UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

1. Chemical food safety, definition of terms, legislative aspects

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

What is Food safety

- **Food safety** is a scientific discipline describing handling, preparation, and storage of food in ways that prevent foodborne illness.
- This includes a number of routines that should be followed to avoid potential health hazards.
- The tracks within this line of thought are safety between industry and the market, and then between the market and the consumer.

Study literature

- Ronald H. Schmidt, Gary E. Rodrick: Food Safety Handbook. Wiley-IEEE, UK, 2005, 0471210641
- Jay, James M. (ed.) Modern Food Microbiology 7th Edition). Springer - Verlag, 2005, 0-387-23180-3
- Watson, D.H. (ed.): Food Chemical Safety, Volume 1 - Contaminants, Woodhead Publishing. UK 2001, 1-85573-462-1
- Watson, D.H. (ed.): Food Chemical Safety, Volume 2 - Additives, Woodhead Publishing. UK, 2002, 1-85573-563-6
- Velíšek J.: The Chemistry of Food, 2013, 978-1-118-38384-1

Information sources

- http://www.efsa.europa.eu/
- http://www.bezpecnostpotravin.cz/
- http://eur-lex.europa.eu/cs/index.htm
- http://www.szpi.gov.cz/

EFSA

European Food Safety Authority

http://www.efsa.europa.eu/

EFSA

- Established in 2002 by the European Parliament and the Council.
- Since 2005, permanent residence in Parma, Italy.
- The task of EFSA is to provide EU institutions and Member States with the best possible scientific advice for the preparation of legislation (opinions that are independent of political will).
- The Office supports and coordinates the development of uniform risk assessment methodologies, searches, collects and analyzes scientific data, and carries out activities leading to the identification and characterization of emerging risks.

EFSA - tasks

- Responsibility for assessing risks in the field of food and feed safety, nutrition, animal health and welfare, plant health and plant health.

- To provide independent scientific advice, scientific and technical support for the activities of the European Community in all areas which have a direct or indirect impact on food and feed safety.

- To prepare the scientific opinions and recommendations that form the basis for EU policies and legislation and support the European Commission, the European Parliament and the EU Member States in taking effective and timely decisions.

EFSA – 10 scientific panels

- Scientific panel for Animal health and welfare - AHAW
- Scientific panel for Food additives and nutrient sources added to food - ANS
- Scientific panel for Biological hazards - BIOHAZ
- Scientific panel for Food contact materials, enzymes, flavourings and processing aids - CEF
- Scientific panel for Contaminants in the food chain - CONTAM
- Scientific panel for Additives and products or substances used in animal feed - FEEDAP
- Scientific panel for Genetically modified organisms - GMO
- Scientific panel for Dietetic products, nutrition and allergies - NDA
- Scientific panel for Plant protection products and their residues - PPR
- Scientific panel for Plant health - PLH

http://www.efsa.europa.eu/en/panels/contam

RASFF
Rapid Alert System for Food and Feed

https://ec.europa.eu/food/safety/rasff_en

RASFF

- RASFF was **established in 1978** for the transmission of information on hazardous food and feed.
- Currently, it is a network that connects EU Member States with the EC and EFSA.
- **The main objective of this system is to prevent the consumer from being harmed by contaminated food or feed.**
- The RASFF system serves for two-way communication between network members and is not directly intended for communication with the consumers.
- The Czech Republic became a member of the RASFF network as a member state of the EU in 2004 and a national contact point for transferring information between the domestic members of the system was established at the CAFIA.

RASFF - tasks

- Announcement of direct / indirect risk to human or animal health or the environment from food / feed.
- Preventing risky food and feed from entering the market, withdrawal of food / feed from the common European market.
- Preventing the consumer from being harmed by contaminated food or (indirect) feed.
- Two-way communication between network members.

RASFF – Types of notifications

Alert notifications are sent when a food or feed presenting a serious health risk is on the market and when rapid action is required.

Information notifications are used when a risk has been identified about food or feed placed on the market, but the other members do not have to take rapid action.

Border rejections concern food and feed consignments that have been tested and rejected at the external borders of the EU (and the European Economic Area – EEA) when a health risk has been found.

Any information related to the safety of food and feed products which has not been communicated as an alert or an information notification, but which is judged interesting for the control authorities, is transmitted to the members under the heading **News**.

RASFF – current report

date	reference	notification type	notified by	subject
9.7.2018	2018.1912	border rejection	Italy	absence of health certificate(s) for rice pasta from China
6.7.2018	2018.1889	alert	France	Diarrhoeic Shellfish Poisoning (DSP) toxins (346 µg/kg - ppb) in live dog cockles (Glycymeris glycymeris) from France
5.7.2018	2018.1881	information for attention	Portugal	unauthorised substance tricyclazole (0.092mg mg/kg - ppm) in parboiled and brown rice from Brazil
3.7.2018	2018.1847	information for follow-up	Germany	unauthorised novel food ingredient mulberry leaves in herbal tea from Moldova, via the Czech Republic
29.6.2018	2018.1823	alert	Sweden	Diarrhoeic Shellfish Poisoning (DSP) toxins (260 µg/kg - ppb) in live mussels (Mytilus edulis) from Sweden
29.6.2018	2018.1829	information for follow-up	Denmark	organic whole wheat flour and organic whole wheat spelt flour from Germany infested with larvae of insects
28.6.2018	2018.1820	alert	Belgium	ethyl carbamate (2.167 mg/kg - ppm) in kirsch from Belgium, with raw material from Germany
27.6.2018	2018.1796	alert	Italy	too high count of Escherichia coli (3300 MPN/100g) in live clams (Chamelea gallina) from Italy
27.6.2018	2018.1797	alert	France	Diarrhoeic Shellfish Poisoning (DSP) toxins (166.3 µg/kg - ppb) in tellinas from France
27.6.2018	2018.1804	information for follow-up	Spain	high count of Escherichia coli (1700;1300 MPN/100g) in chilled clams (Chamelea gallina) from Italy
27.6.2018	2018.1802	alert	Finland	ochratoxin A (6 µg/kg - ppb) in organic gluten-free buckwheat flour from the United Kingdom
27.6.2018	2018.1784	border rejection	Finland	unauthorised substance dinotefuran (0,1 mg/kg - ppm) in green tea from Japan
26.6.2018	2018.1779	information for attention	Netherlands	foodborne outbreak suspected to be caused by and norovirus (presence) in live oysters from France
26.6.2018	2018.1789	alert	France	too high count of Escherichia coli (930 CFU/100g) in live mussels from France
26.6.2018	2018.1781	border rejection	Finland	unauthorised substance dinotefuran (0.046 mg/kg - ppm) in green tea from Japan

RASFF
Rapid Alert System for Food and Feed

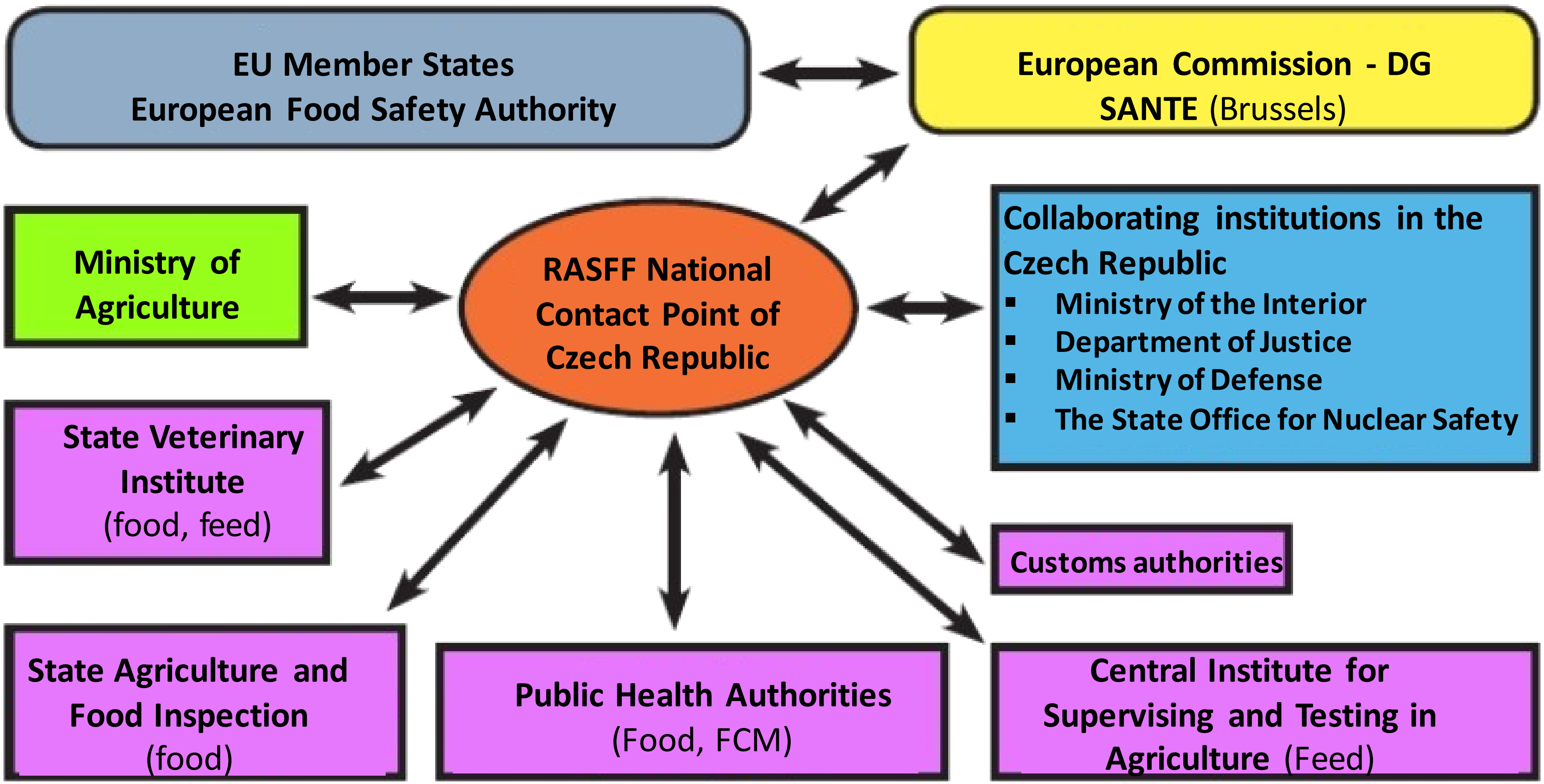
RASFF in Czech Republic

- The functioning of the RASFF in the Czech Republic is regulated by Government Regulation No. 98/2005 Coll., which establishes a system of rapid warning of the risk of danger to human health from food and feed.

- National Contact Point (NCP) in the RASFF according to §15 paragraph. 4 of the Act č.110 / 97 Coll., on food and tobacco products CAFIA. "NKM concentrates information from all supervisory authorities on food and feed in the Czech Republic..

- When the occurrence of a dangerous product is detected by one of the supervisory authorities in the Czech Republic, the CAFIA sends to the European Commission information obtained from individual participants in the national system. The Czech Republic is then informed about the audit findings in the EU Member States.

