14. FOOD CONTAMINANTS

unintentional entry into food chain
• agriculture production
• pollution of environment
• storage, transportation, sale
• technological and cooking practice

classification
• primary contaminants (exogenous) outside sources
• secondary contaminants (endogenous) formation in food

contamination sources

agriculture production
• use of pesticides
• fertilisation
• emission
• water for irrigation
• use of surface water for irrigation
• attack by microorganisms, especially by moulds
• veterinary treatment

storage and processing
• post harvest application of pesticides
• formation from relatively non-toxic pesticides
• attack by microorganisms
• technological and cooking arrangement
• penetration of additives from plastic materials

judgement criteria
• potential risk and effects on human health
• incident frequency, proved as human or animal toxicant
• frequent occurrence in food representing important items of food basket
• persistence and frequency of occurrence in environment, possible conversion to products with higher toxicity, ability to be accumulated in food basket
• amount of entrance environment from industry, agriculture, urban agglomeration and other sources
• importance of food in which the given contaminant is present from the point of international trade

**priority contaminants**
• mycotoxins and other microbial toxins
• toxic elements
• radioactive isotopes
• nitroso compounds
• polycyclic aromatic hydrocarbons
• halogen containing organic compounds
• pesticides residua
• veterinary drug residua
• other contaminants (ethylcarbamate, contaminants from packaging materials)

standards and recommendation - *Codex Alimentarius FAO/WHO* legislation in CZ

**Mycotoxins**
*toxic secondary metabolites of some moulds* (book 3, tab. 12.1), ~ 20 toxicologically important mycotoxins

**producers**
moulds *Aspergillus*
*Penicillium*
*Fusarium*

**occurrence**
• mouldy food
• residua in animal tissues and products
• foods produced by cultural moulds
• biotechnological products

**factors influencing contamination**
• biological
• chemical
• other (water activity, temperature)

**aflatoxins**
• *Aspergillus* sp. (*A. flavus*, *A. parasiticus*), temperature, humidity (subtropical and tropical climate conditions)
• aflatoxins B and G
• high level – corn, groundnut, pistachio
• medium level - almond, walnut, raisin, spices
• toxicity (hepatotoxic, mutagenic, carcinogenic)
aflatoxin B₁

- biotransformation (hydroxylation) in animals - metabolites
- transitional factor = ratio of precursors and metabolites 100:1-300:1 (milk), 1000-14000 (meat)
- inhibitors – preservation agents
- stimulators – higher fatty acids, propionic acid
- detoxication of contaminated materials (very difficult) (extraction by NH₄OH)
- thermal processing – decrease (book 3, tab. 12.2) complexes with proteins

**hygienic limits**
examples. generally 20 - 40 μg.kg⁻¹ (sum)
baby food 2 μg.kg⁻¹ (M₁)
infantile food 1 μg.kg⁻¹ (M₁)

**patulin**
- *Penicillium patulinum, P. expansum*
- apple, grapes, orange, ordinary contaminant of fruit concentrates and juices (< 0.1 mg.kg⁻¹)

- relatively stable at pH 3.0-6.5
- antibiotic, antifungal, antivirus effects vs. cancerogenity, mutagenity

**changes during processing and storage**
- storage – slow decrease
- juice thickening by vacuum distillation under vacuum – decrease for about 25%
- pasteurisation (90°C/10 s) - decrease for about 20%
- ethanol fermentation – rapid degradation
- micro-wave heating - decrease for about 40 - 95%

**hygienic limits**
example generally 0.05 – 0.10 mg.kg⁻¹
infantile food 0.001 mg.kg$^{-1}$

**trichothecenes**
- *Fusarium* sp.
- cereals, oil plants, beer
- deoxynivalenol, nivalenol, T-2 toxin

![Chemical structure of deoxynivalenol](image)

deoxynivalenol, $R^1 = OH$, $R^2 = H$, $R^3 = H$

**hygienic limits**

<table>
<thead>
<tr>
<th>Example</th>
<th>Cereals</th>
<th>2 mg.kg$^{-1}$ (deoxynivalenol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flour</td>
<td></td>
<td>1 mg.kg$^{-1}$</td>
</tr>
</tbody>
</table>

**ochratoxins**
- *Aspergillus ochraceus, Penicillium viridicatum*
- cereals, green coffee, kidney of domestic animals
- nefrotoxicity, hepatotoxicity, carcinogenity, persistency

![Chemical structure of ochratoxin A](image)

**hygienic limits** 5-10 µg.kg$^{-1}$

changes during processing (book 3, tab. 12.3)

**other mycotoxines**
sterigmatocystine, cyclopiazonic acid, zearalenone, citrinine, penicillic acid, fusarin C, alternariols and alterotoxins, ergot alkaloids.

