Updates on Food Processing Contaminants

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- Member of Indonesian Academy of Sciences
- Vice Chair of Codex Alimentarius Commission

“Any substance not intentionally added to food or feed for food producing animals, which is present in such food or feed as a result of the production (including operations carried out in crop husbandry, animal husbandry and veterinary medicine), manufacture, processing, preparation, treatment, packing, packaging, transport or holding of such food or feed, or as a result of environmental contamination. The term does not include insect fragments, rodent hairs and other extraneous matter.”
Food Processing

- Food processing can be considered as a set of practices –using defined technologies and techniques, or unit operation, either individually or in combination, manipulating mass, energy and information- to transform raw food material into the more useful forms.

- Basic unit operations: size reduction, mixing, drying, curing, heating, cooling, freezing, smoking, fermentation, irradiation, Etc.

Food Processing

- Food processing can be considered as a set of practices –using defined technologies and techniques, or unit operation, either individually or in combination, manipulating mass, energy and information- to transform raw food material into the more useful forms.

1. Ensure safety
2. Extend shelf life
3. Maintain or improve sensory properties
   – taste, color, texture
4. Maintain or improve nutritive properties
5. Consistent quality.
6. Provide conveniences
7. Etc. … “other added value”
Food Processing

• The most used food processing: **Heat-treatment**
  • Frying, baking, grilling, toasting, roasting, microwaving, and broiling.
  • Complex chemical changes/reactions → formation of new compounds:
    • Desirable flavors, colors, aromas and textures
    • Undesirable compounds with adverse physiological effects or potential health risks.

Food Processing Contaminants?

• Methods of detection, identification and quantification become available and more sensitive → emerging hazards.
Food Processing Contaminants?
[Also known as; Food Processing Toxicants]

- Methods of detection, identification and quantification become available and more sensitive → emerging hazards.

- Processing toxicants are defined as those substances present in food as a result of food processing/preparation that are considered to exert adverse physiological (toxicological) effects in humans, i.e., substances that create a potential of real risk to human health.

Recent food processing contaminants (FPCs) -as undesirable by-products of thermal treatment- are:

- MCPD (1980)
- Acrylamide (2002)
- Furan (2006)
Recent food processing contaminants (FPCs) -as undesirable by-products of thermal treatment- are:

- MCPD (1980)
- Acrylamide (2002)
- Furan (2006)

Presence of FPCs in food → unavoidable.

Case of “Irreducible level” → unavoidable.

Hariyadi, P. 2017. **Update on Food Processing Contaminants.**
Presented at SEAFAST International Seminar “Current and emerging issues of Food Safety: Innovation Challenges”
**Bogor 20-21 November 2017**
Food Processing Contaminants?
How to manage Risk of FPCs?

ALARA?
• As Low as Reasonably Achievable
• Case of “Irreducible level”
  → that concentration of a substance (hazard) which cannot be eliminated from a food without involving the discarding of that food altogether, severely compromising the ultimate availability of food supplies

Case of “Irreducible level” → unavoidable.

Food Processing Contaminants?
How to manage Risk of FPCs?

ALARA?
• As Low as Reasonably Achievable
• Case of “Irreducible level”
  → The phrase refers to a principle of keeping hazards in food as low as can be achieved, based on technologic and economic considerations
  → f=(BAT : Best Available Technology)

Case of “Irreducible level” → unavoidable.
Food Processing Contaminants?
How to manage Risk of FPCs?

**ALARA?**

<table>
<thead>
<tr>
<th>Level of risk</th>
<th>Sanitary measures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intolerable (&quot;unacceptable&quot;)</td>
<td>Prohibitions and constraints</td>
</tr>
<tr>
<td>Tolerable (&quot;acceptable&quot;)</td>
<td>Optimisation (Reduce risk to that &quot;as low as reasonably achievable&quot;)</td>
</tr>
<tr>
<td>Negligible</td>
<td>No change</td>
</tr>
</tbody>
</table>

Case of “Irreducible level” → unavoidable.

= f(ALOP)
= f(BAT)

CoP: describe and disseminate best practice for the manufacture, for the reduction of hazard level.

Case of “Irreducible level” → unavoidable.

