty acids (MCPDEs) [11], as depicted in Figure 1.



**Figure 1.** Processing contaminants in oils and fats.

Fatty acid (FA) esters of 3-chloropropane-1,2-diol are the compounds with the highest contamination levels. These have been found in refined vegetable oils, fried potatoes, fried chicken, and some infant formulas [14].

Glycidyl fatty acid monoesters (GEs), first identified in 2009 in refined vegetable oils and fats, have raised concerns due to their potential to release the genotoxic carcinogen glycidol (1,2-epoxypropan-3-ol) in animal studies [15]. The level of glycidyl fatty acid esters was found to correlate with the levels of monoacylglycerols and diacylglycerols in the oils [7,16].

The causes of the formation of processing contaminants in oils and fats depend on several factors, most commonly high-temperature treatments such as refining (deodorization) [17], cooking methods like frying, grilling, and baking [18].

Research from the mid-2000s indicated that concentrations of GEs, MCPDEs, and DCPEs were higher in palm oil, rice oil, soybean oil, and corn oil. The highest concentration

of GE, above 30 mg/kg oil, was detected in rice oil and palm oil. The content of DAG precursors for GE was rich in palm and rice oils, ranging from 4 % to 12 %. [19].

High levels of GEs continued to be found in subsequent years, particularly in batches of palm oils [20,21]. Advanced physico-chemical methods for analyzing contaminant content detected high levels of chloropropanol and glycidol esters in refined vegetable oils, fats, and processed fatty foods [15,16, 22, 23]. The concentration values of processing contaminants found in various batches of vegetable oils after 2010 are shown in Table 1.

Table 1

Occurrence of processing contaminants in oils and fats		
Oil type	Determined Concentrations (mg/kg)	References
Refined palm oil	2.54 (3-MCPDEs), 3.19 (2-MCPDEs);	[24]
	5.634 (3-MCPD)	[25]
Refined corn oil	0.503 (3-MCPD), 0.233 (2-MCPD), 0.475 (GEs);	[6]
	2.447 (3-MCPD);	[25]
	0.05-0.37 (3-MCPD), 0.06-0.95 (GEs)	[23]
Refined sunflower oil	0.303 (3-MCPD), 0.218 (2-MCPD);	[6]
	1.817 (3-MCPD);	[25]
	0.02-0.44 (3-MCPD), 0.06-2.42 (GEs)	[23]
Unrefined sunflower oil	0.1-0.4 (chloropropanols)	[26]
Refined soybean oil	1.486 (3-MCPD)	[25]
Olive pomace oil	2.90 (3-MCPD), 1.031 (2-MCPD), 0.70 (GEs);	[27]
	0.573 (3-MCPD)	[25]
Refined olive oil	1.21 (3-MCPD);	[25]
	0.558 (2-MCPD), 0.518 (GEs)	[28]
Cold pressed olive oil	0.093 (3-MCPD)	[25]
Refined peanut oil	0.1-0.9 (3-MCPD), 0.1-0.4 (2-MCPD), 0.4-1.1 (GEs);	[29]
	1.360 (3-MCPDEs), 0.400 (2-MCPDEs);	[30]
	0.90-0.11 (3-MCPD), 1.47- 0.45 (GEs)	[23]
Refined rapeseed oil	1.120 (3-MCPDEs);	[28]
	0.660 (2-MCPDEs)	[30]
Unrefined rapeseed oil	0.022 (3-MCPDEs);	[28]
	0.015 (2-MCPDEs)	[30]
Refined coconut oil	0.2-0.4 (3-MCPD), 0.1-0.2 (2-MCPD), 0.5-3.0 (GEs)	[29]
Refined soybean oil	0.1-0.5 (3-MCPD), 0.4-0.5 (2-MCPD), 0.1-0.6 (GEs)	[29]