**Bacterial toxins**
- exotoxins a endotoxins
- exotoxins – enterotoxins, cytotoxins neurotoxins

**hygienic limits** not determined

**botulotoxins**
- *Clostridium botulinum*
• neurotoxins, polypeptides, 19 amino acids
• non acidic preserved food products (smoked meats)
• anaerobic conditions, pH 4.8-8.5, 30°C
• inactivation 80°C/10 min., 100°C/seconds
• factors water activity, temperature, NaCl, nitrites

**other bacterial toxins**
• *Staphylococcus aureus, C. perfringens, Bacillus cereus*
• infection, propagation and formation of toxins in digestive tract
• *Escherichia coli, Salmonella enteritidis, S. typhimurium*
• primary source meat, milk and eggs

**Nitroso compounds**
• reaction products of secondary amines with nitrosation agents:

\[
\begin{align*}
R^1_2 \text{N-H} &+ X-\text{N}=O \rightarrow R^1_2 \text{N-N}=O + X-\text{H} \\
\text{sekundární nitroační} &\quad \text{N-nitrosamin} \\
\text{amin} &\quad \text{činidlo}
\end{align*}
\]
• secondary amines: amino acids, biogenic amines etc.
• nitrosation agents: nitrosyl cation NO\(^+\), nitrogen oxides
• factors: pH, temperature, time, catalyst, reaction inhibitor

**classification**
• volatile nitrosamines: \(N\)-nitrosodimethylamine
  content (book 3, tab. 12.7)
• non-volatile nitrosamines \(N\)-nitrososarcosine
  content (book 3, tab. 12.8)

**toxicology**
• mutagenic, teratogenic, carcinogenic effects

NDMA = \(N\)-nitrosodimethylamine
NDEA = \(N\)-nitrosodiethylamine
NPIP = \(N\)-nitrosopiperidine
NPYR = \(N\)-nitrosopyrrolidine

**Persistent organochlorine compounds**

**polychlorinated biphenyls**
content in environment (book 3, tab. 12.24)
• 209 congeners
• planar congeners (max. 2 substituents in ortho position)
• indicator congeners: č. 28, 52, 101, 118, 138, 153, 180

\[
\begin{align*}
\text{ring } 1 & \quad \text{ring } 2 \\
\text{C}_{12}\text{H}_{10-(x+y)}\text{Cl}_{x+y}
\end{align*}
\]

\((x+y = 1-10, x = \text{number Cl in circle 1}, y = \text{number Cl in circle 2})\)

physical-chemical properties of technical PCB (kniha 3. tab. 2.19, 2.20, 2.21)

• thermostability and photostability
• incombustible
• chemically inert
• high permittivity and excellent heat properties
• excellent miscibility with organic solvents
• high boiling points

occurance (book 3, tab. 12.24, 12.25, 12.26, 12.28)

in all parts of environment
bioaccumulation

• bioconcentration (passive diffusion)
• biomagnification (due to transfer in food chain)

toxicological judgement

• low acute toxicity of technical mixtures
• carcinogenic risk not confirm
• hygienic limits (sum 7 indicators congeners)
• highest allowable amount 0,2-5 mg.kg\(^{-1}\) fat

polychlorinated dibenzo-\(p\)-dioxines and dibenzofurans

nomenclature (book 3, tab. 2.31, 2.32)
physicochemical properties (book 3, tab. 2.31, 2.33)

17 congeners with high toxicity

formation and main sources

• industrial technologies (production of pesticides, PCB, bleaching of cellulose by chlorine)
• thermal reaction with Cl compounds (combustion, metallurgy)
• photochemical reaction in atmosphere
• secondary food contamination (atmospheric fall out, dump, sediments)

**occurrence in food** (book 3, tab. 12.35)
• levels in range of units to tenth of µg.kg⁻¹ fat
• main sources animal products with higher content of fat