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**Food Processing Contaminants**  
**How to manage Risk of FPCs?**

**ALARA?**
- A voluntary action by country/the food industry: monitored by introducing a minimization concept that measures progress over time.
- Need commitment of country/food industry to investigating all avenues of reduction and will continue to actively share progress → revision of CoP.
- Science-based, open & transparent

**CoP:** describe and disseminate best practice for the manufacture, for the reduction of hazard level.

**Case of “Irreducible level” → unavoidable.**

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**Food Processing Contaminants?**  
**How to manage Risk of FPCs?**

**ALARA?**
- Knowledge is key

**CoP:** describe and disseminate best practice for the manufacture, for the reduction of hazard level.

**Case of “Irreducible level” → unavoidable.**

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Food Processing Contaminants?

How to manage Risk of FPCs?

Preventive strategies
- Ingredient substitution
- Addition of inhibiting or competing ingredients
- Thermal input reduction
- Incorporation of potential precursors
- Creation of unfavourable environmental conditions

Removal strategies
- Formulation
- Processing
- Post-processing
- Physical removal
- Ionizing radiation
- Cooking/warming in open vessel
- Fermentation

General ALARA Strategies

Cases of Acrylamide and MCPD Ester as illustration

General ALARA Strategies

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Acrylamide

- The Swedish National Food Authority and the University of Stockholm (2002):
  - Preliminary findings of acrylamide occurrence in fried and baked foods, notably in the µg/kg to low mg/kg range.
  - Acrylamide is an industrial chemical with well known neurotoxic properties and is classified as a “probable human carcinogen”.
  - Widespread occurrence in many different foods that are consumed daily, including dietary staples such as potatoes, cereals and their products (e.g. French fries, potato crisps, bread, crisp bread, bakery wares) and coffee.

- Mechanism:

\[
\text{Reducing sugar} + \text{Asparagine} \rightarrow \text{Schiff's base} \rightarrow \text{Acrylamide}
\]
Acrylamide

How to manage risk of Acrylamide?

- Knowledge of Critical Factors :
  
  • Free asparagine
  • Free reducing sugar (e.g. glucose, fructose)
  • Low water activity
  • Product temperature > 120°C

Acrylamide

How to manage risk of Acrylamide?

- Knowledge of Critical Factors :
  
  • Asparagin content of wheat flours are widely varies
  • 26 wheat flour samples from France, Poland, UK, Belgium, Finland, Czech Rep. and Italy (2002 Harvest) :

<table>
<thead>
<tr>
<th>Asparagine</th>
<th>Median</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/100 g</td>
<td>7.9</td>
<td>3.0</td>
<td>21.9</td>
</tr>
</tbody>
</table>
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Acrylamide

How to manage risk of Acrylamide?

CIAA. Acrylamide in Biscuits & Cripbread, Geoff Thompson (2011)

Acrylamide

How to manage risk of Acrylamide?


Acrylamide

How to manage risk of Acrylamide?

REDUCE ACRYLAMIDE
GO FOR GOLD
Aim for a golden colour, rather than dark brown, when frying, baking, roasting or toasting.

CODE OF PRACTICE FOR THE REDUCTION OF ACRYLAMIDE IN FOODS
CAC/RCP 67-2009

INTRODUCTION

1. Recent concern over the presence of acrylamide in food dates from 2002. Swedish scientists reported that up to “mg/kg” quantities of acrylamide could be formed in carbohydrate-rich foods during high-temperature cooking, e.g. during frying, baking, roasting, toasting and grilling. These findings were rapidly confirmed by other researchers; subsequently, major international efforts have been mounted to investigate the principal sources of dietary exposure, assess the associated health risks and develop risk management strategies. Details of these global research initiatives are provided on the WHO/FAO Acrylamide Information Network (http://www.acrylamide-food.org/) and the “Acrylamide Information Base” http://ec.europa.eu/food/food/chemicalsafety/contaminants/acryl_database_en.htm. There has also been work on acrylamide mitigation studies which are reported in English in the CIAA Acrylamide Tool Box and at http://ec.europa.eu/food/food/chemicalsafety/contaminants/acrylamide_en.htm and http://www.ciaa.be/asp/documents/brochures_form.asp?doc_id=65.

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Acrylamide

How to manage risk of Acrylamide?