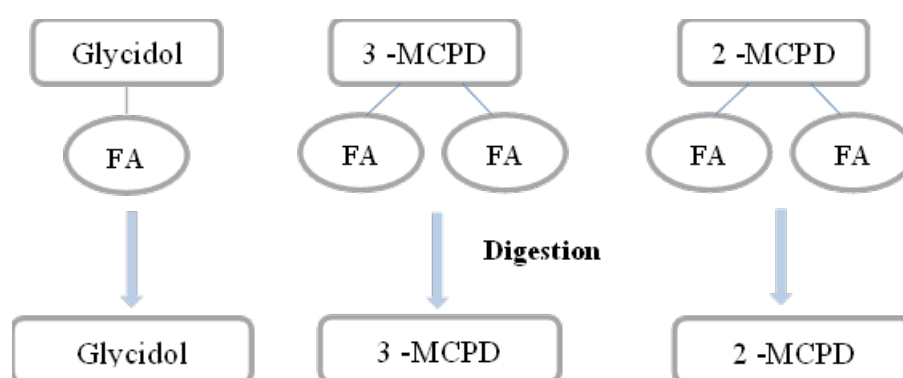
Continuation Table 1

Refined hazelnut oil	19.0 (3-MCPD), 11.0 (2-MCPD), 0.5 (GEs);	[29]
	1.13-2.12 (3-MCPD), 0.54-2.63 (GEs)	[23]
Refined vegetable oils	1.1521 (3-MCPDEs), 1.3172 (GEs)	[22]
Unrefined vegetable oils	0.0974 (3-MCPDEs), 0.1108 (GEs)	[22]
Margarines	0.57- 4.54 (3-MCPD);	[31]
	0.14-1.17 (3-MCPD), 0.41-3.83 (GEs)	[23]
Ghee	0.0148 (3-MCPDEs), 0.0113 (GEs)	[22]
Refined fish oil	1.5-5.5 (3-MCPD);	[32]
	0.7-13.0 (3-MCPD), 0.1-1.2 (2-MCPD), 0.1-1.2 (GEs);	[29]
	0.00-0.11 (3-MCPD), 0.00-0.69 (GEs);	[23]

Research has demonstrated that chloropropanols and glycidols can be introduced into foods along with contaminated oils and fats, or they can form during thermal processing. This occurs through reactions between lipids and intrinsic (or added) components such as chlorine compounds, glycerol, allyl alcohol, chloropropanol esters, propylene glycol, sucralose, carbohydrates, hydrochloric acid, etc. Another way of contamination is the migration of chlorinated propanols from materials that come into contact with food or from food packaging. [30].

### 3. Hazard characterization

The formation of toxic contaminants during the processing of fats and vegetable oils is a concern for consumer health. After oral administration, the esterified forms are almost completely hydrolyzed by digestive enzymes, leading to *in vivo* exposure of consumers to free glycidol and free MCPD, as illustrated in Figure 2 [33,34].



**Figure 2.** Hydrolysis of glycidol and monochloropropanediol esters during digestion (3-chloropropanediol: 3-MCPD, 2-chloropropanediol: 2-MCPD, Fatty acid moiety: FA).

The International Agency for Research on Cancer (IARC) classified glycidol as probably carcinogenic to humans (Group 2A), and considered 3-MCPD as a possible human carcinogen (Group 2B) [35]. According to toxicological studies, 3-MCPDE and 3-MCPD are non-genotoxic carcinogens with adverse effects on the kidneys and male reproductive organs, while glycidol and its esters are genotoxic carcinogens [8,36]. Chloropropanols are toxic to the liver,

kidneys, nervous system, hematological systems, and reproductive system [37,12]. Chronic oral exposure to 3-MCPD causes nephropathy, tubular hyperplasia, and kidney adenomas [38]. A daily dose of 30 milligrams per kilogram of body weight (mg/kg·bw/day) of 3-MCPD in rats resulted in increased relative kidney weight with oxalate crystal deposition and accumulation of 3-MCPD metabolites on the inner membrane of the tubules [39].

Studies have found that 3-MCPD inhibits *in vitro* fertilization and early embryonic development of mouse oocytes and progesterone synthesis. Chloropropanols affect the brain, have a detrimental effect on neurons [40], suppress immunity, and increase the risk of tumor development [41]. Treatment of mice for 28 days with the highest dose of 3-MCPD (100 mg/kg bw/day) induced cardiomyopathy, myofibrillar degeneration, and tissue necrosis [42].

