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JOINT OFFICE: Viale delle Terme di Caracalla 00153 ROME Tel: 39 06 57051 www.codexalimentarius.net Email: codex@fao.org Facsimile: 39 06 5705 4593

**Agenda Item 13**

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## **JOINT FAO/WHO FOOD STANDARDS PROGRAMME CODEX COMMITTEE ON CONTAMINANTS IN FOODS**

**First Session**

**Beijing, China, 16 - 20 April 2007**

### **PROPOSED DRAFT CODE OF PRACTICE FOR THE REDUCTION OF CONTAMINATION OF FOOD WITH POLYCYCLIC AROMATIC HYDROCARBONS (PAH) FROM SMOKING AND DIRECT DRYING PROCESSES**

(N07-2006)

(At Step 3 of the Elaboration Procedure)

Governments and international organizations are invited to submit comments on the following subject matters no later than 15 March 2007, preferably in electronic format, for the attention of Ms. Tanja Åkesson, the Netherlands Secretariat of the Codex Committee on Contaminants in Foods, Fax No.:+31 70 3786141; E-mail:info@codexalimentarius.nl with a copy to the Secretary, Codex Alimentarius Commission, Joint FAO/WHO Food Standards Programme, Viale delle Terme di Caracalla, 00153 Rome, Italy (Fax +39.06.5705.4593; E-mail: Codex@fao.org).

#### **BACKGROUND**

1. The Codex Committee on Food Additives and Contaminants, at its 38<sup>th</sup> Session, agreed to start new work to elaborate a proposed draft code of practice for the reduction of contamination of food with Polycyclic Aromatic Hydrocarbons (PAH) from smoking and direct drying processes and agreed to establish an electronic working group for preparing an initial draft, for circulation, comments at Step 3 and consideration at Step 4 at the First Session of the Codex Committee on Contaminants in Foods (ALINORM 06/29/12 para. 188).
2. The 29th Session of the Codex Alimentarius Commission approved the elaboration of a Code of Practice for the Reduction of Contamination of Food with Polycyclic Aromatic Hydrocarbons (PAH) from Smoking and Direct Drying Processes (N07-2006) as new work for the Committee (see ALINORM 06/29/41, para.124 and Appendix VIII).
3. The Codex Committee on Contaminants in Foods, at its First Session, is invited to discuss the Proposed Draft Code of Practice for the Reduction of Contamination of Foods with Polycyclic Aromatic Hydrocarbons (PAH) from Smoking and Direct Drying Processes as presented in ANNEX to this document. The Committee is also invited to draw its attention to the report of the electronic working group as presented in paras 4 – 12 of this document.

**REPORT OF THE ELECTRONIC WORKING GROUP**

4. As agreed by the Codex Committee on Food Additives and Contaminants, at its 38th Session, the electronic working group, led by Denmark, prepared the Proposed Draft Code of Practice for the Reduction of Contamination of Foods with Polycyclic Aromatic Hydrocarbons (PAH) from Smoking and Direct Drying Processes. The electronic working group includes Australia, Belgium, Cuba, European Community, Ghana, India, Japan, Thailand the Philippines, Poland, Spain, United Kingdom, the United States of America, IFT and INC.

5. At the thirty-sixth session of the Codex Committee on Food Additives and Contaminants (CCFAC), the Delegation of Denmark offered to develop a Code of Practice for reduction of the contamination of food with polycyclic aromatic hydrocarbons (PAH) during food processing. In noting that these substances would be evaluated by Joint Expert Committee on Food Additives (JECFA) in 2005, the Committee considered it premature to start elaboration of a Code of Practice (COP) and agreed to develop a discussion paper to set out the issues concerning PAH in foods for the 37th session of the CCFAC (ALINORM 04/27/12, para. 217).

6. JECFA assessed PAH at its sixty-fourth meeting in February 2005 and concluded that the critical effect of PAH is carcinogenicity and as some PAH are genotoxic. It was not possible to assume a threshold mechanism or to establish a provisional tolerable weekly intake (PTWI). The Committee concluded that the estimated intakes of PAH were of low concern for human health in the case of normal dietary intake, but stated that efforts should be made to reduce contamination with PAH during drying and smoking processes (WHO 2006).

7. At its 37th Session, the CCFAC agreed to establish a working group to revise the Discussion Paper and develop an outline for a COP and a project document for submission to the Codex Alimentarius Commission (CAC). At its 38th Session, the CCFAC agreed to recommend to CAC that the Committee starting up new work on a COP for the reduction of PAH in food and limit its scope to general advice addressing the processes:

- a. Smoking and
- b. Direct drying.

8. Many chemical contaminants are formed during the combustion of fuel. Examples include PAH, dioxins, formaldehyde and nitrogen and sulfur oxides. Furthermore, heavy metals are also found in combustion gasses. The types and amount depend on the fuel used, the temperature and possible other parameters (Nielsen and Illerup, 2003). These contaminants can be food safety problems either as such or due to the reaction of e.g., nitrogen oxide with components in the food leading to the formation of nitrosamines.

9. This COP covers PAH only. However, the possible interplay among levels of contaminants like PAH, heterocyclic amines, and nitrosamines is not always well understood, and it should be emphasized that conditions that lead to a reduction of one contaminant might lead to increases in the levels of other contaminants or could lower the microbiological standard of the products. It should be underlined that any guidance given to minimize PAH should not lead to increase in other contaminants like nitrosamines.

10. This COP is being developed as a means of disseminating strategies that will facilitate the reduction of PAH in internationally traded foodstuffs. The COP discusses those established minimization techniques that have been demonstrated to be effective according to literature and in a commercial setting.

11. The focus of this COP is solely on foods produced by smoking or direct drying processes. It describes some critical elements in Good Manufacturing Practices and how evaluation of the potential contamination of the food with PAH coupled with the choice of processes could reduce the formation of PAH.