CODE OF PRACTICE FOR THE REDUCTION OF ACRYLAMIDE IN FOODS

SCOPE

4. This Code of Practice intends to provide national and local authorities, manufacturers and other relevant bodies with guidance to prevent and reduce formation of acrylamide in potato products and cereal products. The guidance covers three strategies (where information is available) for reducing acrylamide formation in particular products:

i) Raw materials;
ii) Control / addition of other ingredients; and
iii) Food processing and heating.

• The CIAA (Confederation of the Food and Drink Industries of the EU) created a Technical Expert Group → Toolbox.

• Responsible food operators should consider the minimization of acrylamide, by defining and controlling:
  (i) agronomic/raw material
  (ii) recipe design
  (iii) process design, and
  (iv) guidance for finished product preparation.

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**Acrylamide**

**How to manage risk of Acrylamide?**

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Recipe</th>
<th>Process design</th>
<th>Final Preparation</th>
</tr>
</thead>
</table>
| Potato products | • Potato storage temperature  
• Amount of reducing sugars  
• Tuber maturity | • Amino acid or calcium salt addition  
• Lowering pH | • In-line control (elimination of dark crisps)  
• On-pack instructions  
• Color endpoint |
| Bread/ Biscuit/ Bakery wares | • Replacement (or reduction) of NH4CO3  
• Replacement of fructose  
• Use of Ca+ salts | • Pre-treatment (e.g. asparaginase, bleaching)  
• Thermal input (e.g. vacuum frying) | • Follow on-pack instructions  
• Color endpoint |
| Coffee/ Chicory | • Coffee bean maturity  
• Chicory beverage mixtures: Lower the portion of chicory | • Thermal input (roasting time and temperature, but impacts organoleptic quality) | }

Table 1: Selected acrylamide mitigation options tested at pilot or industrial scale. * For certain hard dough biscuit / cereal applications and dough-based potato products

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**3-MCPD**

**How to manage risk of 3-MCPD in Acid-HVPs?**

1978-1980 Hydrolysed vegetable protein, e.g soy sauce (free)

The European Commission’s **Scientific Committee on Food** (SCF, 1994): long-term carcinogenicity assay of 3-MCPD in rats.

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3-MCPD
How to manage risk of 3-MCPD in Acid-HVPs?

3-MCPD was classified by the European SCF as a non-genotoxic, threshold carcinogen (SCF, 2001)

1994
2001

3-MCPD
How to manage risk of 3-MCPD in Acid-HVPs?

- 3-MCPD → results from hydrochloric acid hydrolysis of vegetable protein and mainly occurred in soy sauce.
- Provisional maximum TDI (PMTDI*) : 2 ug/kg bw per day
  → Lowest observed effect level (LOEL): 1.1 mg/kg bw per day
    [for renal tubular hyperplasia and a safety factor of 500].
  → Estimated mean intake of 3-MCPD by consumers of soy sauce would be at or above the PMTDI.

1994
2001
2002

*) PMTDI: Provisional Maximum Tolerable Daily Intake, a recommended maximum tolerable level of a toxic compound.
3-MCPD
How to manage risk of 3-MCPD in Acid-HVPs?

2006:

• JECFA re-evaluated chloropropanols in June 2006 and decided to retain the previously established PMTDI.
• JECFA: reduction in the concentration of 3-MCPD in soy sauce and related products made with acid-HVP could substantially reduce the intake of this contaminant by consumers of these condiments.

3-MCPD
How to manage risk of 3-MCPD in Acid-HVPs?

CODE OF PRACTICE FOR THE REDUCTION OF 3-MONOCHLOROPROPA-1,2-DIOL (3-MCPD) DURING THE PRODUCTION OF ACID-HVPs AND PRODUCTS THAT CONTAIN ACID-HVPs

CAC/RCP 64-2008

INTRODUCTION
1. 3-Monochloropropane-1,2-diol (3-MCPD) is one of a series of compounds referred to as chloropropanols. These compounds are contaminants that are formed during the processing and manufacture of certain foods and ingredients. They were originally discovered in acid hydrolysed vegetable protein (acid-HVP) in the 1980s. Subsequent research in the 1990s revealed their presence in soy sauces manufactured using acid-HVP as an ingredient.