Scheme of RASFF functioning in the Czech Republic



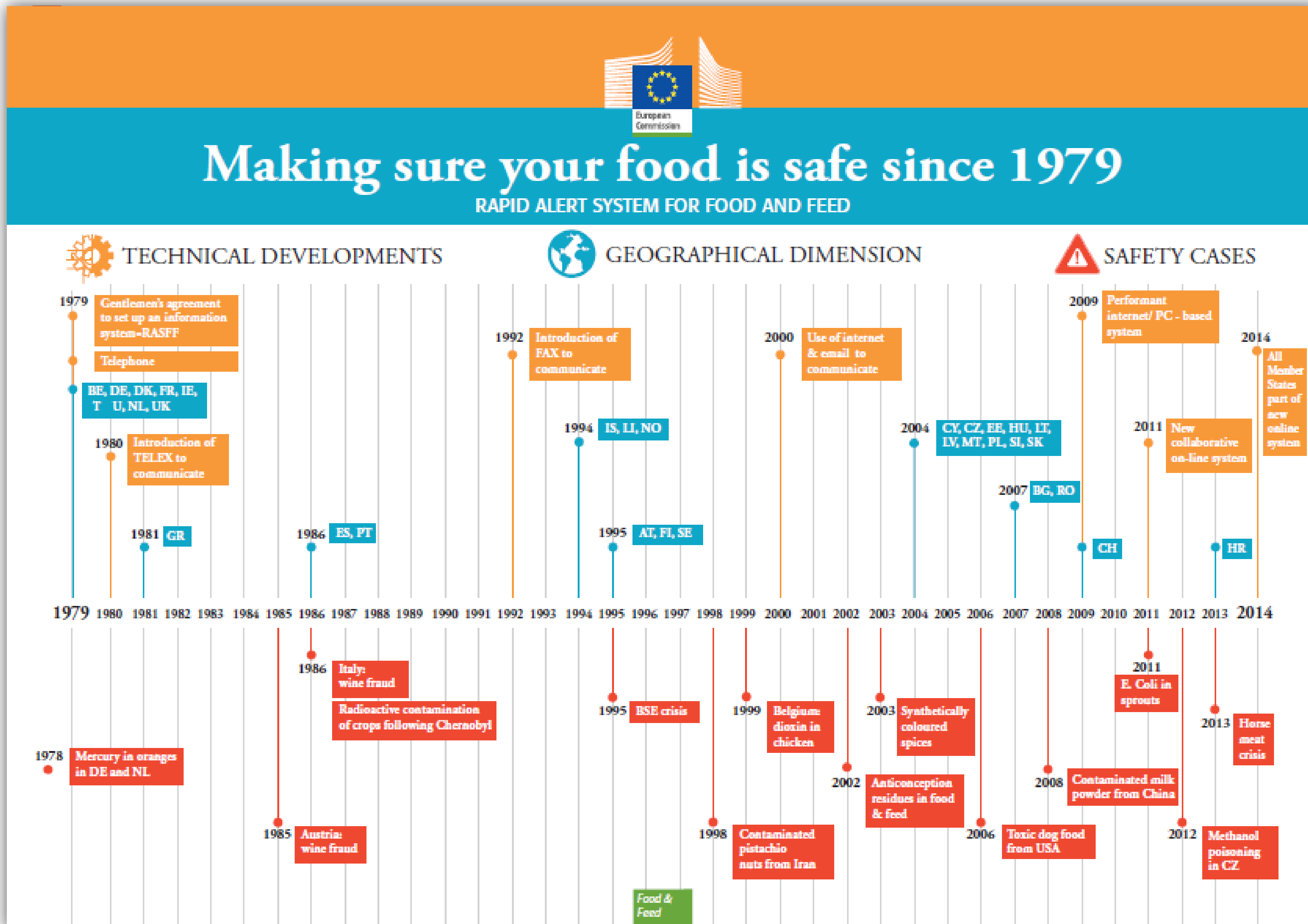
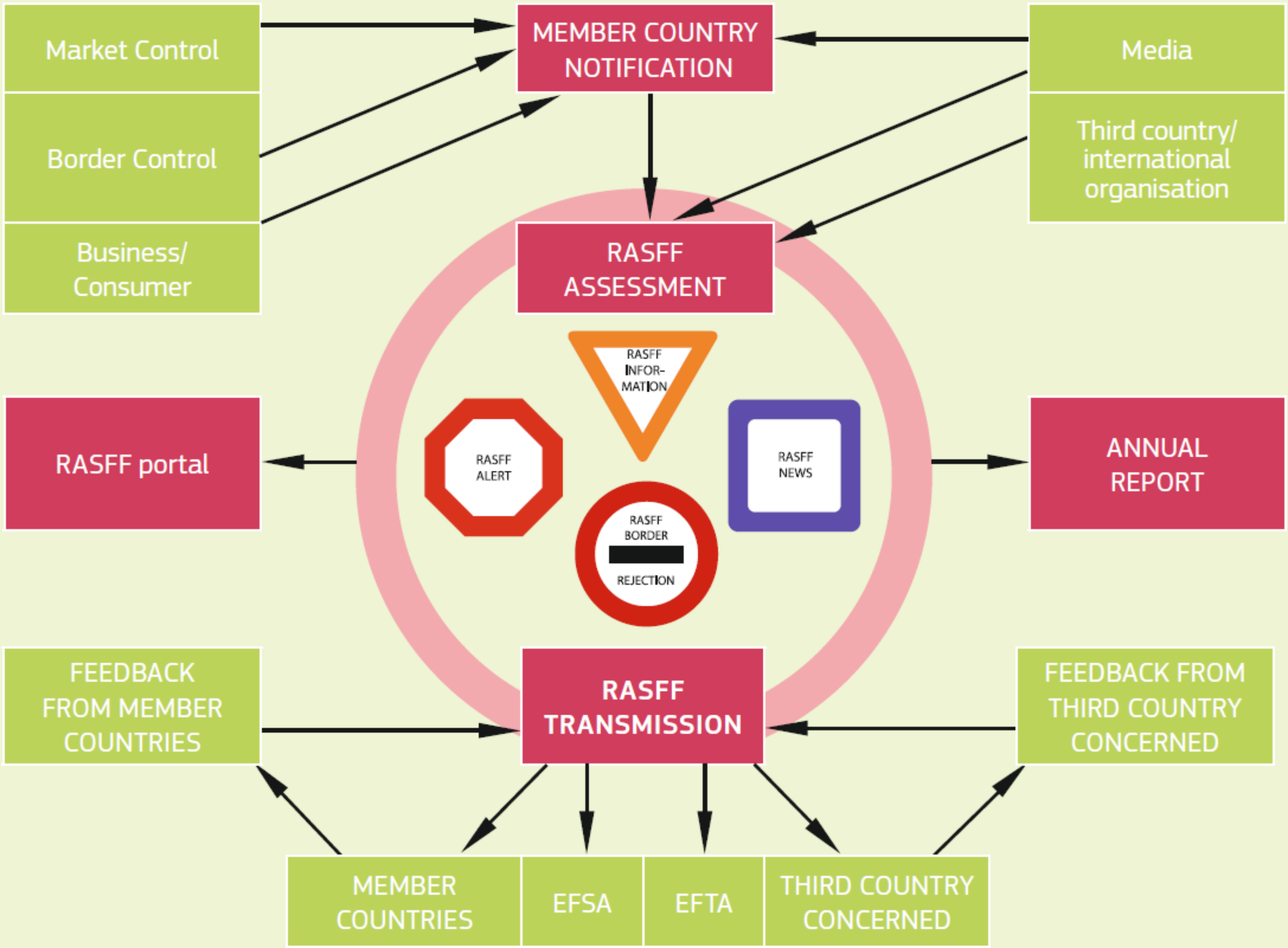
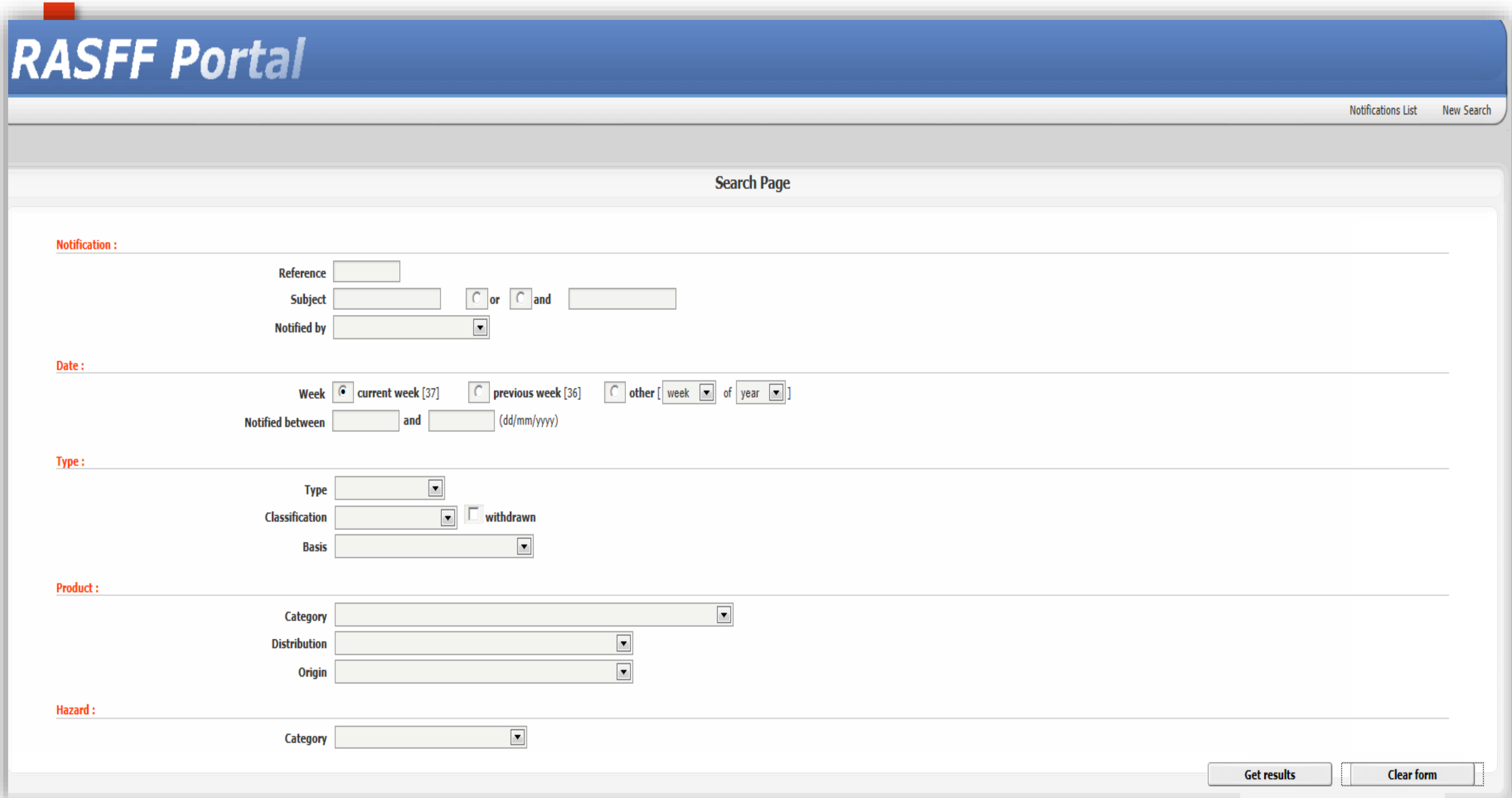