12. This COP is intended to provide tools to optimise smoking and drying processes in order to reduce or eliminate PAH in the final foodstuffs. The COP must recognise the benefits of smoking and drying including the availability of traditional smoked food products, prevention of degradation and microbiological contamination and growth and the potential for lowering the risks to human health from PAH formed in foods during processing.

## ANNEX

**PROPOSED DRAFT CODE OF PRACTICE FOR THE REDUCTION OF CONTAMINATION OF FOOD WITH POLYCYCLIC AROMATIC HYDROCARBONS (PAH) FROM SMOKING AND DIRECT DRYING PROCESSES****INTRODUCTION**

1. PAH constitute a large class of organic compounds<sup>1</sup> containing two or more fused aromatic rings made up of carbon and hydrogen atoms. Hundreds of individual PAH may be formed and released as a result of incomplete combustion or pyrolysis of organic matter, during industrial processes or other human activities, including the processing and preparation of food and the carbonization of wood to make charcoal (WHO, 2006).
2. PAH are chemical contaminants<sup>2</sup>, which can be found in food. Sources of PAH are contamination during food processing or from the environment. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) conducted a comprehensive risk assessment of PAH in 2005 (WHO 2006). JECFA recommended keeping the content of these contaminants in food as low as reasonable achievable. Toxicological information is included in Annex II.
3. The PAH content of thermally treated food differs depending of the processes used and how they are conducted. Occurrence data from the JECFA monograph (WHO 2006) and the EU SCOOP report (European Commission, 2004) and some national studies are found in Annex III.
4. From the data reviewed by the EU Scientific Committee on Food (now the European Food Safety Authority), cereals, vegetables, fats and oils were the major contributors to PAH in the diet, with grilled/smoked /barbequed fish and meat making a relatively low contribution except in cultures where they are a significant part of the diet (European Commission, 2002).
5. As drying processes could be a potential source of PAH in cereals and oil seeds, there is also a need to control the levels of PAH in agriculture crops post-harvest, with particular reference to the source of contamination, as these crops can have a major impact on PAH intake from food.
6. Contamination of food with PAH via environmental contamination is not included in the COP. This contamination should be controlled either by source-directed measures like filtering the smoke from relevant industries (e.g., cement work, incinerator and metallurgy) and limiting the exhaust of PAH from cars. Good agricultural practices (GAPs), when growing crops and when selecting appropriate farmland, could also decrease the environmental contamination of foods with PAH, together with not harvesting shellfish from contaminated water.

**PREVENTIVE MEASURES AND GENERAL CONDITIONS IN GOOD MANUFACTURING PROCESSING OF FOOD.**

7. The food producer should carry out a hazard analysis of the critical points in processes used or intended to be used in food production. The analysis should take into account whether alternative processes could be used to produce the desired result.
8. The hazard analysis should include assessment of the potential formation of process contaminants such as PAH during the process and should address the following points:
  - ⇒ Possible sources of contaminants such as PAH
  - ⇒ Possible formation of contaminants during the process
  - ⇒ Possible effects on consumer health
  - ⇒ Controllability
  - ⇒ Feasibility and effectiveness of controls (cost, commercial availability, occupational hazards)

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<sup>1</sup> A list of PAH included in the JECFA assessment is found in Annex I.

<sup>2</sup> *Contaminant* is defined as “Any substance not intentionally added to food, which is present in such food 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 as a result of environmental contamination. The term does not include insect fragments, rodent hairs and other extraneous matter.” (Codex Alimentarius, Procedural Manual, 14<sup>th</sup> edition 2004).

9. Other factors may also legitimately be considered, such as
- ⇒ Required organoleptic properties of the final food product
  - ⇒ Effects of the processes on organoleptic properties and quality of the product (the ideal method would have no adverse effects on the appearance, odour, taste or nutritional properties of the product.)
  - ⇒ Consumer perception and choice,
10. Considerations should be made as to which process should be used and whether a less contaminating process is available.
11. The effect of any process options on the microbiological status of the food product should also be taken into account.

#### **SCOPE OF CODE OF PRACTICE.**

12. As well as being present in the raw materials, PAH may be formed during food processing in both commercial and domestic food preparation, notably:
- Smoking,
  - Drying,
  - Cooking (Roasting, baking, frying, grilling and barbecuing).
13. The scope of this Code of Practice (COP) is limited to contamination of food with PAH during commercial smoking and direct drying processes.
14. The COP does not cover PAH in food originating from
- a. Use of herbs and spices in the smoking process.
  - b. Other food processes, including cooking in private homes or the catering sector
  - c. Environmental contamination
  - d. Drinking water<sup>3</sup>

#### **EVALUATION OF COMPLIANCE WITH RELEVANT LEGISLATION**

15. Processed food shall be in compliance with relevant national or international legislation and standards, including general requirements for consumer protection.

#### **PAH CONTAMINATION OF FOOD DURING SMOKING AND DRYING PROCESSES, GENERAL REMARKS.**

16. The formation of PAH during smoking and drying is dependent on a number of variables, including
- Fuel (woods, diesel, gases, liquid/solid waste and other fuels)
  - Cooking method (smoking or drying - direct or indirect)
  - The distance between the food and the heat source
  - Position of the food in relation to the heat source
  - Fat content of the food and what happens to it
  - Time for processing
  - Temperature during processing
  - Cleanliness and maintenance of equipment.
17. Changes to cooking or processing techniques can reduce the amount of PAH formed in foods. Alteration could be done in different ways, e.g. by using indirect drying or smoking processes; via the selection of fuel for drying or of wood species in the smoking process; and by adjusting times and processing temperatures. In such cases, it is important to consider potential organoleptic changes in the final food.