3-MCPD
How to manage risk of 3-MCPD in Acid-HVPs?

CODE OF PRACTICE FOR THE REDUCTION OF
3-MONOCHLOROPROPAINE-1,2-DIOL (3-MCPD)
DURING THE PRODUCTION OF ACID-HVPs
AND PRODUCTS THAT CONTAIN ACID-HVPs

SCOPE

11. The purpose of this Code of Practice is to describe and disseminate best practice for the manufacture of acid-HVP and soy sauces and related condiments, whose production involves acid hydrolysis, with the aim of facilitating a reduction in the levels of 3-MCPD. Food ingredients produced using methods that do not involve acid hydrolysis of vegetable proteins are not covered by this Code of Practice.

3-MCPD Esters?

3-MCPD esters were first detected in refined vegetable oils (2004-2006).

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3-MCPD Esters?

(2007) BfR

Infant formula and follow-up formula may contain harmful 3-MCPD fatty acid esters


3-MCPD Esters?

(2007) BfR

tubules in humans has not been described. The latest studies by the official food control authorities identified high levels of 3-MCPD fatty acid esters for the first time in refined edible fats like margarine and oil and in fat-containing foods including infant formula and follow-up formula. BfR has evaluated the data submitted by the food control authorities. It has come to the conclusion that - based on the scientific knowledge currently available - babies in particular may ingest amounts of 3-MCPD esters from infant formula and follow-up formula for which, in the worst case scenario, the margin of safety to the effects observed in animal experiments is deemed to be too small. BfR, therefore, believes there is a need for action to reduce the levels but does not see any acute health risk.
Conclusions: levels of 3-MCPD should be reduced, especially in infant formula and follow-up formula, although no acute danger was expected from current levels.

BfR assumed a “worst-case scenario” that 100% of 3-MCPD esters are cleaved to release free 3-MCPD during digestion.

- The CONTAM Panel confirmed the assessment of BfR (2007) → the need for additional toxicokinetic studies → EFSA
3-MCPD Esters?

ILSI Europe Workshop in 2009

- Although there is a lack of data about 3-MCPD esters for many foodstuffs, it is obvious that thermally processed foods and refined fats and oils (as such or as a component of other foodstuffs) are the most significant sources of 3-MCPD esters for consumers.
- In particular, refined palm oil in different kinds of foodstuffs is responsible for a significant part of the exposure.

3-MCPD Esters?

Codex Committee on Contaminants in Foods (CCCF)

- included 3-MCPD fatty acid esters in the priority list for evaluation by JECFA for toxicological assessment and exposure assessment.
• **BfR opinion**: established a TDI of 2 ug/kg bw per day.

3-MCPD Esters?

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**ILSI Europe**

**MCPD AND GLYCIDYL ESTERS IN FOOD PRODUCTS**

SUMMARY REPORT OF A WORKSHOP HELD IN NOVEMBER 2011

(Published: 2012)

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3-MCPD Esters?

From a limited database of occurrence, the adult exposure to 3-MCPD, assuming complete cleavage of the esters in the gut, could be estimated as 1–9.8 μg/kg bodyweight 3-MCPD/day, which is between 0.5 and 5 times the PMTDI of 3-MCPD. For infants on a diet of infant formula the estimated exposure was 7.3–25 μg/kg bodyweight 3-MCPD/day which is 3.6–7.7 times the PMTDI (Lampen, 2009).

3-MCPD & Glycidyl Esters?

Address issues related to 3-MCPD esters and related compounds:
→ 2-MCPD esters and glycidyl esters

IARC (International Agency for Research on Cancer): there was no evidence to suggest that 3-MCPD is NOT genotoxic.
3-MCPD & Glycidyl Esters?