European Commission
Making sure your food is safe since 1979
RAPID ALERT SYSTEM FOR FOOD AND FEED
TECHNICAL DEVELOPMENTS
GEOGRAPHICAL DIMENSION
SAFETY CASES
1979 Gentlemen's agreement to set up an information system–RASFF
Telephone
BE, DE, DK, FR, IE, IT, LU, NL, UK
1980 Introduction of TELEX to communicate
1981 GR
1986 ES, PT
1992 Introduction of FAX to communicate
1994 IS, LI, NO
1995 AT, FI, SE
2000 Use of internet & email to communicate
2004 CY, CZ, EE, HU, LT, LV, MT, PL, SI, SK
2007 BG, RO
2009 Performant internet/ PC - based system
CH
2011 New collaborative on-line system
HR
2014 All Member States part of new online system
1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014
1978 Mercury in oranges in DE and NL
1985 Austria: wine fraud
1986 Italy: wine fraud
Radioactive contamination of crops following Chernobyl
1995 BSE crisis
1998 Contaminated pistachio nuts from Iran
1999 Belgium: dioxin in chicken
2002 Anticonception residues in food & feed
2003 Synthetically coloured spices
2006 Toxic dog food from USA
2008 Contaminated milk powder from China
2011 E. Coli in sprouts
2012 Methanol poisoning in CZ
2013 Horse meat crisis
Food & Feed

Figure 1 – Schematic representation of the information flow of the RASFF





https://webgate.ec.europa.eu/rasff-window/portal/


PESTICIDES
Pesticides
PESTICIDES
EU Pesticides database
Search active substances
Search products
Search pesticide residues
Download MRLs data
Sustainable use of pesticides
Approval of active substances
Authorisation of Plant Protection Products
Maximum Residue levels
« ALL TOPICS
EU - Pesticides database
ACTIVE SUBSTANCES
Regulation (EC) No 1107/2009
PESTICIDES EU-MRLs
Regulation (EC) No 396/2005
Latest active substance updates
Insertion of Review Reports taken note of by the PAFF in July 2016
21/09/2016
Insertion of Review Reports taken note of by the PAFF in April 2016
01/08/2016
Insertion of Review Reports taken note of by the PAFF in May 2016
07/07/2016
Insertion of the latest publications in the EU Official Journal
29/06/2016
Insertion of the latest publications in the EU Official Journal
14/06/2016
Latest MRL updates
Publication of Commission Regulation (EU) 2015/1910 of 21 October 2015 amending Annexes III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for guazatine in or on certain products
01/09/2016
Publication of Commission Regulation (EU) 2016/71 of 26 January 2016 amending Annexes II, III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for 1-methylcyclopropene, flonicamid, flutriafol, indolylacetic acid, indolylbutyric acid, pethoxamid, pirimicarb, prothioconazole and teflubenzuron in or on certain products
01/09/2016

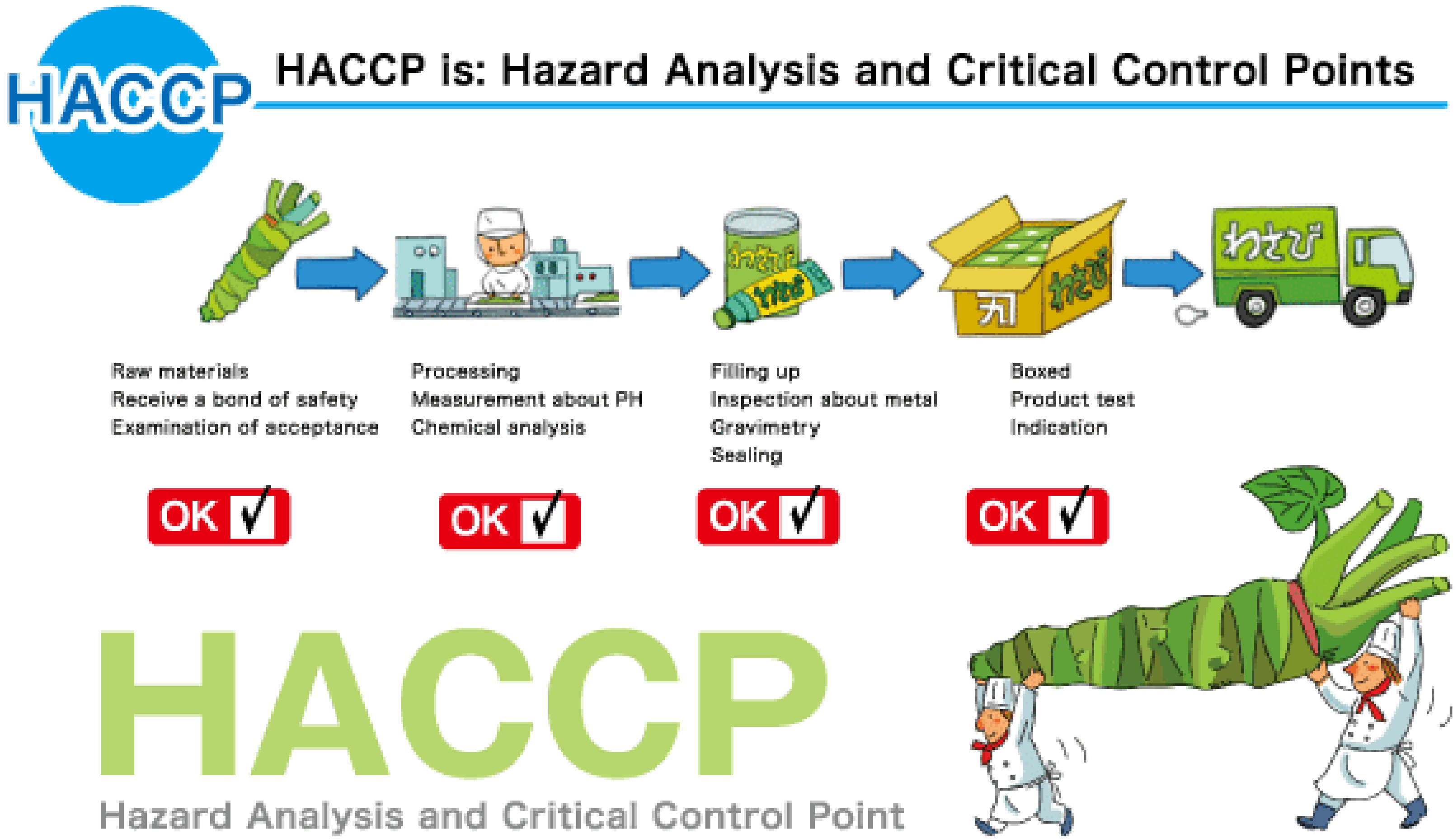
Food Safety Regulation

Food Safety is everyone's responsibility

- In 1963, the **WHO** and **FAO** published the **Codex Alimentarius** which is a collection of guidelines and recommendations relating to food safety.
- **ISO 22000** is a standard developed by the International Organization for Standardization dealing with food safety
- **ISO 22000** specifies the requirements for a food safety management system that involves:
  - **interactive communication,**
  - **system management,**
  - **prerequisite programs,**
  - **HACCP principles**