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<sup>3</sup> *Drinking water* is water, that meets the quality standards of drinking water described in the WHO Guidelines for Drinking Water quality.

## SMOKING AND DRYING PROCESSES, GENERAL REMARKS

18. Traditional processes such as smoking and direct drying provide a wide variety of food textures and flavours and consequently a broader choice for consumers. Many types of smoked and dried foods are highly esteemed traditional food items, where these types of processes have been used to prolong storage times and quality and provide flavour and consistency required by consumers. The extension of shelf life may also have an effect on the nutritional value of foodstuffs, such as the vitamin content.
19. Fuel used will have impact on the potential contaminants of the food, e.g., the PAH contamination of food differs if woods or straw is used (Nielsen and Illerup, 2003).

## SMOKING PROCESS

20. Direct smoking is the traditional type of smoking process where the smoke is developed in the same chamber in which the food is processed; indirect smoking uses smoke generators, with the smoke being developed in a separate chamber and possibly cleaned in various ways before being fed into the smoking chamber. Direct smoking requires less equipment than indirect smoking but can result in higher levels of PAH in the product.
21. Foodstuffs such as meat and fish and some types of cheese have been smoked in many countries for centuries. Originally the purpose was to preserve the food, partly by reducing the moisture content and partly through the transfer of anti-microbiological components such as phenols from the smoke to the food.
22. Smoking is now primarily used to achieve the characteristic taste and appearance of smoked food, with preservation playing a minor role. Nevertheless, smoking can still influence the shelf life of food because components of the smoke may inhibit growth of some microorganisms.
23. In traditional smoking, the main fuel used is various wood species, in some case with herbs and spices, e.g. juniper berries, to give a characteristic flavour. Such herbs and spices may be a potential source for PAH contamination but their use is not considered in this Code of Practice.
24. Woods consists of three main components: cellulose, hemicellulose and lignin (Andersen and Rissum, 1994).
25. Smoke is produced by pyrolysis of the fuel at temperatures of around 300-450°C in the glow zone. The composition of the smoke depends, among other things, on the type and age of wood used, its water content, the amount of oxygen present and the length of time for which it is burned.
26. Smoke consists of liquid and solid particulates suspended in a gaseous phase. Particles in the smoke, generally of a size of 0.2-0.4 µm, are estimated to constitute 90% of its overall weight. The chemical composition of smoke is complex and more than 300 components have been identified (Möhler, K, 1978; Solttes and Elder, 1981; Simko, P, 2005).
27. The main groups of chemicals in the smoke are phenolic and carbonylic compounds, acids, PAH and nitrogen oxides and their reaction products. Some examples of components found to be contributing to the smoke flavour are: phenol, phenolaldehydes, pentenone, vinyl guajacol and alcyphenols of the guajacol type. (Solttes, E.J and Elder, T.J., 1981).
28. The traditional smoking processes are often divided into three group after the temperatures used in the smoke chamber during processes:
  - *Cold* smoking with temperature 18-25 °C. Used for e.g., smoked salmon and salamitype sausages
  - *Semi-warm* with temperatures around 40°C. Used for e.g. bacon and pork loin
  - *Warm* smoking is smoking combined with heating resulting in a temperature of 70-90°C. Used for e.g. herrings, eel and frankfurter type sausages.
29. The organoleptic properties of the final products will differ and changes of the methods might not necessary result in the requested products.

30. Differences in the smoking processes can lead to highly variable PAH levels in the final food product (European Commission, 2002). Factors that influence this variability include
- The type and composition of wood used to smoke foods,
  - The use of other fuels
  - Whether smoking is direct or indirect,
  - Use of a washing/water cooling procedure after the smoking process,
  - The type of generator used,
  - The accessibility of oxygen
  - Temperature, and
  - Smoking time.

The scientific background and data to illustrate the exact influence of the use of different types of fuel, time, temperature etc. is limited and specific testing is needed in the hazard analysis of the individual processes.

31. The different variables in the processes used should be assessed in relation to a hazard analysis of the parameters critical for potential formation of PAH in a specific process used.

### **COP FOR PRODUCTION OF SMOKED FOOD**

32. The choice of technology for processing is very important for the final concentration of PAH.

#### *Fuel*

33. It is recommended to use hardwoods as fuel for smoking of foods. Hard woods can be used in form of chips or sawdust.
34. Maga et al (1986) reported that the use of the soft wood species: mesquite wood resulted in increased levels of benzo[a]pyrene compared to the use of hard wood and charcoal. Maga, 1988 proposed to use hard woods instead of soft woods to reduce the PAH content. However, limited investigations are conducted and they are not in total agreement (Guillén et al., 2000).
35. The conclusion is that the wood species have an influence, in general. However, it has not been possible to find references to recommend the use of more specific wood species and recommendation is, that the individual species of woods have to be studied in relation to PAH formation before use.
36. Treated wood should not be used, since treatments with chemicals for preserving, waterproofing, fireproofing etc. may result in tainting of the food as well as the introduction of other contaminants e.g. dioxin from woods treated with pentachlorophenol (PCP) (Hansen and Hansen, 2003).
37. For some foods, the effect of fuel choice on taste may be the critical factor in choosing a fuel. In any event, fuels like e.g., diesel, old tires or waste oil should generally not be used even as a partial component, as these might well lead to increased PAH levels, and must be specifically assessed and analysed if their use is considered.

#### *Process: direct versus indirect*

38. Replacing direct smoking with indirect smoking can significantly reduce contamination of smoked foods. In modern industrial kilns, an external smoke generator can be operated automatically under controlled conditions to clean the smoke and regulate its flow as it is brought into contact with the food. For more traditional or smaller scale operations, this may not, however, be an option.
39. When possible, washing or water-cooling of smoke should be used to reduce the content of PAH in the final food. Water-cooling is already used in the meat industry, and this kind of washing of the product after the process may remove PAH-containing particles from the surface of the product (Fabech, B and Larsen, J.C., 1986).
40. The type of generator used should be based on an assessment of possible reduction of the PAH content in the final food and where possible include washing of the smoke after the generator and before the smoke chamber.

