

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

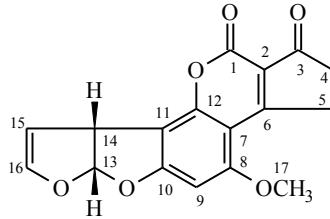
- mouldy food
- residua in animal tissues and products
- foods produced by cultural moulds
- biotechnological products

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

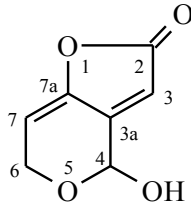
- biotransformation (hydroxylation) in animals - metabolites
- transitional factor = ratio of precursors and metabolites 100:1-300:1 (milk), 1000-14000 (meat)
- inhibitors – preservation agents
- stimulators – higher fatty acids, propionic acid
- detoxication of contaminated materials (very difficult) (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 (M ₁)
	infantile food	1 µg.kg ⁻¹ (M ₁)

patulin

- *Penicillium patulinum*, *P. expansum*
- apple, grapes, orange, ordinary contaminant of fruit concentrates and juices (< 0,1 mg.kg⁻¹)



4-hydroxy-4*H*-furo(3,2-*c*)pyran-2(6*H*)-on (patulin)

- relatively stable at pH 3.0-6.5
- antibiotic, antifungant, antiviral effects *vs.* cancerogenicity, mutagenicity

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

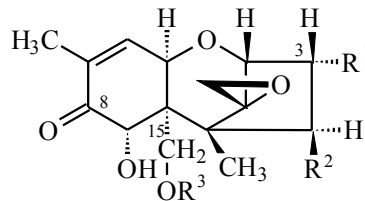
example	generally	0.05 – 0.10 mg.kg ⁻¹
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infantile food

0.001 mg.kg⁻¹

trichothecenes

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



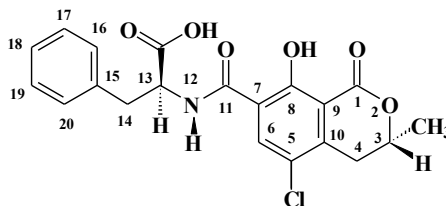
deoxynivalenol, R¹ = OH, R² = H, R³ = H

hygienic limits

example	cereals	2 mg.kg ⁻¹ (deoxynivalenol)
	flour	1 mg.kg ⁻¹

ochratoxins

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



ochratoxin A

hygienic limits 5-10 µg.kg⁻¹
changes during processing (book 3, tab. 12.3)

other mycotoxines

sterigmatocystine, cyklopiazonic 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*

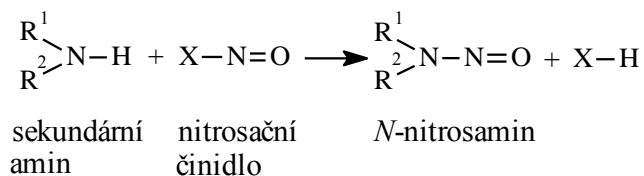
- neurotoxins, polypeptides, 19 amino acids
- non acidic preserved food products (smoked meats)
- anaerobic conditions, pH 4.8-8.5, 30°C
- inactivation 80°C/10 min., 100°C/seconds
- factors water activity, temperature, NaCl, nitrites

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:



- 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

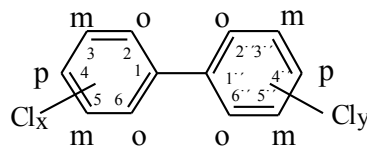
Persistent organochlorine compounds

polychlorinated biphenyls

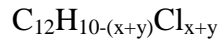
content in environment (book 3, tab. 12.24)

- 209 congeners
- planar congeners (max. 2 substituents in *ortho* position)