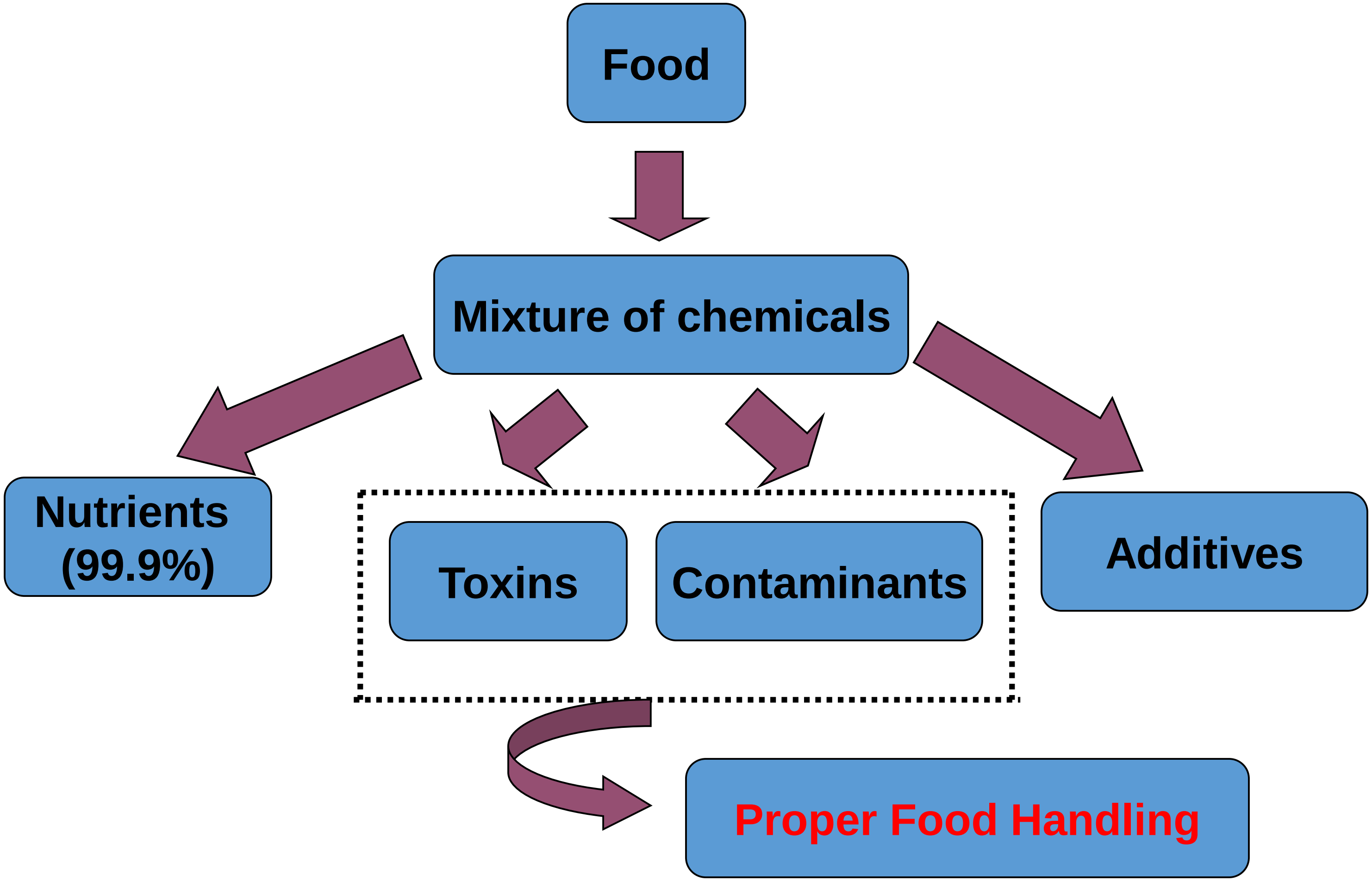
HACCP

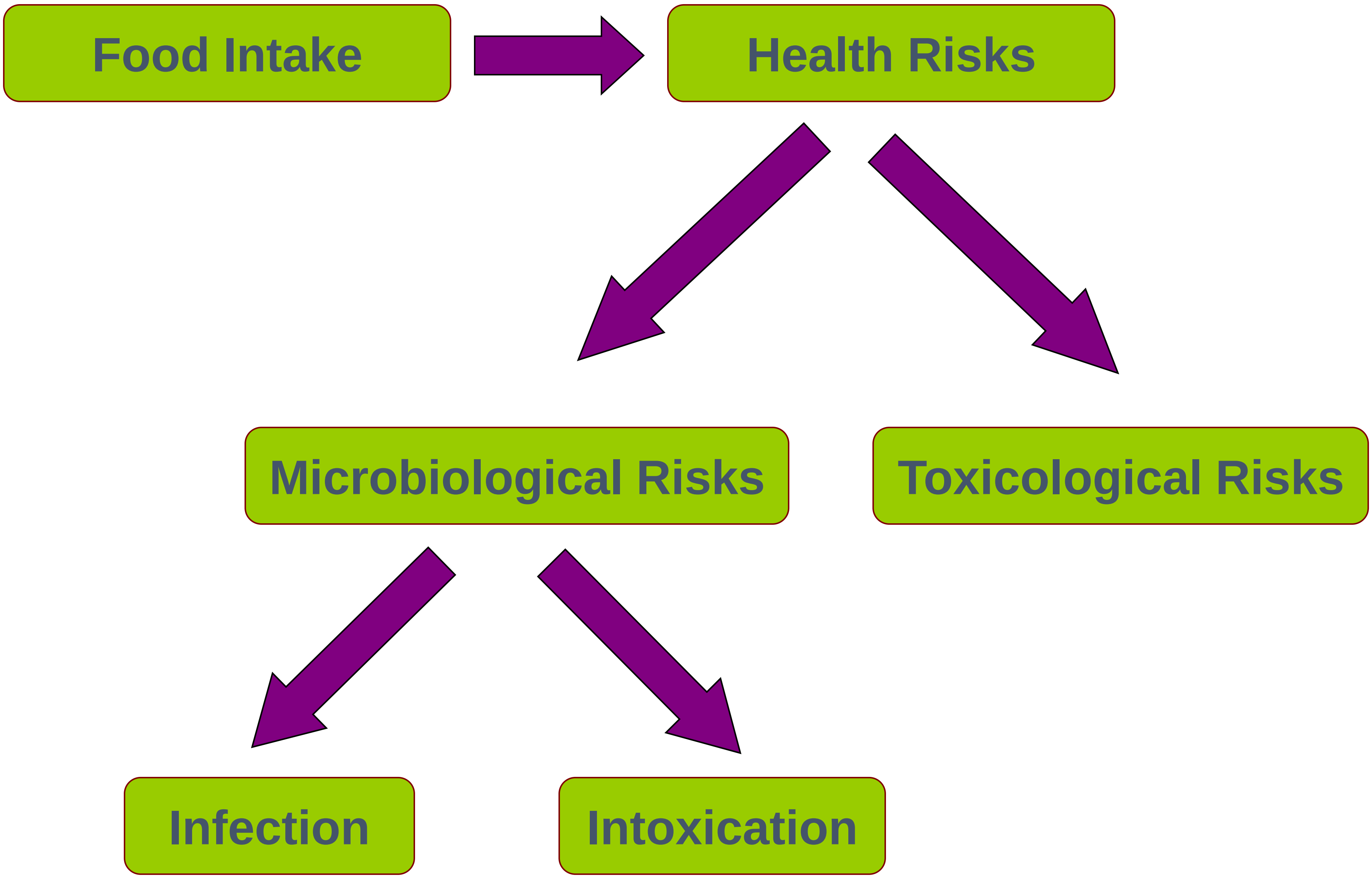
- HACCP is current food regulation program



FOOD

- Food is of fundamental importance to life
- Humans consume 30 tons of food during their lifetime





Food Intake
Health Risks
Microbiological Risks
Toxicological Risks
Infection
Intoxication

Types of toxicants

- **Carcinogens**: cause cancer
- **Mutagens:** cause mutations in DNA
- **Teratogens:** cause birth defects
- **Allergens:** cause unnecessary immune response
- **Neurotoxins:** damage nervous system
- **Endocrine disruptors:** interfere with hormones

Routes of Exposure

Ingestion (water and food)

Absorption (through skin)

Inhalation (air)

Duration & Frequency of Exposure

Duration and **frequency** are also important components of exposure and contribute to dose.

Acute exposure - less than 24 hours; usually entails a single exposure

Repeated exposures are classified as:

- Subacute - repeated for up to 30 days
- Subchronic - repeated for 30-90 days
- Chronic -repeated for over 90 days

Definitions. Risk and Hazard

- **Hazard**: a biological, chemical or physical agent in, or condition of, food with the **potential** to cause an adverse health effect (the nature of that effect)

- **Risk**: a function of the **probability** of an adverse health effect and the severity of that effect, consequential to a hazard(s) in food

  (FAO/WHO 1995)

No Observed Effect Level (NOEL)

- The NOEL is the greatest concentration or amount of an agent, *found by study or observation, that causes no detectable, usually adverse alteration of morphology, functional capacity, growth, development or lifespan of the target.*

The Acceptable Daily Intake

- **ADI:**

  an estimate … of the amount of a food additive, expressed on a bodyweight basis, that can be ingested daily over a lifetime without appreciable health risk (JECFA)

  The concentration or amount of a chemical that can be consumed **daily for a lifetime in the practical certainty, on the basis of all known facts, that no harm will result (JMPR)**

- **ARfD:**

  the amount of a chemical that can be consumed at one meal/in one day in the practical certainty…….

Tolerable Intakes: Definitions

- Tolerable daily intake (TDI) - similar to ADI, but not the same.
  - **ADI** refers to chemicals that have been deliberately added to a product or ingredient, or which are found in food because of, for example, crop treatment with pesticides or antifungal preparations.
  - **TDI** is an estimate of the amount of chemical contaminant that we are exposed to from environmental contamination and which, when in food, can be consumed daily during life without posing a significant health risk.
  - Exposure to these contaminants is undesirable but cannot be ruled out because some of these substances are found in food due to environmental pollution (e.g. lead, dioxins)

Toxicity Classes

LD_{50} (rat, oral)	Correlation to Ingestion by 150 lb Adult Human	Toxicity
<1mg/kg	a taste to a drop	extremely
1-50 mg/kg	to a teaspoon	highly
50-500 mg/kg	to an ounce	moderately
500-5000 mg/kg	to a pint	slightly
5-15 g/kg	to a quart	practically non-toxic
Over 15g/kg	more than 1 quart	relatively harmless

Toxic Potency

Agent	LD_{50} (mg/kg)	
Ethyl alcohol	10,000	slight
Sodium chloride	4,000	
BHA/BHT (antioxidants)	2,000	
Morphine sulfate	900	moderate
Caffeine	200	
Nicotine	1	high
Curare	0.5	Extremely high (<1 mg/kg)
Shellfish toxin	0.01	
Sarin	0.001	
Botulinum toxin	0.00001	

The published materials are intended for students of the University of Chemistry and Technology, Prague as a study material. Some text and image data contained herein are taken from public sources. In the case of insufficient quotations, the author's intention was not to intentionally infringe the possible author(s) rights to the original work.

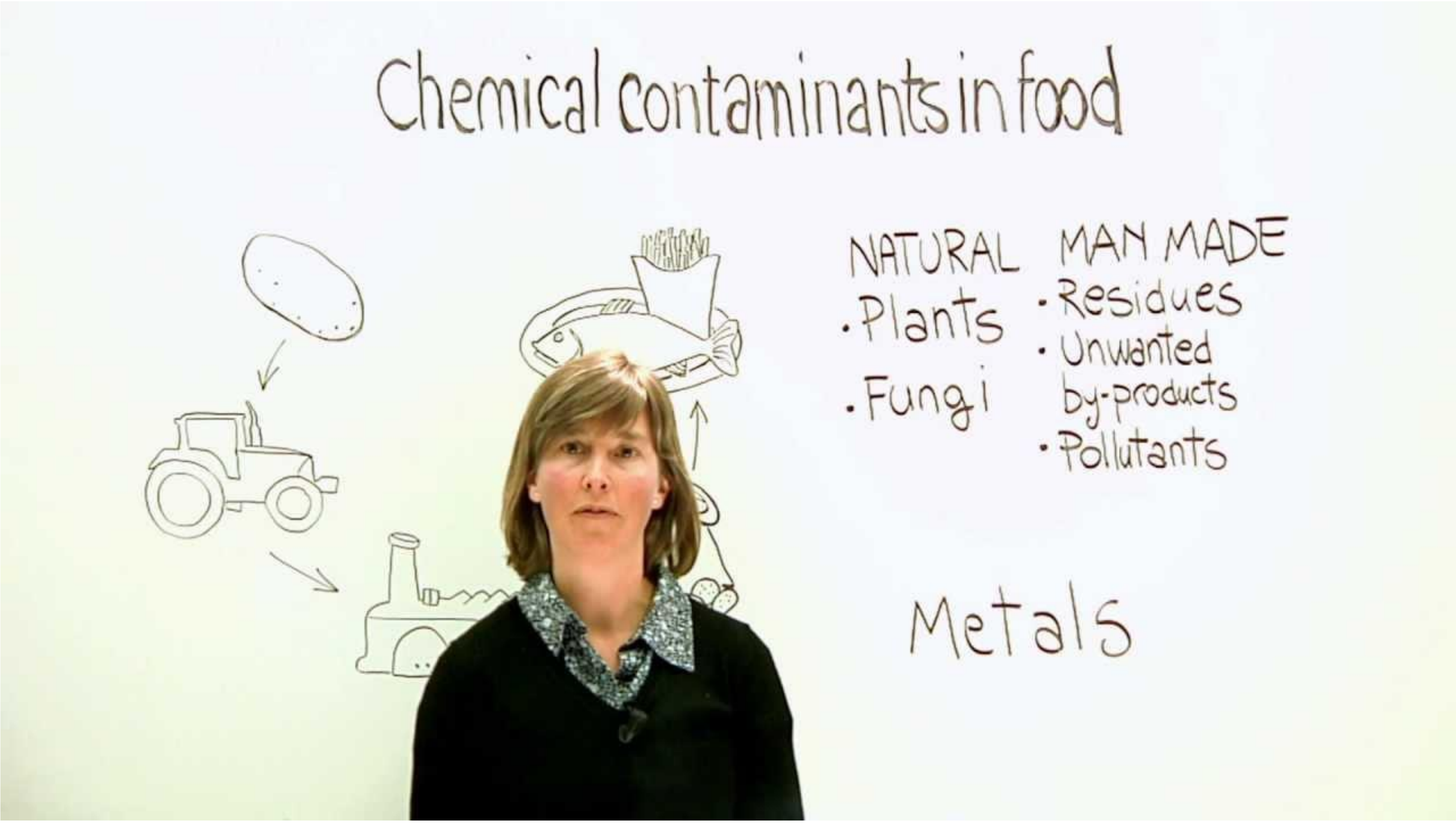
If you have any reservations, please contact the author(s) of the specific teaching material in order to remedy the situation.

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

2. Overview of important groups of compounds associated with chemical food safety

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS


Chemical contaminants in food
NATURAL
· Plants
· Fungi
MAN MADE
· Residues
· Unwanted by-products
· Pollutants
Metals

FOOD: A COMPLEX COCKTAIL OF CHEMICALS

Food fiber

NATURAL COMPONENTS

CONTAMINANS

Natural toxins / antinutrients

Nutrients

Proteins
Lipids
Sugars
Minerals
Vitamins

Primary flavor compounds

Biologically active compounds, beneficial (antioxidants...)