41. As PAH are particular bound, a filter may be used to remove particulate material from the smoke. This should reduce potential contamination with PAH.
42. Oxygen needs to be adequate to ensure complete combustion of the fuel. A lack of oxygen may lead to the formation of more PAH in the smoke, as well as producing carbon monoxide, which may be hazardous to operators.

#### *Temperature*

43. Temperature is of importance for the complete combustion of the fuel. The composition of the smoke depends of the temperature, and the temperature should be adjusted to minimize PAH formation. However, more data is needed to document which temperatures would be recommendable.

#### *Time*

44. In principle, the smoking time should be as short as possible to minimize the exposure of the food surfaces to PAH-bearing smoke. However, in the case of hot smoking, when the product is being cooked at the same time, it will be essential to allow sufficient time for the product to be cooked thoroughly. Time dependency of smoking and charcoal grilling is illustrated by data obtained (by Chen and Lin, 1997).

#### *Microbiology*

45. The microbiological quality of the final food product must be evaluated to ensure that there is no potential growth of pathogens during processing and in the final food.

#### **Summary of COP and critical points:**

PAH content of smoked can be minimised by

- a. Use hard wood rather than soft wood to generate smoke
- b. Don not use fuels as diesel fuel, waste products, especially tyres and waste oil which may already contain significant levels of PAH
- c. To use indirect smoking when possible instead of direct smoking
- d. Selection of smoke generators should include assessment of the resulting PAH content in the smoke
- e. Filter or cool the smoke where possible
- f. Wash or water-cool products after smoking where possible
- g. Reduce the time that food is in contact with smoke

#### **Smoke flavourings as alternative to the smoking process.**

46. As an alternative to the smoking process, smoke flavouring can be added to food. There are various types of smoke flavour including smoke extract and mixtures of chemicals. In principle, both types of flavourings, especially smoke extracts, may contain PAH. However, levels are tightly regulated through EU legislation<sup>4</sup>.
47. The use of smoke flavourings is generally considered to be of lesser health concern than the traditional smoking process. In the production of smoke flavourings, PAH can be removed, and maximum limits for e.g. benz[a]pyrene can be established and met.
48. The use of smoke flavourings does not necessarily provide the preservative/anti-microbial effect of actual smoking. The microbial food safety of the food must therefore be taken into account in any change from actual smoking to the use of smoke flavouring.

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<sup>4</sup> *Smoke flavourings* are regulated under the EU directive for flavourings. The regulation includes a limit for the content in the flavour preparation/condensate on benzo(a)pyrene of 10 micrograms/kg and benz(a)anthrazene of 20 micrograms/kg, EC Regulation No 2065/2003 of the European Parliament and the Council of 10 November 2003 on smoke flavourings used or intended for use in or on foods.

**DIRECT DRYING**

49. Drying of food can take place either by indirect or direct drying processes. In the direct drying process the combustion gasses are in direct contact with the foods, while this is not the case in the indirect drying, where e.g. the heat is in a closed system and not coming into direct contact with the foods.
50. With regard to direct and indirect drying processes, direct drying requires less equipment than indirect but could result in higher levels of PAH in the final, dried food.
51. Replacing direct drying with indirect drying can significantly reduce contamination of dried foods. As indirect drying is not regarded as a significant source of PAH, it is not covered by the COP and will not be addressed in this paper.

*Fuel to be used.*

52. The type of fuel used for direct drying of foods has an influence on the formation of PAH (Nielsen and Illerup, 2003). As the fuel used in drying processes may affect the flavour of the final product, this point is also relevant to consider.

*Process: direct versus indirect*

53. Direct drying is used to dry grains, seeds, oils, milk powder etc. Common direct drying/heating operations and applications include drying to remove water (and/or other solvents/chemicals) added, left or produced during processing. During direct drying, hot air is blown directly into the foodstuffs and combustion products can therefore directly enter the food. One example of PAH contamination from direct drying in contamination of vegetable oils (including olive residue oils) in which oil has been contaminated with PAH during technological processes (Antonopoulos, K et al., 2006; Menichini, S. et al., 1991).
54. The hot drying gasses can be produced by using various types of fuel resulting in different types of contaminants in the air.

The heat energy of a system must:

- Heat the dryer feed to the vaporization temperature of the "light" components
- Vaporize and/or free the liquid/by-products above the solids surface
- Heat solids to the final desired temperature, for the desired duration of time, and
- Heat the vapour to the final desired temperature.

Numerous factors, including equipment cost and availability of energy sources often result in similar foods being dried in very different ways.

55. For most non-meat products benzo[a]pyrene levels were low (Kazerouni et al., 2000). From the SCOOP project average a benzo[a]pyrene levels of 0.2 µg/kg were reported for both bread and rolls (n = 103) and cereals (n = 63) (European Commission, 2004). For popcorn benzo[a]pyrene concentrations of 0.5 µg/kg was found. The bread/cereal/grain intake for humans has been found to cover approximately 30 % of the total intake of benzo[a]pyrene (Larsson, 1986; Kazerouni et al., 2001, European Commission, 2002; Duedahl-Olesen et al., 2006), even though individual items in this food group have low levels of benzo[a]pyrene, see also Annex III.
56. For dried fruits 71 % of 158 samples had benzo[a]pyrene levels below 2 µg/kg. However 10 % of the total number of samples had concentrations of benzo[a]pyrene above 100 µg/kg (European Commission, 2004). No comments or explanation of the increased levels was included.
57. Van der Wielen and co-workers (2006) reported benzo[a]pyrene concentrations up to 85 µg/kg in olive oils (n=170), while other vegetable oils (n=170) for human consumption only showed benzo[a]pyrene concentrations up to 9 µg/kg. Benzo[a]pyrene concentrations ranging from not detected levels to 64 µg kg-1 have been reported previously for vegetable oils (Dennis et al., 1991, Moret et al., 2000; European Commission, 2004), see also Annex III.