A series of research findings over several years in mice and rats have demonstrated the high toxicity of glycidol [35], which have demonstrated carcinogenic and genotoxic activity with both *in vitro* and *in vivo* studies [43]. Oral exposure to glycidol has caused benign or malignant tumors in mice and rats, affecting the mammary glands, stomach (papilloma or carcinoma), thyroid gland, brain (glioma) in both male and female rats. Additionally, the skin and sebaceous glands have been affected. Glycidol has caused Zymbal gland cancer and testicular tumors in rats, intestinal tumors, oral cavity carcinoma. In mice, oral exposure to glycidol has also induced uterine and genital organ cancer, subcutaneous tissue tumors (sarcoma or fibrosarcoma) in females, and lung tumors in males. Furthermore, exposure to glycidol has caused glandular stomach cancer (fibrosarcoma) in female rats and bladder cancer (carcinoma) and testicular sarcoma in male mice [35,44].

#### **4. Formation of process-induced contaminants in oils and fats**

The mechanism of formation of processing contaminants in food products has not been fully elucidated. Available data on the content of GEs, MCPDEs, and DCPEs in foods mostly refer to refined vegetable oils, refined edible fats, and oil-based food products. Research has shown that notable amounts of MCPDEs and GEs are formed during the processing of oils, particularly during the deodorization stage, where oils are heated at high temperatures (240-270 °C) [45]. Deodorization of oil represents a final and essential step in the refining process of edible oil to remove odoriferous substances and other unwanted components (pesticide residues, pigments, free fatty acids, and other polar compounds). In crude or unrefined oils and fats, such as extra virgin olive oil, no GEs have been detected, and only traces of GEs have been found in some batches [24].

Based on research, it has been concluded that the formation of processing contaminants occurs at high temperatures in the presence of precursors contained in the raw material and crude oil. In model system experiments, chlorinated propanols 3-MCPD and 2-MCPD were formed when lipids, glycerol, triolein, and lecithin were heated in the presence of hydrochloric acid [20]. It is presumed that 2- and 3-MCPD are generated from glycerol through the formation of the unstable intermediate glycidol [46]. Glycidol has long been recognized as a carcinogen, but it has only relatively recently been shown to be associated with 3-MCPD in foods. It was found that at high temperatures, in the presence of chlorine ions or free radicals, glycidols and chloropropanols can mutually transform into each other [15, 47].

A series of research studies have shown that the formation of harmful contaminants, such as 3-MCPDEs and GEs, in vegetable oils and fats is influenced by various factors. These factors include high temperature, in the range of 180-200 °C for 3-MCPDE and above 230 °C

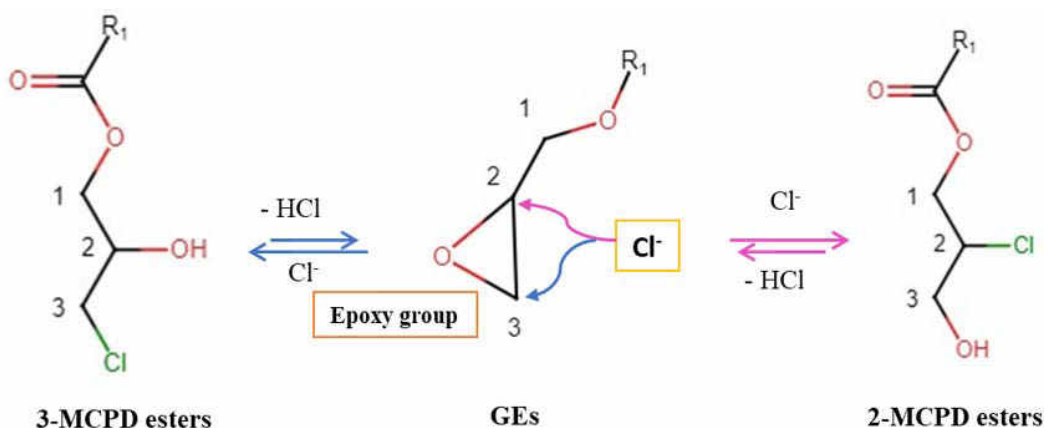
for GEs, the duration of heat treatment, the presence of precursors such as monoacylglycerols (MAG), diacylglycerols (DAG) and glycerols, pH conditions, chlorine content, the presence of metal ions, and water quality [8,20,48]. Data regarding the correlation between the level of glycidol esters with the concentration of MAG and especially DAG in oils have been confirmed by other researchers as well [7,17].