Environmental contaminants

Pesticide / vet. drugs residues

Migrants from food contact materials

Toxic metals

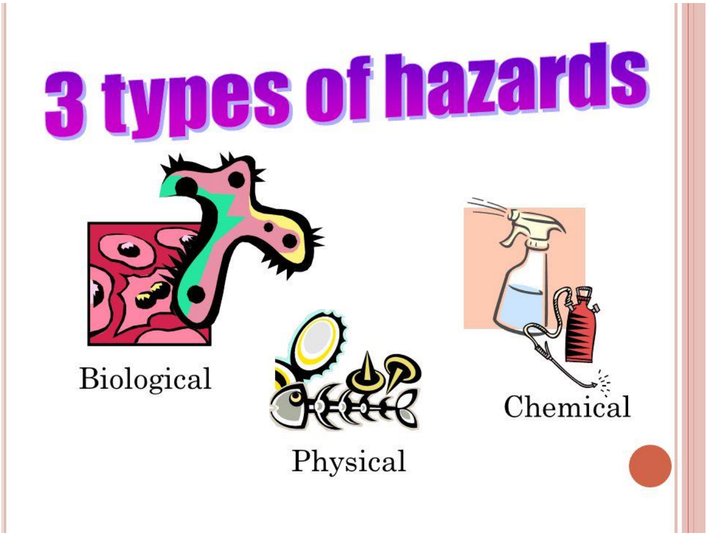
Products originated during processing

Food additives

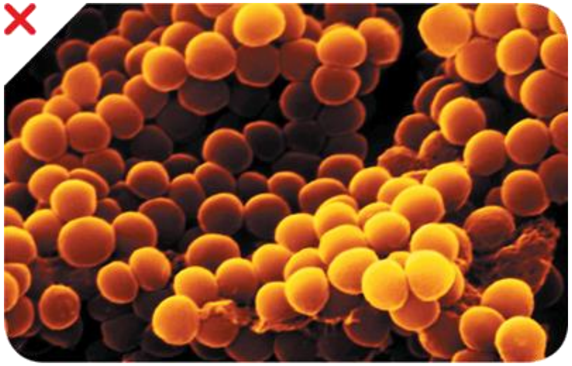
Products of biotechnologies (GMO...)

Types of hazard in food

- **Biological hazard**
- **Chemical hazard**
- **Physical hazard**



Biological Hazards



Biological hazards include:

- Viruses (Rotavirus, Norwalk virus..)
- Bacteria (Salmonella, E. coli, Listeria...)
- Parasites (Toxoplasma gondii, Trichinella spiralis..)
- Fungi (Aspergillus flavus..)

Microorganisms such as viruses and bacteria are the most common causes of food poisoning.

Foodborne illness causing agents

Microorganism	Source	Symptoms	Onset Time
Norwalk-like viruses	Feces, vomitus Contaminated foods	Nausea, vomit, diarrhea, abdominal cramps, headache	12-48 hrs
Campylobacter Jejuni	Raw or undercooked poultry, water, milk, feces	Diarrhea, abdominal cramps, fever, nausea	2-5 days
***Salomonella* spp.**	Poultry and egg, milk, beef, fruits	diarrhea, fever, cramps	12-36 hrs
***E. Coli* O157:H7**	Ground beef, fruits, vegetables, milk, water	Watery or bloody diarrhea, nausea, cramps Hemolytic Uremic Syndrome	2-5 days
Clostridium botulinum	Raw fish and meat Fruits and vegetables	Paralysis, diarrhea	12-36 hrs
Staphylococcus aureus	Human nose, throat, ears, skin Septic wounds Animals and raw milk	Vomiting Abdominal pain Low temperature	1-7 hrs

Chemical Hazards

- Household chemicals include those used:
  - to clean kitchen surfaces and equipment
  - as pesticides, flame retardants, cooling agents....
- Chemicals can be very harmful if they are:
  - spilt on or near food
  - mistaken for food or drink.
- Toxins are poisonous substances produced by some micro-organisms, plants and animals.
- Most toxins that cause food poisoning are tasteless and remain toxic even after cooking

Physical Hazards

- Foreign matter can:

– physically injure people

– introduce harmful bacteria into food.

- Examples of foreign matter include:

– dead insects

– hair

– jewellery

– glass

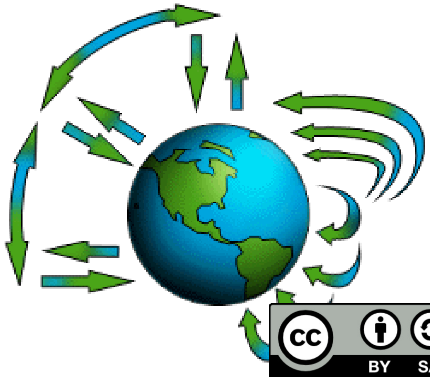
– pieces of metal.

Contaminants classification

- Primary contaminants (**exogenous**) external sources
- Secondary contaminants(**endogenous**) formed in food during processing

Contaminants classification

- **By origin**: whether they are natural or man-made (synthetic).
- **By effect**: on an organ, specie, or an entire ecosystem.
- **By properties**: mobility, persistence, toxicity.
- **By controllability**: ease or difficulty of removal.



Types of pollutants

pollutants

Inorganic

metals/metaloids, nutrients/salts, acids, greenhouse gases, radionuclides, nanoparticles

Organic

sewage/manure, VOC, hydrocarbons (aliphatic, cyclic, polycyclic, heterocyclic), POPs, organo-metals, pharmaceuticals, personal care products, pesticides

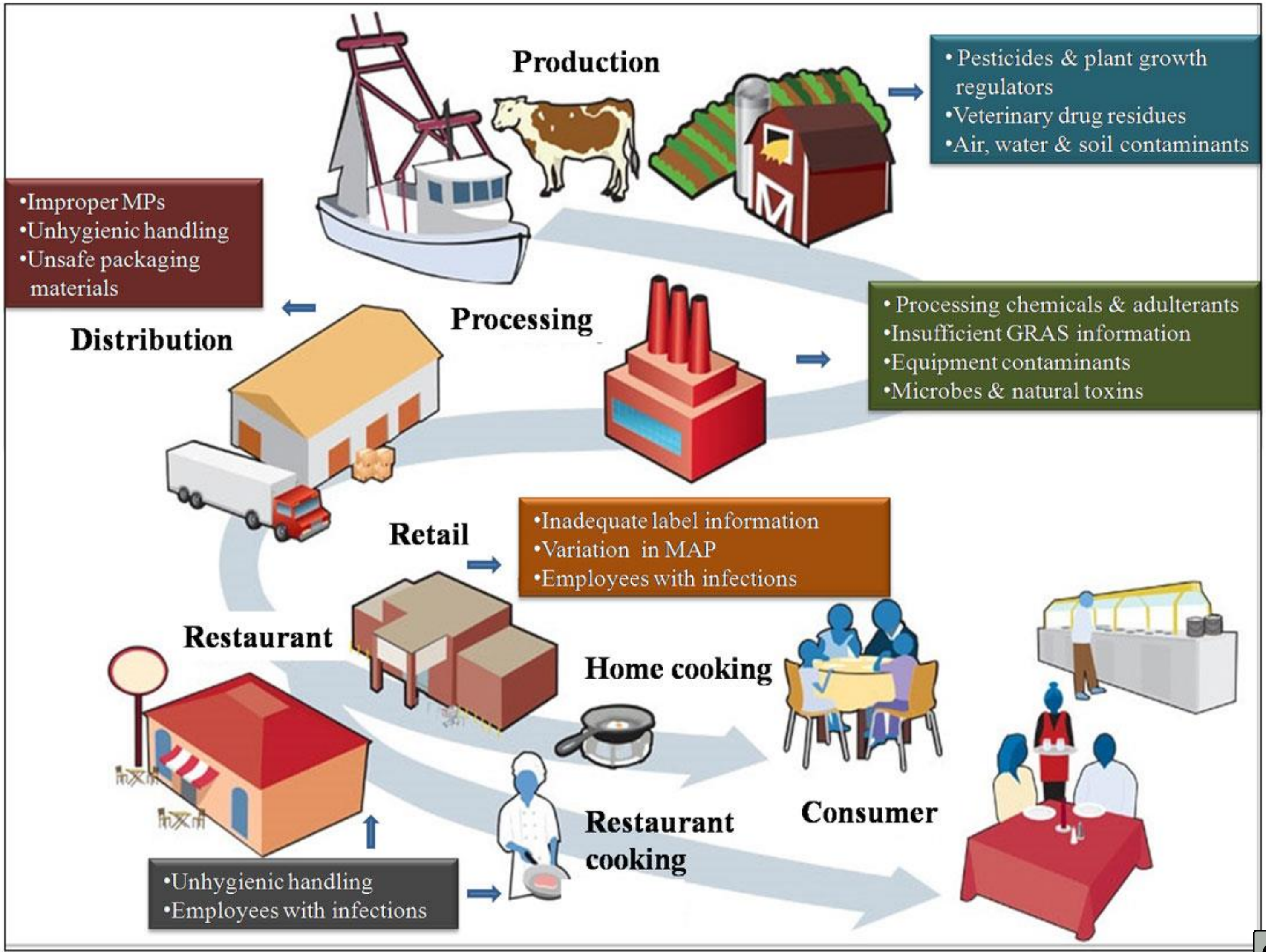
Biological

microorganisms (and their toxins)

Other

sound, light, heat

Food contamination pathway



Sources of potential toxicants in food

- **Naturally occurring toxicants**
  - intrinsic and exogenous (e.g. mycotoxins)
- **Added intentionally and purposefully**
  - food additives, nutritional supplements
- **Present purposefully but not intentionally**
  - pesticide residues, veterinary drug residues
- **Present without purpose and unintentionally**
  - environmental contaminants in the food chain (both anthropogenic and natural/geological)
- **Produced during cooking/processing**
  - acrylamide, furan…

Important groups of food contaminants

- Naturally occurring contaminants
- Environmental contaminants
- Process contaminants




Naturally occurring toxicants

- naturally present in plants & animals
- at least 2 000 different plant species are considered to be poisonous





- and approximately 1 200 species of poisonous animals




Naturally occurring toxicants

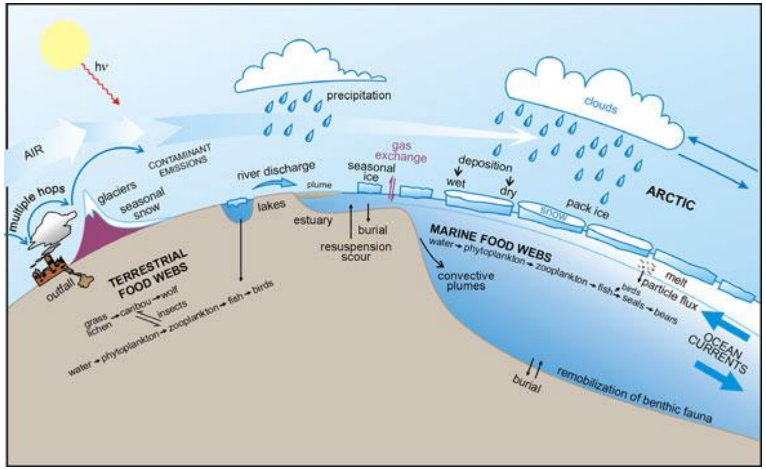
- Naturally present in plants & animals
- Long term ingestion of natural toxins in commonly eaten foods → risks to human health?
- Usually, natural toxins are not acutely toxic, except in a few cases in animals.
- Most of them induce adverse effects only after chronic ingestion or by allergic reactions.