**polycyclic aromatic hydrocarbons (PAH)**

**physical-chemical properties** (book 3, tab.12.9)
**sources** (book 3, tab.12.10)
compounds with 2-6 condensed benzene rings

- formation by pyrosynthesis of organic matter (500-900°C, for example by combustion of fossil fuels)
- some have mutagenic, carcinogenic activity

**possible ways of food contamination by PAH** (book 3, tab. 12.14, 12.15)

**pesticides**
• higher harvest
• negative influence of agricultural chemisation

**classification** (book 3, tab. 12.38, 12.39)
• according to activity
  insecticides
acaricides 
fungicides 
herbicides 
molusccocides 
rodenticides 
regulators of plant growth, dessicators

**insecticides**
- interaction with cell membranes, neurotoxicity (persistent chlorinated hydrocarbons)
- inhibition of acetylcholinesterase, neurotoxicity (organophosphates, carbamates, pyrethroids)
- inhibition of chitin biosynthesis (esters of benzoylcarbamide)

**herbicides**
- interference with biosynthesis of nucleic acids (phenoxyalkanoic and benzoic acids)
- interference with photosynthesis (triazines, uracils)
- reaction with cell membranes (bipyridyls)
- retardation of germination (nitroanilines)

**fungicides**
- inhibition of enzymatic systems (ethylenebisdithiocarbamates, phtalimides)
- interference with DNA biosynthesis (benzimidazoles)

**perzistent chlorinated hydrocarbons** (book 3, tab.12.40)  
**physicochemical properties** (book 3, tab.12.41),

contact insecticides  
DDT, aldrin, dieldrin, toxafen, heptachlor, hexachlorbenzen (HCB), γ-HCH, lindan, hexachloran, pentachlorfenol

\[
\text{pp}^\prime\prime\text{-DDT} \quad \text{pp}^\prime\prime\text{-DDD (TDE)} \\
\text{pp}^\prime\text{-DDD} (\text{TDE}) \quad \text{pp}^\prime\text{-DDE}
\]

products of \(p, p'\)-DDT transformation
**modern pesticides**

**insecticides**

- Heptachlor
- HCB

- Chlorpyrifos (organophosphate)

- Aldicarb (carbamate)

- Permethrin (pyrethroid)

**herbicides**

- 2,4-D (fenoxyalkanoic acid)

**fungicides**

- Atrazine (triazine)

- Zineb (ethylenebisdithiocarbamate, M = Zn)
transformation pesticides

- formation of products with lower toxic or non toxic compounds (hydrolysis of permethrin)
- formation of products with increased toxic effects (dicofol from DDT, paraoxon from parathion, carbofuran from carbosulfan)

**influence of technological and home operation**

- degradation, volatilisation, selection of eating part
- concentration of residuum in given part
- formation of toxic degradation products (ethylenethiourea from ethylenedithiocarbamate)

**toxicological judgement**

- inhibition of acetylcholinesterase
- inhibition of oxidative phosphorylation
- potential human carcinogens
- estrogenic activity

**other contaminants**

**ethylcarbamate**

\[
\text{CH}_3\text{CH}_2\text{O} \overset{\text{O}}{\text{C}} \overset{\text{O}}{\text{NH}_2}
\]

- natural compound of product of fermentation
- potential human carcinogen
- hygienic limits for wine, fruit distillates

**formation and main sources**

**influence of technological operations**

- light, temperature of fermentation
- special cupreous catalysts
- lowering of precursors

contaminants from packaging materials

corrosion, migration

- metals
- glass and ceramics
- paper
- wood
- polymeric materials
  - residua of raw materials
  - residua of auxiliary substances (additives)
  - residua of degradation products or additives
phtalates
- plasticizer of plastics
- possible teratogenic, carcinogenic effects
- estrogenic activity
- hygienic limits (book 3, tab.12.59) permitted level, alc. drinks=1.0 mg.kg$^{-1}$ (DBP+ DEHP)

\[
\text{COOR} \quad \text{COOR}^1
\]

dibutylphthalate \quad R = R^1 = (\text{CH}_2)_3\text{CH}_3

bis(2-ethylhexyl)phthalate \quad R = R^1 = \text{CH}_2\text{CH(CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3

occurrence in food
- contamination of raw materials
- contamination of finished products from packaging material

factor influencing migration
- kind of polymers
- kind of food
- temperature
- time of contact
- quantity in food and others.