Several authors have noted that pure triacylglycerols (TAGs) remain stable during thermal treatment at 235 °C for 3 hours and therefore are not involved in the formation of GEs [49]. However, the results of experiments on model systems of thermally treated oil, consisting of 100 % TAG, revealed the occurrence of small amounts of GEs [47].

Currently, the formation mechanism of GEs intermediates and the relationship between GEs and 3-MCPDEs are still unclear. Fourier-transform infrared (FTIR) research suggests that the formation of GEs from TAG may proceed through the high-temperature decomposition steps of TAG to DAG and MAG [50]. Additionally, it has been demonstrated that 3-MCPDEs in refined oils can be obtained from TAG [51].

Researchers have proposed a series of reaction mechanisms for the formation of contaminants during processing [47,12], which may occur simultaneously.

- The formation of the unstable intermediate glycidol with the epoxide group (1,2-epoxypropane-3-ol) from glycerol. Glycidol, being reactive, in the presence of chlorine, generates 3-MCPD and 2-MCPD [46,52]. In acidic conditions, in the presence of chlorine ions, the conversion rate of glycidol into 3-MCPD was higher than that of 3-MCPD into glycidol [53]. Monoesters of glycidol can form from MAG and DAG during reactions. The opening of the epoxy ring of GEs in the presence of chloride ions leads to 3-MCPDEs or 2-MCPDEs, Figure 3.



**Figure 3.** The transformation of the Glycidol monoesters (GEs) in 3- chloropropanediol (3-MCPD) and 2- chloropropanediol (2-MCPD) esters [50].

- Nucleophilic substitution of hydroxyl or ester groups in MAG, DAG, and TAG by chloride ion [54].
- Cation-mediated mechanisms, involving the formation of cyclic acyloxonium or epoxide cation intermediates from DAG. The opening of these cycles in the presence of chloride ions generates monoesters and diesters of chloropropanols [55,56].
- Free radical-mediated mechanisms involve the formation of cyclic acyloxonium radicals or epoxide radicals from TAG or DAG. The opening of these cycles in the presence of free chlorine radicals leads to the formation of monoesters and diesters of chloropropanols and GEs [57-59].

## 5. Control and regulating strategy

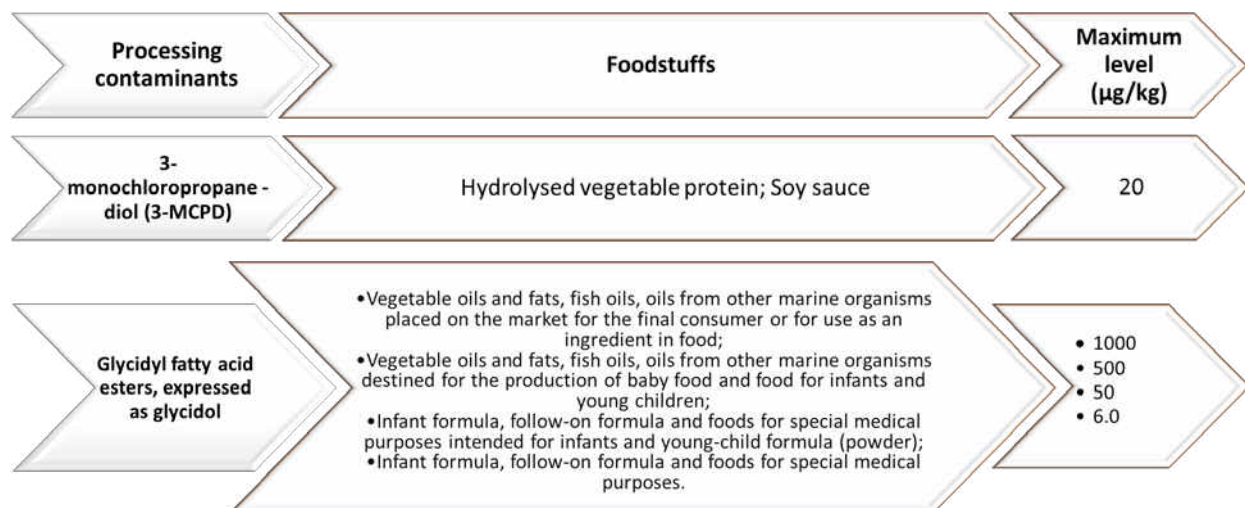
The effect of food contamination with chloropropanols (found in hydrolyzed vegetable protein and soy sauce) was first examined by JECFA in 1993 (FAO/WHO 1993), with the unique recognition of renal toxicity of 3-MCPDEs, and carcinogenic potential for both 3-MCPD and 1,3-DCP. It was concluded that these substances are undesirable contaminants and measures should be taken to regulate permissible concentrations. In 1996, the United Kingdom Food Advisory Committee recommended that the levels of 3-MCPD in hydrolyzed vegetable protein and soy sauce should be reduced to 0.01 mg/kg [60]. The concentration of total chloropropanols (free and esterified) determined in foods was expressed as 3-MCPD equivalents [6]. The proposed European Union (EU) limit at this time for 3-MCPD was 0.02 mg/kg. There was no proposed EU limit for 1,3-DCP [61].