Groups of naturally occurring toxicants

- **Mycotoxins** – aflatoxins, fumonisins, ochratoxin, trichothecenes (DON, T2 etc.)
- **Phytoestrogens** – e.g. soybean estrogens
- **Cyanogenic glycosides** – e.g. linamarin, amygdalin
- **Alkaloids** – e.g. solanine, morphine, caffeine
- **Biogenic amines** – e.g. serotonin, histamine, tyramine, tryptamine
- **Algal toxins** (phycotoxins) – diarrhetic, paralytic (saxitoxin), amnesic (domoic acid)
- **Bacterial toxins** – e.g. botulotoxin
- **Mushroom toxin** – e.g. phaloidine, muscarine

Environmental contaminants

- harmful chemicals present in soil, air and water.
- may come directly from human sources: industrial manufacturing, agricultural run-off and wastewater discharge
- may originate from natural sources, such as the taste and odor-causing chemicals in water generated by algae and bacteria blooms



Important groups of environmental contaminants

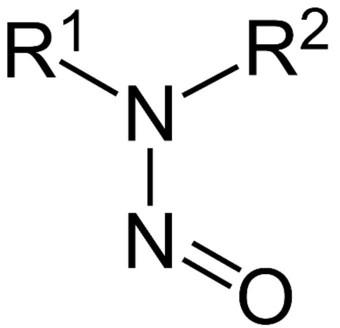
- **Inorganic pollutants**
  - Heavy metals – Hg, Pb, Cd, As, Cu
  - Greenhouse gasses – CO_2 , N_2O
  - Radionuclides – ^{90}Sr, ^{134}Cs, ^{137}Cs , ^{241}Am
- **Organic contaminants**
  - Persistent organic pollutants (POPs) – PCB, PCDD/PCDF, BFR
  - Polycyclic aromatic hydrocarbons (PAHs)
  - Pesticides

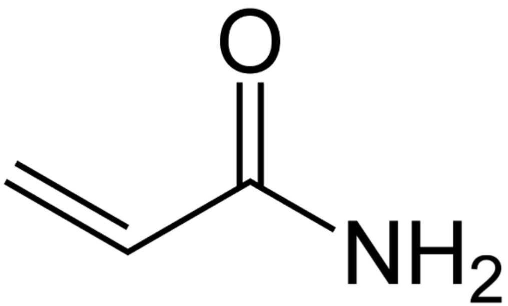
Process contaminants

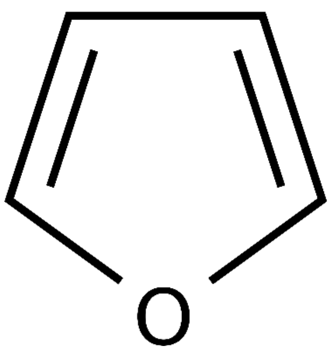
- Toxicants/carcinogens produced during cooking/processing
- Processing methods include fermentation, smoking, drying, refining and high-temperature cooking.

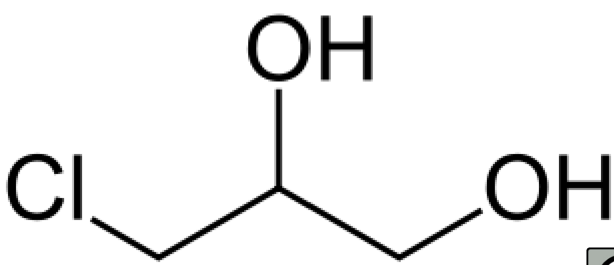
Important process contaminants

- Nitrosamines in cured meats
- Acrylamide
- Furan
- 3-MCPD









UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

3. Substances produced in the production of food - process contaminants

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS


PROCESS CONTAMINANTS
FOOD PROCESSING
- fermentation
- smoking
- drying
- cooking (+120°C)
ACRYLAMIDE
FURAN
EXAMPLES
- acrylamide
- furan

Food processing contaminants

- Process contaminants refer to chemicals formed unintentionally during food manufacturing, cooking (including home cooking), packaging and other processing activities.

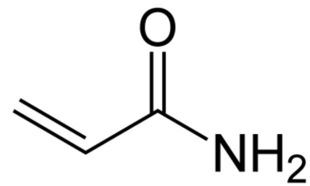
- Some of the chemicals are harmful and may even cause cancer.

Examples of process contaminants produced by dry-heat cooking include **acrylamide** in French fries and **PAHs** in roasted pork

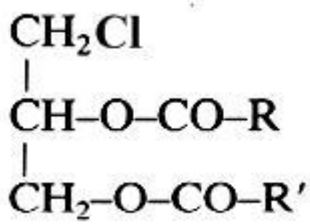
Process contaminants such as **ethyl carbamate** may be generated during fermentation in wine and soy sauce and **3-MCPD** during acid hydrolysis in soy sauce

Food processing contaminants

- **Acrylamide**

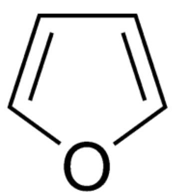


- **3-MCPD**



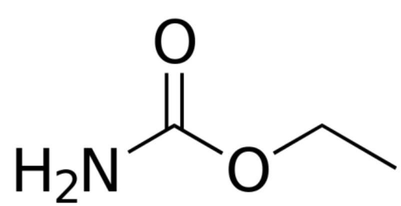
3-MCPD-esters

- **Furan**

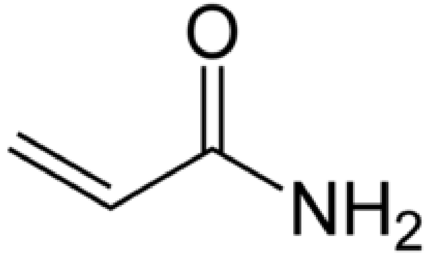


- **Polycyclic aromatic hydrocarbons**

- **Ethyl carbamate**



ACRYLAMIDE



Prop-2-enamide

Acrylamide – food carcinogen???

1997 Hallandsås***:*** during the building of a tunnel in Sweden, concern was raised on the use of acrylamide and related compounds as building materials (as a component of grout)

"For 23 subjects there was strong evidence indicating that *peripheral nervous functions* were impaired due to occupational exposure to NMA or acrylamide. Environmental effects due to contamination of the drinking water were also observed that led to the development of *severe neurological symptoms* among cows and the death of fish downstream."

2002 SWEDEN : *occurrence of acrylamide in starch rich food*

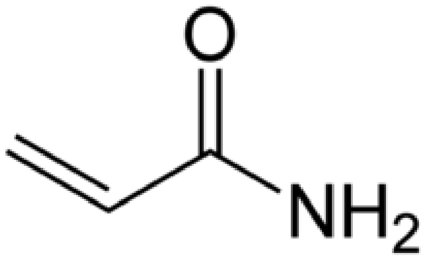
CONCERNS:

- **Carcinogenic, neurotoxic and genotoxic**
- **probable human carcinogen**
  (IARC 1994, group 2A)

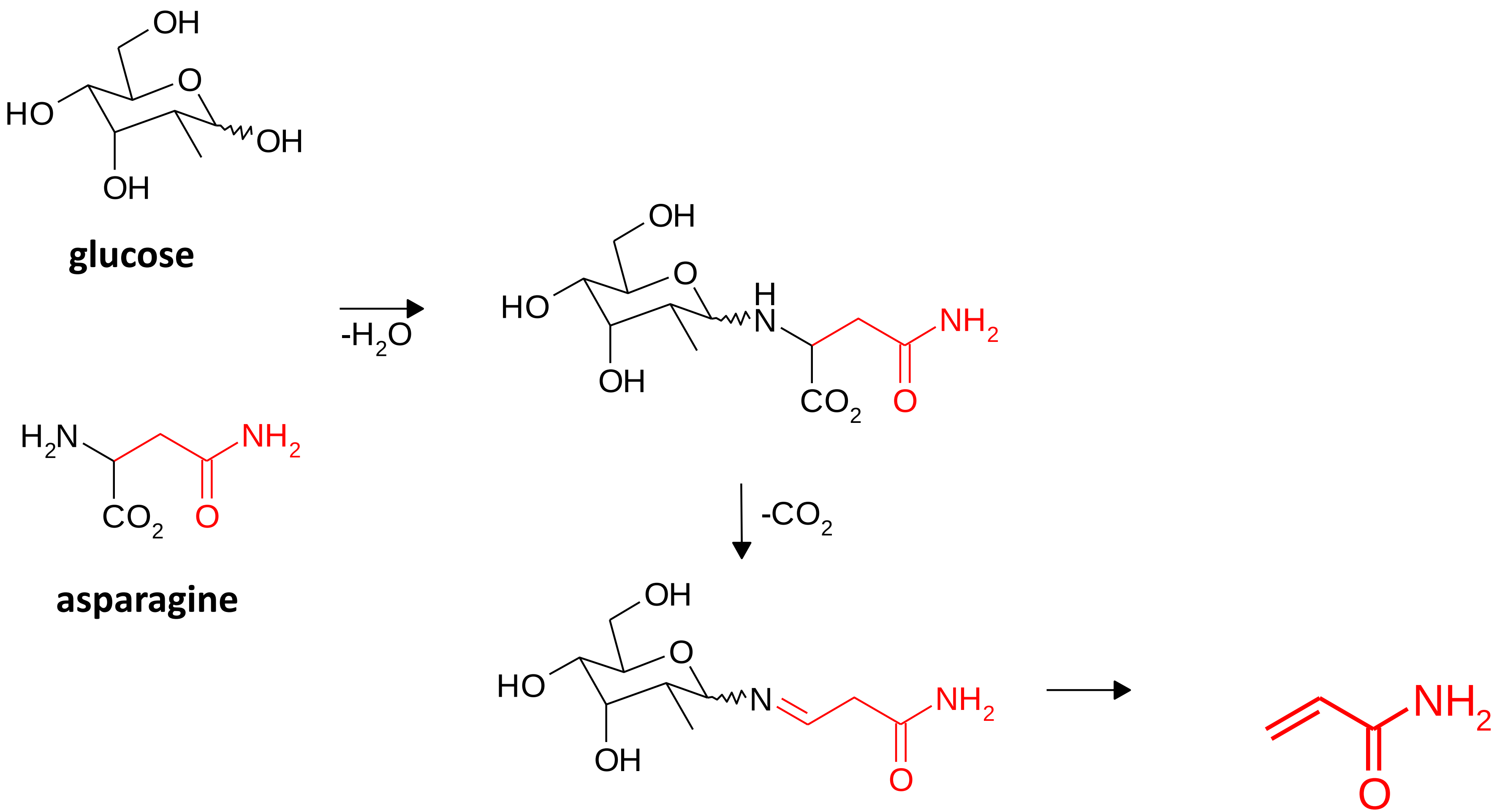
'2002 NFA and Stockholm University – source of acrylmide is DIET'

Acrylamide

- Probable human carcinogen (group 2A – IARC)
- Chemical compound occurring in starchy foods after cooking (frying, baking, grilling)
- Not found in any of the raw foods or cooked foods (potatoes, rice, pasta)
- Heat treatments have been used for several centuries, so it is not easy to reduce the amount of acrylamide in food