**COP FOR PRODUCTION BY USING DIRECT DRYING**

58. Direct drying can be done either using drying in the sun or using hot combustion gasses from burning gases, oil, wood, solid/liquid waste etc.



59. Sun drying with crops exposed directly to the sun/air should not take place near industrial point sources of combustion off-gas, such as incinerators, coal-fired power stations, cement works etc. However, covered dryers may protect crops from industrial sources to some extent. Avoid drying of the products (cacao pods for example) directly on the asphalt or bitumen which is a source of PAH
60. The type and composition of fuel used in the drying process has an influence on the formation of PAH, but insufficient data are available to recommend specific fuels and furthermore, some types of fuel might result in specific contaminants in contact with some types of foods.
61. It is recommended to make a risk assessment of the fuel intended to be used, the actual process and foodstuffs to be dried. This assessment should take into account the benefit of using filtering of the gasses.
62. Use of other types of fuel can lead to increased content of PAH, and has to be specifically assessed and analysed if they are considered to be used.
63. Temperature should be optimal for drying without the opportunity for PAH formation. A good homogeneity of the temperature of the air is important to avoid overheating.
64. The drying time should be as short as possible to decrease the exposure of the food with the potential contaminating gasses as much as possible.
65. The use of active carbon is required for oil seeds and pomace olive oil as the only way to reduce the PAH content when direct drying processing is used. A monitoring system for the PAH content should be established and additional refining steps (with active carbon) must be used when the PAH level in the food is unacceptable.

**Summary of COP and critical points:**

PAH content of dried foods can be minimised by

- a. Make a risk assessment of the fuel used in contact with the foods to be dried
- b. Do not use diesel fuel, waste products, especially waste oil or old tyres which may already contain significant levels of PAH
- c. Do not dry near industrial point sources of combustion off-gas, such as incinerators, coal-fired power stations, cement works etc.
- d. Reduce the time that food is in contact with combustion gasses
- e. Keeping equipment clean and well maintained (especially driers).

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## ANNEX I

## Polycyclic aromatic hydrocarbons included in the JECFA Risk Assessment summary.

Common name	CAS name	CAS Registry No.	Abbreviation
Acenaphthene	Acenaphthylene	83-32-9	AC
Acenaphthylene	Acenaphthylene, 1,2-dihydro-	208-96-8	ACL
Anthanthrene	Dibenzo[ <i>def,mno</i> ]chrysene	191-26-4	ATR
Anthracene	Anthracene	120-12-7	AN
Benz[ <i>a</i> ]anthracene	Benz[ <i>a</i> ]anthracene	56-55-3	BaA
Benzo[ <i>a</i> ]fluorene	11 H-Benzo[ <i>a</i> ]fluorene	238-84-6	BaFL
Benzo[ <i>b</i> ]fluorene	11 H-Benzo[ <i>b</i> ]fluorene	243-17-4	BbFL
Benzo[ <i>b</i> ]fluoranthene	Benz[ <i>e</i> ]acephenanthrylene	205-99-2	BbFA
Benzo[ <i>ghi</i> ]fluoranthene	Benzo[ <i>ghi</i> ]fluoranthene	203-12-3	BghiF
Benzo[ <i>j</i> ]fluoranthene	Benzo[ <i>j</i> ]fluoranthene	205-82-3	BjFA
Benzo[ <i>k</i> ]fluoranthene	Benzo[ <i>k</i> ]fluoranthene	207-08-9	BkFA
Benzo[ <i>ghi</i> ]perylene	Benzo[ <i>ghi</i> ]perylene	191-24-2	BghiP
Benzo[ <i>c</i> ]phenanthrene	Benzo[ <i>c</i> ]phenanthrene	195-19-7	BcPH
Benzo[ <i>a</i> ]pyrene	Benzo[ <i>a</i> ]pyrene	50-32-8	BaP
Benzo[ <i>e</i> ]pyrene	Benzo[ <i>e</i> ]pyrene	192-91-2	BeP
Chrysene	Chrysene	218-01-9	CHR
Coronene	Coronene	191-07-1	COR
Cyclopenta[ <i>cd</i> ]pyrene	Cyclopenta[ <i>cd</i> ]pyrene	27208-37-3	CPP
Dibenz[ <i>a,h</i> ]anthracene	Dibenz[ <i>a,h</i> ]anthracene	53-70-3	DBahA
Dibenzo[ <i>a,e</i> ]pyrene	Naphtho[1,2,3,4- <i>def</i> ]chrysene	192-65-4	DBaeP
Dibenzo[ <i>a,h</i> ]pyrene	Dibenzo[ <i>b,def</i> ]chrysene	189-64-0	DBahP
Dibenzo[ <i>a,i</i> ]pyrene	Benzo[ <i>rst</i> ]pentaphene	189-55-9	DBaiP
Dibenzo[ <i>a,l</i> ]pyrene	Dibenzo[ <i>def,p</i> ]chrysene	191-30-0	DBalP
Fluoranthene	Fluoranthene	206-44-0	FA
Fluorene	9H-Fluorene	86-73-7	FL
Indeno[1,2,3- <i>cd</i> ]pyrene	Indeno[1,2,3- <i>cd</i> ]-pyrene	193-39-5	IP
5-Methylchrysene	Chrysene, 5-methyl-	3697-24-3	5-MCH
1-Methylphenanthrene	Phenanthrene, 1-methyl-	932-69-9	1-MPH
Naphthalene	Naphthalene	91-20-3	NA
Perylene	Perylene	198-55-0	PE
Phenanthrene	Phenanthrene	85-01-8	PHE
Pyrene	Pyrene	129-00-0	PY
Triphenylene	Triphenylene	217-59-4	TRI

## TOXICOLOGICAL CONSIDERATIONS, Summary.

JECFA reviewed PAH in February 2005 (WHO 2006).