The emergence of potential carcinogens, glycidols, and chloropropanols in edible oils, fats, and oil-based food products, especially in infant formulas, has focused attention on the oil processing industry since the early 2000s [35]. Researchers' concerns about the possible health risks associated with processed edible oils and fats contamination initiated a series of actions by the European Commission, scientists, and the industry aimed at regulating the concentration of chloropropanols and glycidols in foods [52, 61].

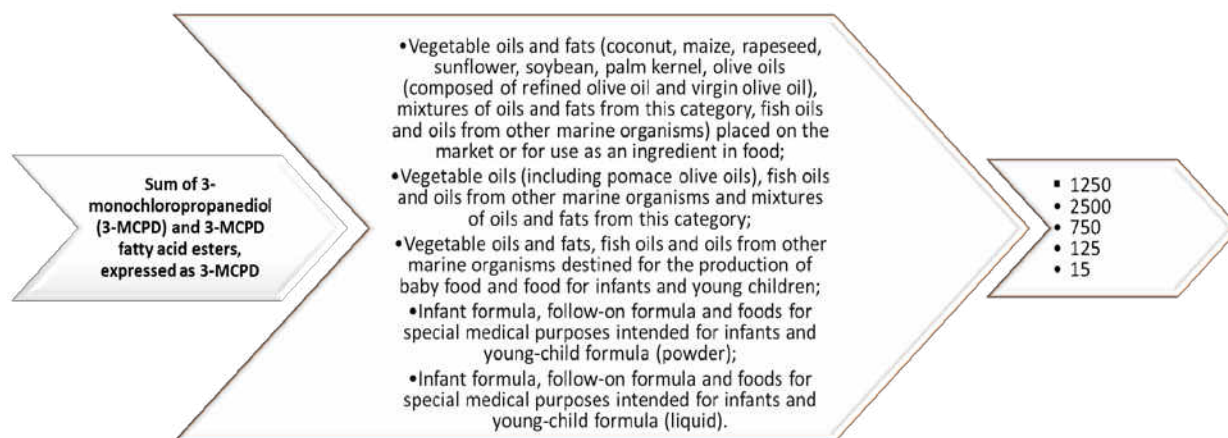
In 2016, the World Health Organization (WHO) and Food and Agriculture Organization (FAO) of the United Nations set a maximum total daily intake (TDI) value reported on body mass of 4  $\mu\text{g}/\text{kg}\cdot\text{bw}/\text{day}$  for 3-MCPD and its corresponding esters. As recently as 2018, the EFSA updated the TDI of 3-MCPD value to 2  $\mu\text{g}/\text{kg}\cdot\text{bw}/\text{day}$  [62].

Following a series of animal studies, further adjustments to the TDI of 3-MCPD were made in 2020, reducing it to 0.8  $\mu\text{g}/\text{kg}\cdot\text{bw}/\text{day}$ . No TDI has been applied for glycidol, but intake should be "as low as reasonably achievable" [63].