**Abstract**
EFSA was asked to deliver a scientific opinion on free and esterified 3- and 2-monochloropropane-1, 2-diol (MCPD) and glycidol esters in food. Ester(s) of 3- and 2-MCPD and glycidol are contaminants of processed vegetable oils; free MCPDs are formed in some processed foods. The Panel on Contaminants in the Food Chain (CONTAM Panel) evaluated 7,175 occurrence data. Ester(s) of 3- and 2-MCPD and glycidyl esters were found at the highest levels in palm oil, but most vegetable oil/fats contain substantial quantities. Mean middle bound (MB) dietary exposure values to total 3-MCPD, 2-MCPD and glycidol, respectively, across surveys and age groups in μg/kg body weight (bw) per day were 0.2-1.5, 0.1-0.7 and 0.1-0.9; high exposure (HP) values were 0.3-2.6, 0.2-1.2 and 0.2-2.1. Animal studies show extensive hydrolysis of esterified 3-MCPD and glycidol following oral administration; esterified and free forms were assumed to contribute equally to internal exposures. Nephrotoxicity was consistently observed in rats treated with 3-MCPD. Data on 2-MCPD toxicity were insufficient for dose-response assessments. Chronic treatment with glycidol increased the incidence of tumours in several tissues of rats and mice. Test via a germinotrop mode of action. The Panel selected a BMDL$_{01}$ value for 3-MCPD of 0.077 mg/kg bw per day for induction of renal tubular hyperplasia in rats and derived a tolerable daily intake (TDI) of 0.8 μg/kg bw per day. The mean exposure to 3-MCPD was above the TDI for ‘Infants’, ‘Toddlers’ and ‘Other children’. For glycidol, the Panel selected a TDI value of 10.2 μg/kg bw per day for neoplastic effects in rats. The margins of exposure (MoEs) were 11,393-102,000 and 4,960-51,000 across surveys and age groups at mean and HPs exposures, respectively. An exposure scenario for infants receiving formula only resulted in MoEs of 5,560 (mean) and 2,100 (HP). MoEs of 25,000 or higher were considered of low health concern.

**3-MCPD & Glycidyl Esters?**

- Esters of 3- and 2-MCPD and glycidyl esters were found at the highest levels in palm oil/fat, but most vegetable oil/fats contain substantial quantities.
- Animal studies show extensive hydrolysis of esterified 3-MCPD and glycidol following oral administration; esterified and free forms were assumed to contribute equally to internal exposures.
- 3-MCPD ester and free forms are nephrotoxic.
- Tolerable daily intake (TDI) of 0.8 μg/kg bw per day.
- The mean exposure to 3-MCPD was above the TDI for ‘Infants’, ‘Toddlers’ and ‘Other children’.

3-MCPD & Glycidyl Esters?

Experimental evidence indicates that 3-MCPD esters are substantially hydrolysed to 3-MCPD in the gastrointestinal tract and elicit toxicity as free 3-MCPD. The Committee therefore based its evaluation on the conservative assumption of complete hydrolysis of 3-MCPD esters to 3-MCPD. Whereas the experimental data supporting substantial hydrolysis are derived from studies with post-weaning animals, the Committee concluded that the capacity of the neonate to hydrolyse fatty acids in the gut is efficient, and therefore the same assumption of substantial hydrolysis could be extended to this age group.

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3-MCPD & Glycidyl Esters?

JECFA/83/SC

3-Monochloro-1,2-propanediol (3-MCPD) esters are processing-induced contaminants found in various refined oils and fats and are formed from acyglycerols in the presence of chlorinated compounds during deodorization at high temperature. "3-MCPD esters" is a general term for 3-MCPD esterified with one (sn1- and sn2-monoesters) or two identical or different fatty acids (diesters). Depending on the fatty acid composition of the oil or fat, a variety of different 3-MCPD esters can be formed during processing. In foods that contain refined vegetable oils or fats, mainly diesters are found. Concentrations of 3-MCPD esters in refined oils increase incrementally in the following order: rapeseed oil < soya bean oil < sunflower oil < safflower oil < walnut oil < palm oil.

REP17/CF (APPENDIX X)

Project Document

Proposal for new work on a Code of Practice for the reduction of 3-monochloropropane-1,2-diol esters and glycidyl esters in refined oils and products made with refined oils, especially infant formula

1. The purpose and scope of the project

The purpose of the proposed new work is to develop a Code of Practice (COP) for the reduction of 3-monochloropropane-1,2-diol esters (3-MCPDE) and glycidyl esters (GE) in refined edible oils and products containing refined oils or products made with these oils, especially infant formula, in light of the conclusions of the Joint FAO/WHO Expert Committee on Food Additives (JECFA). In the Summary and Conclusions of its 83rd Session (November 2016), JECFA stated that (1) formula-fed infants can exceed the provisional maximum tolerable daily intake (PMTDI) for 3-MCPDE and (2) the margins of exposure (MOE) for GE for infants, children, and adults may be a health concern. The scope of the new work encompasses measures applicable to agricultural practices, oil milling and refining processes, and sources and uses of the refined oils in products made from these oils, especially infant formula.