Acrylamide- reaction pathway



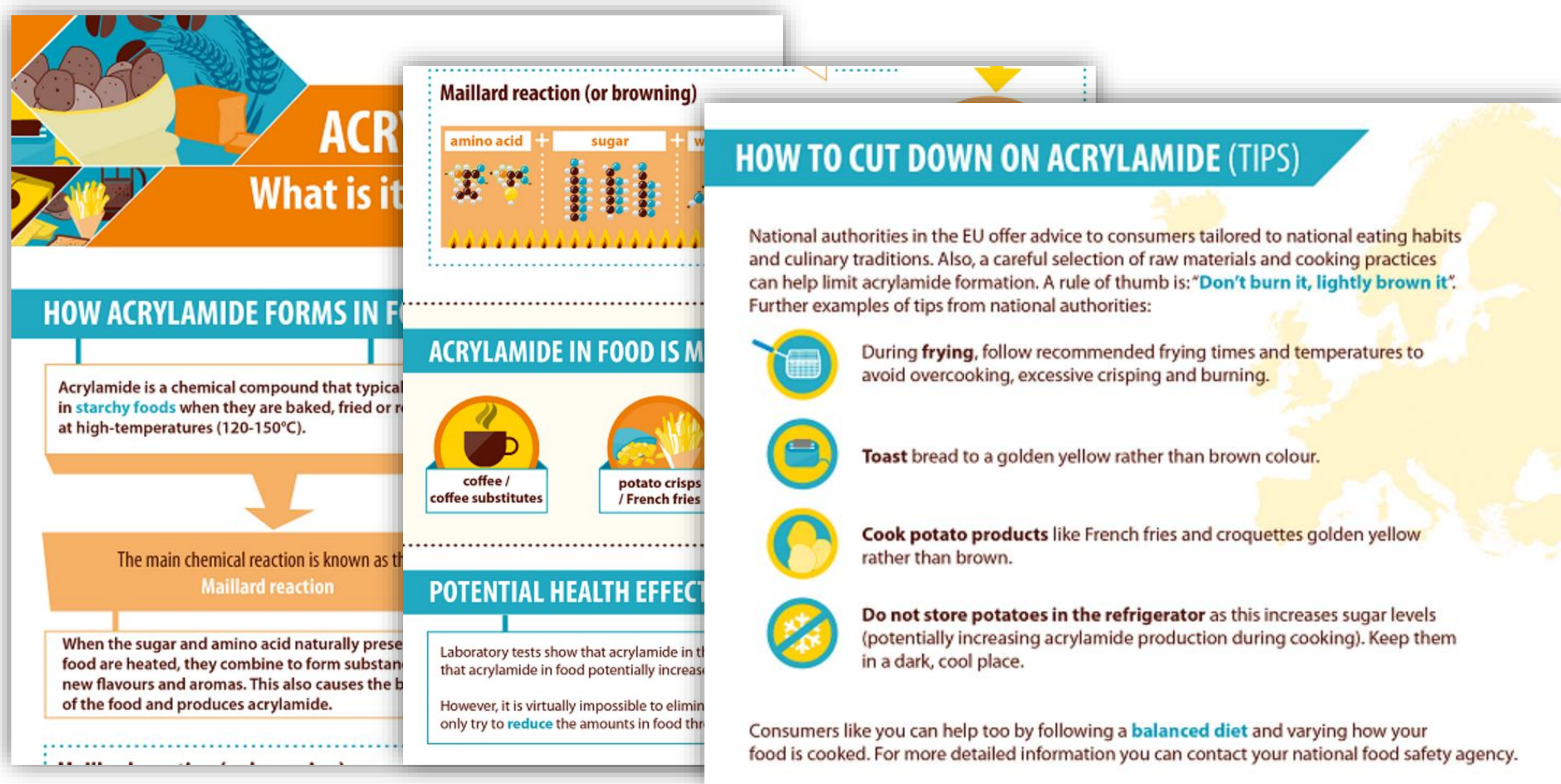
acrylamide

Stadler R. H., Blank I., Varga N., Robert F., Hau J., Guy A. P., Robert M.-C., Riediker S.: Acrylamide from Maillard reaction products, Nature, 2002, 419, 449-450.

In what foods was it found?

- Starchy foods and their products (potatoes, cereals)
- Fried potato chips
- Fried potatoes
- Bread
- Roasted coffee
- Biscuits, candies, waffles
- Breakfast cereals
- Baby food

EFSA – Information about acrylamide



Legislation

- There are currently no regulatory maximum limits for acrylamide in food.
- COMMISSION RECOMMENDATION 2007/331/ES of 3 May 2007 on the monitoring of acrylamide levels in food
- COMMISSION RECOMMENDATION 2010/307/ES of 2 June 2010 on the monitoring of acrylamide levels in food
- The European Commission (EC) has introduced 'indicative values' for those food groups considered to contribute the most to consumer dietary exposure to acrylamide (CR 2013/647/EU).

12.11.2013 EN Official Journal of the European Union L 301/15

RECOMMENDATIONS

COMMISSION RECOMMENDATION

of 8 November 2013

on investigations into the levels of acrylamide in food

(Text with EEA relevance)

(2013/647/EU)

12.11.2013 EN Official Journal of the European Union L 301/15

RECOMMENDATIONS

COMMISSION RECOMMENDATION

of 8 November 2013

on investigations into the levels of acrylamide in food

(Text with EEA relevance)

(2013/647/EU)

Indicative Acrylamide Values Recommended by European Union

Foodstuff	Indicative Acrylamide Value (µg/kg)
French fries ready-to-eat	600
Potato crisps from fresh potatoes and from potato dough Potato-based crackers	1000
Soft bread ☐ Wheat based bread ☐ Soft bread other than wheat based bread	 80 150
Breakfast cereals (excl. porridge) ☐ bran products and whole grain cereals, gun puffed grain ☐ wheat and rye based products (non-whole grain and/or non-bran) ☐ maize, oat, spelt, barley and rice based products (non-whole grain and/or non-bran)	 400 300 200
Biscuits and wafers	500
Crackers with the exception of potato based crackers	500
Crispbread	450
Ginger bread	1000
Products similar to the other products in this category	500
Roast coffee	450
Instant (soluble) coffee	900
Coffee substitutes ☐ coffee substitutes mainly based on cereals ☐ other coffee substitutes	 2000 4000
Baby foods, other than processed cereal foods ☐ not containing prunes ☐ containing prunes	 50 80
Biscuits and rusks for infants and young children	200
Processed cereal based foods for infants and young children, excl. biscuits and rusks	50

How to reduce AA levels in French fries???

A “Toolbox
Acrylam
Produ

Acrylamide
Acrylamide is a su
in foods as a result
baking, grilling, c
cancer in animals a
cause cancer in h
probably been par
cooking, because
experts have rec
levels of acrylamid

Acrylamide has be
including those pr
at home. It is fou
potatoes as well a
as crisps, biscuits a

FOODDRINK EUROPE

Annex 1 to FCP/AATEC/033/11

Methods of Reduction for finished French Fries

The following “Tools” have been used successfully to reduce levels of acrylamide in French fries. Manufacturers are advised to select those “Tools” that are most suitable to their type of product, process methods and product quality specification. euppa@fvphouse.be

Raw Materials Selection	Recipe Design	Process Design	Finished Product Attributes*
• Only use (low sugar) potato varieties suitable for fried potato products • Store potatoes climate controlled > 6° C: check temperature and humidity • Suppress sprouting in stored potatoes using CIPC or equivalent • Check in-coming potato lots at plant through fry colour testing or other tools to measure reducing sugars • Remove immature tubers	• Cut thicker French fries; thicker French fries contain less acrylamide than thinly cut French fries through the surface area/volume effect	• Blanching potato strips in water is the most important tool to control reducing sugar levels before frying • Addition of disodium diphosphate directly after blanching can reduce acrylamide levels in the final product through pH effect	• Give clear cooking instructions on pack: fry at max 175 °C; do not overcook; aim for light golden colour; when cooking smaller amounts reduce cooking time • Check final colour against product specification after frying according to cooking instruction

* This is intended for the final preparation before consumption

Acrylamide in Food on European market

Table 3: Number of analytical samples for each sampling year by the respective coun

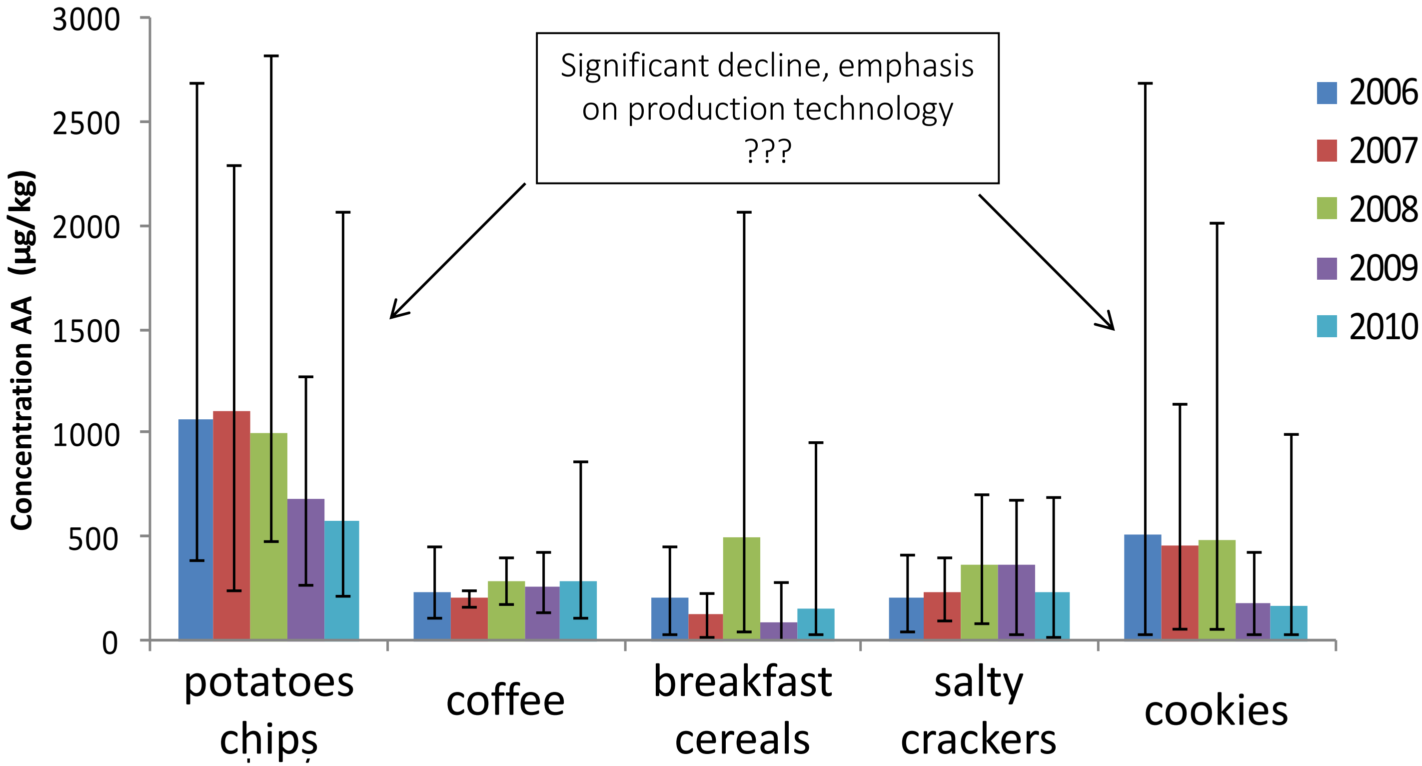
Country	2010	2011	2012	2013	Total
Austria	99	73	82	-	**254**
Belgium	169	192	175	-	**536**
Bulgaria	-	44	-	-	**44**
Cyprus	41	43	42	-	**126**
Czech Republic	45	78	63	-	**186**
Denmark	120	117	118	-	**355**
Estonia	30	42	12	-	**84**
Finland	-	120	10	6	**136**
France	56	165	176	-	**397**
Germany	812	986	1 065	-	**2 863**
Greece	80	52	50	-	**182**
Hungary	30	36	48	-	**114**
Ireland	66	54	49	-	**169**
Italy	165	155	217	-	**537**
Lithuania	10	42	40	-	**92**
Netherlands	62	-	-	-	**62**
Norway	51	-	-	-	**51**
Poland	-	141	-	-	**141**
Romania	-	80	86	40	**206**
Slovakia	125	99	115	54	**393**
Slovenia	41	128	77	-	**246**
Spain	107	41	76	44	**268**
Sweden	56	104	96	-	**256**
United Kingdom	93	199	250	-	**542**
Total	**2 258**	**2 991**	**2 847**	**144**	**8 240**