In EU Regulation 2020/1322, permissible limits for the content of total chloropropanols expressed in 3-MCPD equivalents in oils and fats were established. Accordingly, the permissible limit of 1250  $\mu\text{g}/\text{kg}$  (1.25 mg/kg) was set for refined palm oil, rapeseed oil, coconut oil, maize oil, sunflower oil, soybean oil, olive oil, and the mixture of oils and fats from this category; 2500  $\mu\text{g}/\text{kg}$  (2.5 mg/kg) in pomace olive oil, fish oil, and the mixture of oils and fats from this category. These limits are further reduced to 750  $\mu\text{g}/\text{kg}$  (0.75 mg/kg) in oils and fats intended for the production of food for infants and young children (Figure 4).







**Figure 4.** The permissible limits for the content of 3-monochloropropanediol (3-MCPD), 3-MCPD fatty acid esters, and glycidyl fatty acid esters [63].

In the recently consolidated version of 10.08.2023, the EU regulation established maximum permissible values for glycidyl esters, expressed as glycidol, at 1000  $\mu\text{g}/\text{kg}$  of oil in vegetable oils and fats sold on the market for consumption or used as an ingredient in food. The maximum level for GEs has been set at less than 500  $\mu\text{g}/\text{kg}$  of oils and fats, fish oils and oils from other marine organisms intended for the production of infant food and processed cereal-based food for infants and young children [64], as shown in Figure 4.

Due to the implemented strategy, starting from 2016, the concentration of processing contaminants in foodstuffs in EU countries' stores has significantly decreased. For instance, in 2019, determinations in 45 infant formula products purchased from German supermarkets showed that average contaminant concentrations in all samples were below the permitted limit. When comparing the data collected in 2019 with those from 2015, it was found that average bound 3-MCPD and glycidol concentrations in infant formula products had decreased (from 0.094 to 0.054  $\mu\text{g}/\text{g}$  and from 0.010 to 0.006  $\mu\text{g}/\text{g}$ , respectively). This confirms that the measures to control and reduce contaminant concentrations have been effectively implemented over the 4-year period [65].

## 6. Factors Favoring the Formation of Processing Contaminants in Vegetable Oils and Mitigation Strategy

The production of vegetable oils includes the following stages: cultivation of oilseed plants, harvesting (fruits, seeds), transportation of fruits (palm, olive) and seeds; sterilization of fruits, crushing, cleaning, grinding of seeds; pressing or steam extraction of crude oil, and refining of crude oil.

The refining of edible oils can be performed through two methods: chemical refining and physical refining.

Chemical refining includes degumming (removal of phospholipids with water or acid solutions); neutralization (addition of sodium hydroxide solution to neutralize free fatty acids, oxidation products, certain pigments); bleaching (using bleaching clay) for decolorization and neutralization of residual salts, phospholipids, trace metals, and degradation products; deodorization (steam distillation of oil at low pressures and high temperatures (1.5-6.0 mbar, 180-270  $^{\circ}\text{C}$ )) for the removal of colorants, free acids, volatile compounds, and other.

Physical refining is carried out at higher temperatures (240-270  $^{\circ}\text{C}$ ) than chemical refining, as it does not have the neutralization step. The physical refining of the oil includes

the stages of degumming, bleaching and deodorization and is more commonly applied to oils with a low phospholipid content [48].

It is known that refining is essential to eliminate the anti-nutritional factors of oils; however, during this process, in the presence of precursors (chlorine compounds), processing contaminants are formed, among which chlorinated propanols are the most widespread. It has been mentioned that these can form endogenously in foods during the processing of oils/fatty foods at high temperatures, or exogenously when contaminated raw materials are added. Understanding and managing the presence of chloride ions in edible oils is crucial to minimize the formation of chloropropanols and glycidols during processing [1,13,15,48].

The concentration of precursors, particularly chlorine compounds in raw materials, depends on several factors, listed below.