3-MCPD & Glycidyl Esters?

**REP17/CF (APPENDIX X)**

**PROJECT DOCUMENT**

Proposal for new work on a Code of Practice for the Reduction of 3-monochloropropene-1,2-diol esters and glycidyl esters in refined oils and products made with refined oils, especially infant formula

1. The purpose and scope of the project

3. Main aspects to be covered

The COP will address measures, supported by scientific data, to reduce 3-MCPDE and GE in refined oils. Although 3-MCPDE and GE are produced primarily during deodorization, measures applicable to agricultural practices (e.g. harvesting and storage of fruit), oil milling and refining processes (e.g., fruit selection and processing, degumming/bleaching, deodorization) and sources and uses of the refined oils, including in other products, especially infant formula (e.g. oil selection, processing modifications), will be addressed.

9. The proposed timeline for completion of the new work, including the starting date, proposed date for adoption at Step 5 and the proposed data for adoption by the Commission

Work on the COP will commence following approval by the Codex Alimentarius Commission in July 2017. Final adoption by the Commission can be expected by 2020.
3-MCPD & Glycidyl Esters?

• Need a multifaceted approach:
  • beginning with a reduction of chloride application in fertilizer, continuing with the use of plant varieties low in MAG and DAG precursors, the selection of young fruit of good quality and technical changes to the refining steps, and ending with the removal of the esters using inorganic adsorbents.

Integrated R&D - on farm → off farm
### 3-MCPD & Glycidyl Esters?

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Structure</th>
<th>Source</th>
<th>Possible Mitigation Strategies</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-MCPD Esters</td>
<td>Monoesters</td>
<td>Formed during deodorization (beginning at 140°C) when DAGs or MAGs undergo chloride substitution</td>
<td>• Reduce DAG levels in crude oil by changing harvesting practices or using enzymatic treatment. &lt;br&gt;• Wash raw oils to remove chloride precursors. &lt;br&gt;• If possible, use chemical rather than physical refining. &lt;br&gt;• Use neutral rather than activated bleaching earth to minimize chloride ions. &lt;br&gt;• Remove 3-MCPD esters from refined oil with adsorbents.</td>
</tr>
<tr>
<td></td>
<td>Diesters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycidyl Esters</td>
<td></td>
<td>Formed during deodorization (beginning at 230°C) from DAGs by radical mechanism</td>
<td>• Reduce DAG levels in crude oil by changing harvesting practices or using enzymatic treatment. &lt;br&gt;• If possible, use chemical rather than physical refining. &lt;br&gt;• Minimize deodorization temperatures or use two-step deodorization. &lt;br&gt;• Remove glycidyl esters from refined oil with absorbents or by acid-catalyzed degradation.</td>
</tr>
</tbody>
</table>
3-MCPD & Glycidyl Esters?

<table>
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| 3-MCPD Esters | Monoesters Diesters | Formed during deodorization (beginning at 140°C) when DAGs or MAGs undergo chloride substitution | • Reduce DAG levels in crude oil by changing harvesting practices or using enzymatic treatment.  
• Wash raw oils to remove chlorine precursors.  
• If possible, use chemical rather than physical refining.  
• Use neutral rather than activated bleaching earth to minimize chloride ions.  
• Remove 3-MCPD esters from refined oil with adsorbents. |
| Glycidyl Esters |          | Formed during deodorization (beginning at 230°C) from DAGs by radical mechanism | • Reduce DAG levels in crude oil by changing harvesting practices or using enzymatic treatment.  
• If possible, use chemical rather than physical refining.  
• Minimize deodorization temperatures or use two-step deodorization. |

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Conclusion: How to manage Risk of FPCs?

General ALARA Strategies

Conclusion: How to manage Risk of FPCs?

General ALARA Strategies

Thank you
Terimakasih

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