- a. The Committee concluded that the critical effect of PAH is carcinogenicity. As a number of PAH are also genotoxic, it is not possible to assume a threshold mechanism and a PTWI could not be established. Most epidemiological data refer to occupational and environmental exposure. The available evidence regarding oral exposure to PAH was indirect and did not include data on quantitative exposure, and thus was not suitable for use in the risk assessment for PAH.
- b. JECFA used benzo[*a*]pyrene as a marker of the carcinogenic PAH and evaluated results of recent carcinogenicity studies in mice and rats on benzo[*a*]pyrene and used a margin of exposure approach for the risk assessment of PAH.
- c. The present JECFA evaluation focused on 13 PAH that the Committee identified as being genotoxic and carcinogenic: benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, chrysene, dibenzo[*a,h*]anthracene, dibenzo[*a,e*]pyrene, dibenzo[*a,h*]pyrene, dibenzo[*a,i*]pyrene, dibenzo[*a,l*]pyrene, indeno[1,2,3-*cd*]pyrene and 5-methylchrysene.
- d. JECFA compared mean and high-level intakes of PAH with the calculated benchmark dose lower confidence limit for PAH and calculated margins of exposure (MOEs) of 25 000 and 10 000, respectively. The MOEs were based on available intake data, and can be a useful tool to prioritize risks. Based on these MOEs, JECFA concluded that the estimated intakes of PAHs were of low concern for human health.
- e. JECFA noted that measures to reduce intake of PAH could include avoiding contact of foods with flames, and cooking with the heat source above rather than below the food. Efforts should be made to reduce contamination with PAH during drying and smoking processes, e.g., by replacing direct smoking (with smoke developed in the smoking chamber, traditionally in smokehouses) with indirect smoking. Washing or peeling fruits and vegetables before consumption would help to remove surface contaminants.
- f. JECFA recommended that future monitoring should include, but not be restricted to, analysis of the 13 PAH identified as being genotoxic and carcinogenic, i.e. benzo[*a*]anthracene, benzo[*b*]-, benzo[*j*]-, and benzo[*k*]fluoranthene, benzo[*a*]pyrene, chrysene, dibenzo[*a,h*]anthracene, dibenzo[*a,e*]-, dibenzo[*a,h*]-, dibenzo[*a,i*]- and dibenzo[*a,l*]pyrene, indeno[1,2,3-*cd*]pyrene and 5-methylchrysene. In addition, analysis of benzo[*c*]fluorene in food may help to inform future evaluations.
- g. In the European Union, thirty-three PAH were evaluated by the Scientific Committee on Food (European Commission, 2002). Among these, 15, namely benzo[*a*]anthracene, benzo[*b*]-, benzo[*j*]- and benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, chrysene, cyclopenta[*cd*]pyrene, dibenzo[*a,h*]anthracene, dibenzo[*a,e*]-, dibenzo[*a,h*]-, dibenzo[*a,i*]-, dibenzo[*a,l*]pyrene, indeno[1,2,3-*cd*]pyrene and 5-methylchrysene, show clear evidence of mutagenicity/genotoxicity in somatic cells in experimental animals *in vivo*.
- h. For most PAH, the carcinogenic potential constitutes the critical effect for the hazard and risk characterization. In general, the evidence of genotoxicity shows considerable overlapping with carcinogenicity in agreement with the mechanistic link between DNA adduct formation, mutations, and cancer outcome following PAH exposure.
- i. With the exception of benzo[*ghi*]perylene, the 15 genotoxic PAH (evaluated by the European Union Scientific Committee on Food) have also shown clear carcinogenic effects in various types of bioassays in experimental animals. Although only benzo[*a*]pyrene has been adequately tested using dietary administration, these compounds may be regarded as potentially genotoxic and carcinogenic to humans. They represent a priority group in the assessment of the risk of long-term adverse health effects following dietary intake of PAH.
- j. In the JECFA Summary report (Joint FAO/WHO Expert Committee on Food Additives, February 2005), the Committee note that they have not received any data on occurrence in the GEMS/food format. However, based on data from the European Union SCOOP task force and from IPCS reports, it was

noted that the major foods containing higher concentrations of PAH are meat and fish products, particularly grilled and barbecued products, oils and fats, cereals and dry foods.

k. Some examples are given of the content of PAH in foods after processing of food such as drying and smoking and cooking of foods at high temperatures (grilling, roasting, frying):

- In uncooked foods the average background values are usually in the range 0.01 -0.1 µg/kg.
- In barbecued meat levels of the individual PAH, benzo[*a*] pyrene have been found as high as 157µg/kg.
- In traditional smoked food, an average of benzo[*a*]pyrene was 1.2 µg/kg with a sum of carcinogenic compounds of 9 µg/kg. For modern kilns the values were 0.1 µg/kg and 4.5 µg/kg respectively.
- A level of 10.7 µg/kg of benzo[*a*]pyrene as been reported in corn oil.

However, national studies has shown much higher concentrations, like e.g. in Finland<sup>5</sup> where in a study from 2003 the concentrations of benzo [a] pyrene varied from zero to 34 µg /kg and that of the total PAH compounds (19 compounds) from 42 to 9000 µg /kg. The study shows that the total PAH concentrations can be very high for instance in smoked meat products.