- *Soil and water contamination.* Depending on geographical location and environmental conditions, soils and water can contain higher amounts of chloride ions.
- *Agrochemicals.* The use of certain fertilizers and pesticides in agriculture can introduce chloride ions into the plant, and consequently, into the oil extracted from these plants.
- *Cleaning agents.* During the processing of edible oils, cleaning agents or sanitizers containing chloride ions may be used to clean equipment and machinery. Residual chloride ions from these cleaning agents can potentially end up in the final product.
- *Water used in processing.* Water is often used in various stages of processing, including washing and refining. If the water contains chloride ions, they can be transferred to the oil.
- *Transport and storage.* Contamination can occur during the transportation and storage (in the presence of kitchen salt, *etc.*) of raw materials or finished products.
- *Multiple processing steps.* If the oil undergoes multiple processing steps, each step has the potential to introduce or concentrate chloride ions. For instance, if a crude oil with chloride contamination is used as a starting material, the concentration may increase during refining.

In Codex Alimentarius CXC 79-2019 [8], measures to reduce the concentration of toxic contaminants in vegetable oils were outlined, as shown in Table 2. Special attention is drawn to the elimination of precursors such as chloride ions from the raw material and crude oil. In addition to reducing 3-MCPDEs and GEs, it is also important to consider other factors that influence the quality of refined oils and oil-based products, such as odor and taste, oxidative status, free fatty acid profile, concentration of nutrients, pesticides, mycotoxins, *etc.* Experience in mitigating 3-MCPDE and GE from palm oil may be applicable to reducing concentrations of processing contaminants in other refined oils (Table 2).

Table 2

**Recommended measures to reduce 3-MCPDE and GE from oils and fats [8]**

Production Stage	Mitigation Measures
Agricultural practices for vegetable oils	Selecting the seed material; selecting and planting oil palm plant varieties with low lipase activity. Lipases cleave ester bonds, forming di-, mono-acylglycerols (MAG, DAG), glycerol, and free fatty acids (FFA). Minimizing the use of plant tending procedures involving fertilizers, pesticides and irrigation water containing excessive amounts of chlorine compounds during the cultivation of oil plants/trees. Restricting

Continuation Table 2

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	<p>chlorinated pesticides and fertilizers helps reduce the concentration of toxic processing contaminants in raw materials and food products. Harvesting the seeds/fruits of oleaginous plants in the phase of optimal maturity. Avoiding excessive handling and fruit damage. Pre-cooling the raw material before transportation is recommended. Transportation of seeds/fruits to oil mills in the shortest possible time to obtain oil from freshly harvested raw material.</p>
	<hr/> <p><i>Crude Oil Production and Treatment</i></p> <p>Storage of oleaginous raw materials at low temperatures and dry conditions. Sterilization of oil palm fruits. Cleaning, selection, drying and heating of oilseeds/fruits at optimal temperatures for lipase inactivation. Washing raw materials (oil palm fruit) with water or 75% ethyl alcohol leads to a 20-25% reduction in 3-MSPDEs concentration [66]. Washing the crude vegetable oil with chlorine-free water helps to reduce the concentration of the precursors. Washing crude oil with water or sodium carbonate/bicarbonate solutions significantly decreases the level of 3-MCPDEs [67].</p> <p>Not to use residual vegetable oil recovered from solvents or other extractions, as it will increase the contaminant content of the finished product.</p> <p>Monitoring the concentration of precursors (e.g. DAG, FFA and chlorine compounds) in batches of crude vegetable oil (or fish oil) allows to adjust the refinement parameters. Precursors can be removed by washing the crude oil with 5-10% hot water (90-95 °C) [68].</p>
Oil milling and refining	<p>The crude oil destined for refining should contain a very low concentration of precursors.</p> <p><i>Degumming</i></p> <p>Carrying out the degumming process with water or in milder, less acidic conditions. Water degumming, without the addition of acids, yields positive results, reducing 3-MCPDEs by 78 % and GEs by 53 % [69]. Reducing the degumming temperature in vegetable oils.</p> <p><i>Neutralization</i></p> <p>The reduction of temperature and acidity in the refining process is achieved by applying the chemical refining process (i.e. neutralization) as an alternative to the physical refining of vegetable oils or fish oils.</p> <p><i>Bleaching</i></p> <p>Using a greater amount of bleaching clay in vegetable oils and fish oils. Clays with a neutral pH are used to reduce the acidity of the oils. The water degumming stage reduces by 84 %, while bleaching with synthetic magnesium silicate resulted in a further 10 % reduction in 3-MCPDEs in the oil [70].</p> <p><i>Deodorization</i></p> <p>Deodorization of oils at low temperatures. Deodorization process temperatures below 180 °C do not favor the formation of detectable concentrations of chloropropanols [71]. The concentration of</p>