- indicator congeners: č. 28, 52, 101, 118, 138, 153, 180



ring 1 ring 2



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

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

occurrence (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

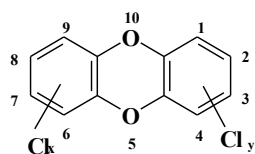
- low acute toxicity of technical mixtures
- carcinogenic risk not confirm
- hygienic limits (sum 7 indicators congeners)
- highest allowable amount $0,2-5 \text{ mg.kg}^{-1} \text{ fat}$

polychlorinated dibenzo-*p*-dioxines and dibenzofurans

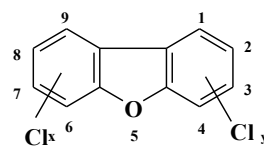
nomenclature (book 3, tab. 2.31, 2.32)

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

17 congeners with high toxicity



PCDD



PCDF

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)

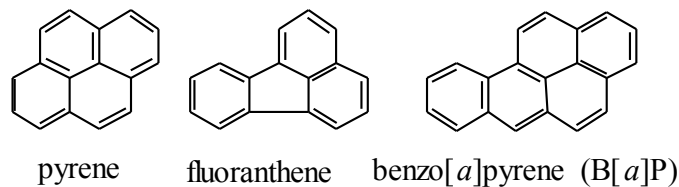
- levels in range of units to tenth of $\mu\text{g.kg}^{-1}$ fat
- main sources animal products with higher content of fat

polycyclic aromatic hydrocarbons (PAH)

physical-chemical properties (book 3, tab.12.9)

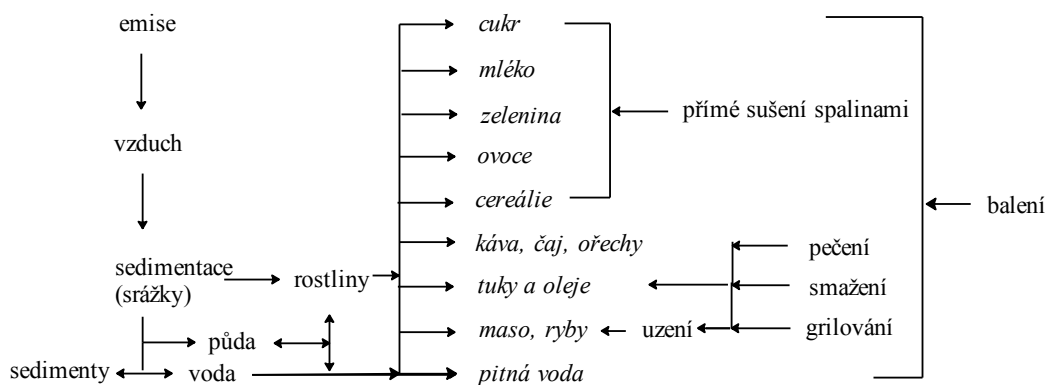
sources (book 3, tab.12.10)

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
 molluscicides
 rodenticides
 regulators of plant growth, desiccators

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

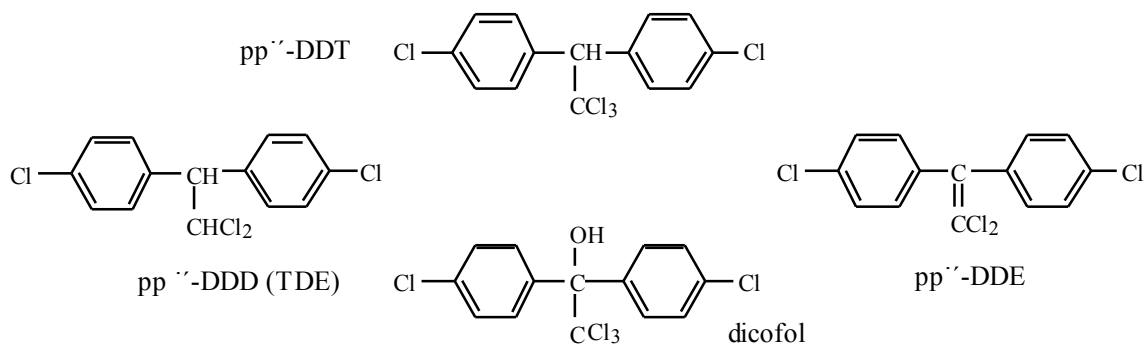
- inhibition of enzymatic systems (ethylenebisdithiocarbamates, phthalimides)
- interference with DNA biosynthesis (benzimidazoles)