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<sup>5</sup> National Food Agency, Finland, 2003.

## ANNEX III

## PAH CONTENT IN SOME SMOKED AND DRIED FOODS.

- a. Examples of the effect that differences in smoking process can have on PAH levels, are the content of 12 PAH in smoked fishery products from modern smoking kilns that use external smoke generation and have procedures in place to remove compounds with high boiling points such as PAH and particles potentially containing PAH has been compared with products from traditional smoking kilns where the smoke is generated in direct contact with the product.
- b. The average benzo [a] pyrene concentration determined was 1.2 µg/kg for the traditional kilns and 0.1 µg/kg for the modern kilns (Karl and Leinemann, 1996). Levels of benzo[a]pyrene being higher for traditional smoked fish compared to external smoked fish were confirmed by results on eel (n=7) and salmon (n=3), with even lower concentrations of benzo[a]pyrene for cold smoked salmon (Karl and Leinemann, 1996).
- c. In 2005, Yurchenko and Mölder confirmed the trend, where cold smoked mackerel (n=6) and herring (n=4) did not have detectable levels of benzo[a]pyrene (< 0.2 µg/kg) in comparison to varieties (n=4) processed by hot smoking with benzo[a]pyrene concentrations of 0.7 µg/kg. Analysis of herring (n=7) and mackerel (n=9) produced by either direct or indirect smoking did however not show statistically significant different average concentrations of benzo[a]pyrene (Duedahl-Olesen et al., 2006). Increased levels were however found for both one mackerel (0.7 µg/kg) and one herring (3.9 µg/kg) smoked by a direct smoking processes using common alder wood for smoke formation. Recent results on studies on different processing methods of fish are listed in table 1.
- d. Furthermore, collection of data in the European Union Scientific Cooperation Task (European Commission, 2004) revealed an average benzo[a]pyrene concentration for fresh fish of 0.2 µg/kg (n=454) including 11 samples from monitoring in contaminated areas. For smoked fish average concentrations of benzo[a]pyrene for fish smoked with unknown smoking methods (n=127) and for fish smoked by traditional methods (n=213) were reported as 1.4 µg/kg and 5.3 µg/kg, respectively (European Commission, 2004). In comparison addition of liquid smoke flavouring to fish (n=12) resulted in average benzo[a]pyrene concentrations of 0.03 µg/kg.
- e. For fish with edible parts exposed to the smoke increased benzo[a]pyrene concentrations were found. This is illustrated by mackerel fillets with concentrations of benzo[a]pyrene of 0.4 and 0.9 µg/kg compared to <0.08 µg/kg for whole mackerel (Duedahl-Olesen et al., 2006). In 1996, Karl and Leinemann reported that external smoking of mackerel fillets resulted in a benzo[a]pyrene concentration of 0.15 µg/kg (n=11), while traditional smoking of mackerel fillets resulted in levels of 0.6 µg/kg (n=7).
- f. Benzo[a]pyrene levels of smoked meat products produced today do not seem to impose problems. The concentration of benzo[a]pyrene is well below 5 ppb. Duedahl-Olesen and co-workers reported benzo[a]pyrene levels for Danish produced products such as bacon, small sausages and salami well below the maximum of 0.6 µg/kg reported by WHO in 1998 for meat, fish and poultry. Jira (2004) found benzo[a]pyrene concentrations of 0.12 µg/kg ranging from 0.05 to 0.35 µg/kg for smoked ham and sausage (n=18).
- g. Larsson concluded already in 1983 that the benzo[a]pyrene formation in meat is largely affected by the cooking method and the time for which it is cooked. Kazerouni et al (2001) reported concentrations of benzo[a]pyrene for other commercially produced products such as bacon, salami, smoked ham and sausages prepared as package directions of less than 0.1 µg/kg.
- h. In the tables below, both drying and smoking terms such as direct or indirect drying or smoking are used. For direct or traditional smoking or drying the smoke formation source is placed in the same chamber as the final food product, while for indirect smoking or drying, a generator forms smoke externally.

Table 1. Fish

Benzo[a]pyrene concentrations in fish smoked under different processing conditions ( $\mu\text{g}/\text{kg}$ ) n.d. not detected

Food item	Indirect	Direct	Other	Reference
Fresh fish			0.2 ( $\pm$ 0.7)	European Commission, 2004
Smoked fish	1.4 ( $\pm$ 7.2) (method unknown)	5.3 ( $\pm$ 21.7) (traditional)	0.03 ( $\pm$ 0.02) (liquid smoke flavouring)	European Commission, 2004
Mackerel	<0.08 (n = 5)	0.18 (n = 4)	One sample, direct 0.72	Duedahl-Olesen et al., 2006
Herring	<0.10 (n = 3)	0.15 (n = 4)	One sample, direct 3.9	Duedahl-Olesen et al., 2006
Mackerel fillets		0.44 – 0.93		Duedahl-Olesen et al., 2006
Mackerel fillets	0.15	0.6		Karl and Leinemann, 1996
Eel	0.02 (n.d. – 0,1)	1.1 (0.3 – 3.9)		Karl and Leinemann, 1996
Salmon	0.06	1.0	0.04 (cold smoked)	Karl and Leinemann, 1996
Herring/mackerel		0.7 (hot smoked)	n.d. (cold smoked, LOD = 0.24 ) n.d. (Fresh herring)	Yurchenko and Mölder, 2005
Salmon		0.8 (hot smoked)	0.4 (cold smoked)	Yurchenko and Mölder, 2005



Table 2. Meat  
Benzo[a]pyrene concentrations ( $\mu\text{g}/\text{kg}$ ) in meat products smoked or grilled under different conditions