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	<p>chloropropanols significantly increases at temperatures ranging between 180-270 °C.</p> <p>Deodorization of vegetable oils in 2 steps as an alternative to traditional deodorization. For the evaporation of volatile compounds, much lower pressures are applied, thus the deodorization temperature will be considerably reduced.</p> <p>An alternative to deodorization is short-term distillation to reduce overheating of the fish oil.</p>
Treatment post refining	<p>Repeated bleaching and deodorization after the refining process reduce the concentration of contaminants in vegetable oil (especially palm oil). Applying activated bleaching clay to refined vegetable oils helps reduce the concentration of contaminants. Treating refined oil with calcinated zeolite and synthetic magnesium silicate reduces the concentration of 3-MCPD esters and similar compounds by over 40 % [72].</p> <p>Using short-path distillation on bleached and deodorized vegetable oils. Treating the medium-chain triglycerides from refined oil with fatty acids, in the presence of cations and alkaline bases, converts 3-MCPDEs into MAG, DAG, and TAG, and GEs into DAG.</p>
Selection of refined oil	<p>Selecting refined vegetable oils or fish oils with lower concentrations of 3-MCPDEs and GEs.</p> <p>Reducing the amount of refined oils in finished products. Using cold pressed oils from high quality raw materials</p>

For the production of safe foods, each manufacturing step implements quality control measures, including the testing of raw materials and monitoring processing conditions to reduce the risk of toxic contaminants in the final product. Identification of chloropropanols, glycidols, and their esters in food products, particularly in edible oils, is typically carried out using advanced instrumental physico-chemical method [73]. These methods include Gas Chromatography-Mass Spectrometry [74-77], High-Performance Liquid Chromatography [78,79], Enzyme-Linked Immunosorbent Assay [80], Capillary Electrophoresis, Nuclear Magnetic Resonance Spectroscopy [81], Supercritical Fluid Chromatography (SFC) coupled with Triple Quadrupole Mass Spectrometry [82], among others.

In recent years, many countries have established regulatory limits for chloropropanols in edible oils [14,22-27,65,83,84]. However, currently, there are no universal, global regulations limiting the maximum allowable concentrations of glycidyl esters in edible oils. In many non-EU countries, insufficient research has been conducted to assess the risk of consumer exposure to toxic food processing contaminants such as chloropropanols and glycidols.

In order to reduce the risk of exposure to chloropropanols and glycidols, consumers can take the following measures:

- avoiding the consumption of processed foods rich in fats and oils;
- reducing cooking, baking, and frying temperatures, especially for foods high in oils and fats (such as biscuits, pies, crackers, fried potatoes), avoiding deep frying, *etc.*;
- limiting the consumption of grilled foods;
- using moist-heat cooking methods, such as steaming and stewing;

- decreasing the use of kitchen salt and adding salt at the end of cooking;
- maintaining a balanced and varied diet to reduce the intake of glycidyl esters and MCPD esters [8,85].

### Conclusion

The toxic contaminants, chloropropanols and glycidols, formed during food processing, especially during the refining of vegetable oils and fats, can critically impact food safety.

The purpose of this review was to assess current research findings regarding the occurrence of processing contaminants - chloropropanols and glycidols - in refined vegetable oils and fats, hazard characterization, formation mechanisms, control and regulatory strategies, factors favoring the formation of toxic contaminants in food, as well as mitigation strategies.

The material is also aimed at researchers, nutritionists, and professionals in the domestic food industry and oil industry, who should pay more attention to the health risks posed by processing contaminants and the methods of eliminating them from raw materials and oil. Chloropropanols, glycidols, and their esters, as minor components in refined oils, raffinated fats, and processed fatty foods, raise concerns for heightened health risks due to their advanced toxicity.

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