persistent chlorinated hydrocarbons (book 3, tab.12.40)

physicochemical properties (book 3, tab.12.41),

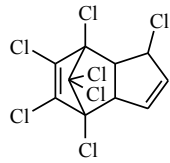
contact insecticides

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

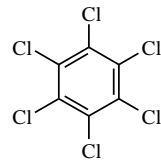


products of *p,p'*-DDT transformation

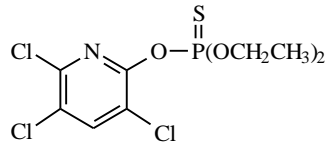
**modern pesticides
insecticides**



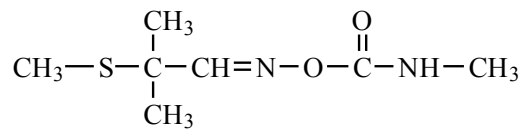
heptachlor



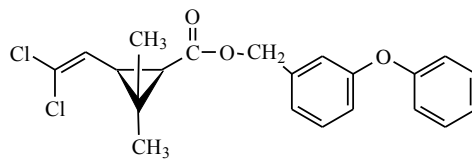
HCB



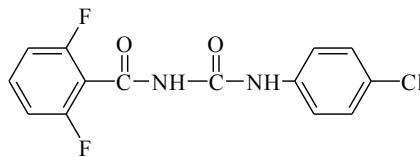
chlorpyrifos (organophosphate)



aldicarb (carbamate)

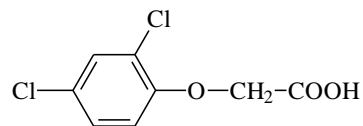


permethrin (pyrethroid)

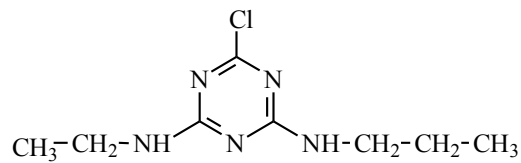


diflubenzuron (esters benzoylcarbamide)

herbicides

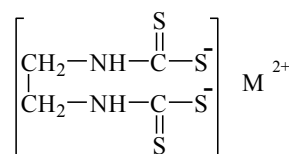


2,4-D (fenoxyalkanoic acid)



atrazine (triazine)

fungicides



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

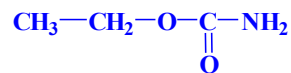
- degradation, volatilisation, selection of eating part
- concentration of residuum in given part
- formation of toxic degradation products (ethylenethiourea from ethylenedithiocarbamate)

toxicological judgement

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

other contaminants

ethylcarbamate



- 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 catalyts
- lowering of precursors

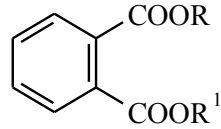
contaminants from packaging materials

corrosion , migration

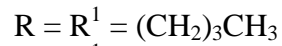
- metals
- glass and ceramics
- paper
- wood
- polymeric materiales
 - residua of raw materials
 - residua of auxiliary substances (additives)
 - residua of degradation products or additives

phthalates

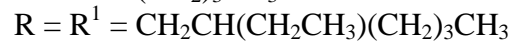
- plasticizer of plastics
- possible teratogenic, carcinogenic effects
- estrogenic activity
- hygienic limits (book 3, tab.12.59) permitted level, alc. drinks=1.0 mg.kg⁻¹ (DBP+ DEHP)



dibutylphthalate



bis(2-ethylhexyl)phthalate



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.