Food item				References
Smoked meat products	1.7 $\pm$ 6.7 (n= 145, method unknown)	3.3 $\pm$ 11.7(n = 1023, Traditional smoking)	0.02 $\pm$ 0.03 (n=198, Liquid flavouring)	European Commission, 2004
Frankfurter	0.3 (charcoal fire) 0.2 (electric oven) 0.1 (frying pan)	54.2 (log fire) 7.7 (log fire embers) 17.6 (cone fire)		Larsson et al., 1983
Hamburger	0.01 (oven-broiled)	0.01 (pan-fried)	Grilled/barbecued 0.09 (medium), 0.6 (well), 1.5 (very well)	Kazerouni et al., 2001
Hamburger, restaurant grilled/barbecued	0.73 (medium)	1.2 (well)	1.4 (very well)	Kazerouni et al., 2001
Steak	0.01 (Oven-broiled)	0.01 (pan-fried)	4.2 (medium) 4.8 (well) (grilled/barbecued)	Kazerouni et al., 2001
Meat, barbecued	1.5			Lodovici et al., 1995
Pork, barbecued	0.1			Lodovici et al., 1995
Cooked Pattie (70-90% lean)	n.d. – 0.1 (hardwood, charcoal)	26 – 42 (mesquite wood)		Maga, 1986
Smoked meat products	0.12 (smoked cured ham n=8, smoked raw sausage, n=10)			Jira., 2004
Lamb sausage	0.32 $\pm$ 0.02 (standard barbecue practice)	2.81 $\pm$ 0.04 (barbecued under severe conditions)		Mottier et al., 2000
Pork products	0.5 – 2.3 (wood smoked)	2.5 (grilled)	0.2 (liquid flavourings)	Gomaa et al., 1993
Chicken with skin and bone	0.08 (oven-broiled)	0.12 (pan-fried)	4.6 (grilled/barbecued)	Kazerouni et al., 2001
Chicken, whole	0.01 (stewed)	0.01 (roasted)		Kazerouni et al., 2001
Chicken boneless	0.12 (Oven-broiled)	0.10 (pan-fried)	0.4 (grilled/barbecued)	Kazerouni et al., 2001
Duck breast steak	6.9 (0.5 hr smoking) 6.9 (1 hr smoking)	9.0 (1.5 hr smoking) 10.6 (2 hr smoking)	13.9 (3 hr smoking)	Chen and Lin, 1997
Duck breast steak	9.2 Charcoal grilled without skin (0.5 hr) 3.7 Charcoal grilled with skin (0.5 hr)	8.4 Charcoal grilled without skin (1 hr) 5.0 Charcoal grilled with skin (1 hr)	8.5 Charcoal grilled without skin (1.5 hr) 5.0 Charcoal grilled with skin (1.5 hr)	Chen and Lin, 1997
Chicken	n.d. – 0.1 (flavouring, wood smoked)	0.7 – 0.8 (barbecued)		Gomaa et al., 1993
Turkey breast, sausage and bacon	0.1 – 0.4 (wood smoked)		n.d. (LOD = Liquid flavouring)	Gomaa et al., 1993

Table 3. Average, ranges and median of benzo[a]pyrene concentration in µg/kg for vegetable oils analyzed with country of origin including values for references (from Fromberg et al., 2007)

Vegetable oil	N	Average	Range	Median	Origin
Olive oil, extra virgin	46	0.15	<0.2-0.4	0.10	IT, ES, GR, FR, NL
Olive oil	6	0.12	<0.2-0.2	0.10	IT, ES
Rapeseed oil	8	0.15	<0.2-0.3	0.10	DK, BE, DE, AT
Sunflower oil	3	0.4	<0.2-0.8	0.3	IT
Sunflower oil	1	11			NL
Grape seed oil	4	1.0	0.2-1.8	1.0	IT, ES, BE
Sesame oil	1	0.2			DE
<b>Reference</b>					
Virgin olive oil	671	0.4	0.015 - 32	0.2	European Comm., 2004
Virgin olive oil	2		<0.02 - 0.7		Hopia et al., 1986
Virgin olive oil	52		<0.015 - 1.2		Moret et al., 1997
Virgin olive oil	6		< 3		Menichini et al., 1991
Virgin olive oil	3	0.1			Lodovici et al., 1995
Olive oil	280	1.7	0.03 - 89	0.3	European Comm., 2004
Olive oil	32		0.5 - 164		Pupin and Toledo, 1996
Olive pomace oil	268	18	<0.1 - 206	9.6	European Comm., 2004
Olive oil	7	0.7	0.2 - 1.2		Speer et al., 1990
Rapeseed oil, deod.	2	0.8	0.3 - 1.3		Larsson et al., 1987
Rapeseed oil	18	0.3	<0.03 - 1.3	0.1	European Comm., 2004
Refined rapeseed oil	24	1.8	0.3 - 69		Dennis et al., 1991
Sunflower oil	5	0.7	<0.1 - 0.8		Speer et al., 1990
Sunflower oil	201	3.1	<0.015 - 232	0.4	European Comm., 2004
Grape seed oil	92	4.2	0.05 - 73	0.6	European Comm., 2004
Grape seed oil	20	20	8.6-44		Moret et al., 2000

Deod. = deodorized oil.

Origin codes: AT = Austria, BE = Belgium, DE = Germany, DK = Denmark, ES = Spain, FR = France, GR = Greece, IT = Italy, NL = Holland.

Table 4. Other foodstuffs. Benzo[a]pyrene concentrations (µg/kg) in other types of food.

Food item	N	BaP	Median	Reference
Bread and rolls	103	0.16 (±0.55)	0.05	European Commission, 2004
Cereals	63	0.16 (± 0.31)	0.05	European Commission, 2004
Dried fruits	158	48.1 (±5.30)	0.25	European Commission, 2004