Table 6: Distribution of acrylamide (AA) levels in µg/kg

	Food category[k]	n[a]	LC[b]	Mean MB [LB-UB][c]	P95 MB [LB-UB][c]
1	**Potato fried products (except potato crisps and snacks)**	**1 694**	**14.3**	**308 [303–313]**	**971**
1.1	French fries and potato fried, fresh or pre-cooked, sold as ready-to-eat	877	12.7	308 [302–314]	904
1.2	French fries and potato fried, fresh or pre-cooked, sold as fresh or pre-cooked, analysed as sold	74	40.5	367 [362–372]	1 888
1.3	French fries and potato fried, fresh or pre-cooked, sold as fresh or pre-cooked, prepared as consumed[d]	557	15.3	239 [236–242]	656
1.4	French fries and potato fried, fresh or pre-cooked, sold as fresh or pre-cooked, preparation unspecified	90	15.6	368 [361–375]	1 468
1.5	Other potato fried products[e]	96	2.1	606 [606–607]	1 549
2	**Potato crisps and snacks**	**34 501**	**0.2**	**389 [388–389]**	**932**
2.1	Potato crisps made from fresh potatoes	31 467	0.1	392	949
2.2	Potato crisps made from potato dough	2 795	0.5	338	750
2.3	Potato crisps unspecified	216	7.9	519 [516–521]	1 465
2.4	Potato snack other than potato crisp	23	4.3	283	-
4	**Soft bread**	**543**	**48.8**	**42 [36–49]**	**156**
4.1	Wheat soft bread	302	45.0	38 [33–44]	120
4.2	Other soft bread	107	40.2	57 [51–62]	240
4.3	Soft bread unspecified	134	64.2	40 [31–50]	141

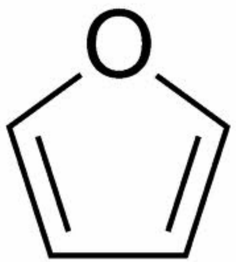
efsa
European Food Safety Authority

Monitoring of acrylamide levels (2006 – 2010)



Acrylamide monitoring (2006 – 2010), altogether 526 samples, 18 foods categories

FURAN



Furan

- Furan and its derivatives are naturally occurring compounds. They are found in a very low concentration in a variety of food and beverages where they are involved in taste and smell.

- They are formed during thermal technological or culinary processing of food and food raw materials (baking, frying, grilling, roasting or pasteurization and sterilization.
- They are the major group of substances that are formed during the Maillard reaction.

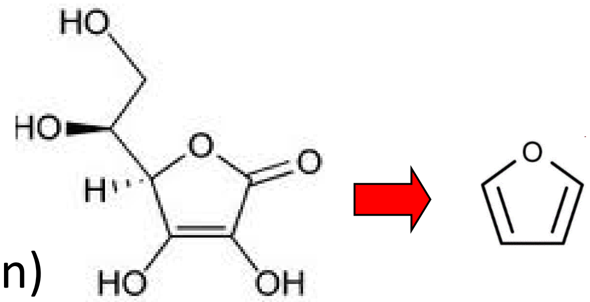
- Potential human carcinogen, genotoxic and hepatotoxic, toxic are primarily intermediates resulting from biotransformation.

Highest furan findings

- Roasted coffee
- Bread crust
- Preserved products
- Baby food
- Soy sauce
- Caramel
- Potato chips
- Cookies

UCT PRAGUE

Formation of furan in food



- Precursors
  - Amino acids
    - (Strecker degradation, Maillard reaction)
- Carbohydrates (MR)
- Ascorbic acid
- Lipids:
  - Carotenoids
  - Polyunsaturated fatty acids

- Maillard reaction of reducing sugars and amino acids
- Degradation of some amino acids
- Degradation of reducing sugars
- Oxidation of ascorbic acid
- Oxidation of carotenoids
- Oxidation of polyunsaturated fatty acids

European Food Safety Authority

EFSA Journal 2011; 9(9):2347

SCIENTIFIC REPORT OF EFSA

Update on furan levels in food from monitoring years 2004-2010 and exposure assessment[1]

European Food Safety Authority[2, 3]

European Food Safety Authority (EFSA), Parma, Italy

ABSTRACT

Furan, which can be formed in a variety of heat-treated commercial foods, has been shown to be carcinogenic in animal experiments. The current report provides an update to include all data sampled and analysed between 2004 and 2010 and, in addition to previous reports, presents exposure estimates for different populations. The analysis includes a total of 5,050 analytical results for furan content in food submitted by 20 countries. The highest furan levels were found in coffee with mean values varying between 45 µg/kg for brewed coffee and 3,660 µg/kg for roasted coffee beans. The highest 95th percentile was reported for roasted coffee beans at 6,407 µg/kg. In the non-coffee categories, mean values ranged between 3.2 µg/kg for infant formula and 49 µg/kg for jarred baby food 'vegetables only', the latter also with the highest 95th percentile of 123 µg/kg. Mean furan exposure across surveys was estimated to range between 0.03 and 0.59 µg/kg b.w. per day for adults, between 0.02 to 0.13 µg/kg b.w. per day for adolescents, between 0.04 and 0.22 µg/kg b.w. per day for other children, between 0.05 to 0.31 µg/kg b.w. per day for toddlers and between 0.09 and 0.22 µg/kg b.w. per day for infants. A major contributor to exposure for adults was brewed coffee with an average of 85% of total furan exposure. Major contributors to furan exposure in toddlers and other children were fruit juice, milk-based products and cereal-based products, whereas in addition for toddlers jarred baby foods were major contributors. To reduce uncertainty associated to exposure estimates future testing should preferably target food products where limited results are available.

Furan in food

efsa
European Food Safety Authority

Product category	Furan content µg/kg							
	N	P05	P25	Median	Mean	P75	P95	Max
Coffee instant[1]	57	2.8-3	72	271	569	850	2118	2200
Coffee, roasted bean[1]	15	38	905	3998	3611	5303	6407	6407
Coffee, roasted ground[1]	88	19	296	1695	1786	2610	5749	6900
Coffee, not specified[1]	478	13	933	1819	1850	2481	4783	6500
Coffee ready-to-drink	68	0-5	0-5	11	37-40	53	154	360
Baby food	1322	0-2	4-6.6	22	28-29	42	79	224
Infant formula	11	0-2.2	0-2.5	0-2.5	0.2-3.2	0-2.5	2.2-10	2.2-10
Baked beans	56	0-4	5-10	21	23-24	32	57	80
Beer	102	0-1.6	0-2	0.14-3	3.3-5.2	4-8	13	28
Cereal product	181	0-0.3	0-4	5-10	15-18	20-20.5	60	168
Fish	43	0-0.3	0-1.2	2.4-4.3	17-18	16	86	172
Fruit juice	246	0-0.7	0-1.42	0-2	2-5	1.4-5	8-10	90
Fruits	108	0-1	0-2.4	0-5	2-5	2-6	13	36
Meat products	133	0-0.32	0-2	3-10	17-19	22	85	160
Milk products	64	0-0.18	0-0.32	0.4-0.9	5-6	7	20	80
Sauces	245	0-2.3	0-3.2	2.4-8	8.5-11	11	30	175
Soups	245	0-1.4	2.5-5	17	23-24	34	72	225
Soy sauce	51	0-3	13	19	23-24	33	55	78
Vegetable juice	45	0-1	0-3	0-5	2-6	0-9	14	20
Vegetables	156	0-0.32	0-3	0-5	7-9	6-8	39	74
Others	471	0-0.32	0-2.4	7-8	15-16	22	61	164

[1]Coffee results reported for solid coffee

Furan in food

- According to the *efsa* estimated daily intake of furan is:
  - For ADULTS 0.26 *μg/Kg b.w.*
  - For CHILDREN 0.19 *μg/Kg b.w.*
  - For INFANTS 0.09 *μg/Kg b.w.*
- Some useful recommendations to reduce the amount of furan assumed are:
  - Allow the evaporation of furan opening and removing the product from jar a few minutes before consumption (heating it to 50°C in an open pan you can have a 46% reduction of the furan).
  - Prefer medium roast coffee and take care of very finely grind well in advance of consumption.

medium roast

EFSA

- From the point of view of food safety:

  FURAN = serious problem

- Collaboration with EU Member States - collecting furan data in different foods.
- Provides scientific advice for risk assessment.
- The necessity to monitor baby food (average of 25 µg / kg) also cereal products and roasted coffee.

Call for furan and its methyl analogues (2-methylfuran and 3-methylfuran) occurrence data in food

(M-2016-0012/ Furan and its methyl analogues in food)

Deadline for data submission: 31 July 2016

Background

Furan occurs in a variety of foods such as coffee, canned and jarred foods including baby food containing meat, and various veg
3-methylfuran, have been found con
during thermal processing and are like

The Scientific Panel on Contaminants
report on provisional findings on fura
data it appeared that there is a relativ
and the doses in experimental anim
genotoxic mechanism. However, a reli
toxicity and exposure.

SCIENTIFIC OPINION

EFSA Journal

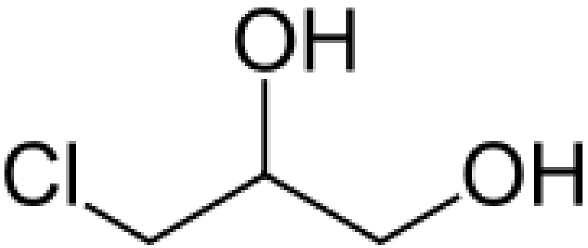
ADOPTED: 20 September 2017

doi: 10.2903/j.efsa.2017.5005

Risks for public health related to the presence of furan and methylfurans in food

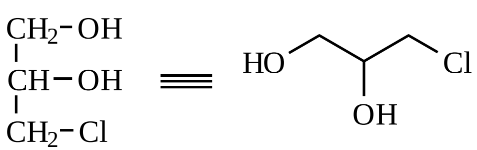
EFSA Panel on Contaminants in the Food Chain (CONTAM),
Helle Katrine Knutsen, Jan Alexander, Lars Barregård, Margherita Bignami, Beat Brüschweiler, Sandra Ceccatelli, Bruce Cottrill, Michael Dinovi, Lutz Edler, Bettina Grasl-Kraupp, Christer Hogstrand, Laurentius (Ron) Hoogenboom, Carlo Stefano Nebbia, Isabelle P Oswald, Annette Petersen, Martin Rose, Alain-Claude Roudot, Tanja Schwerdtle, Christiane Vleminckx, Günter Vollmer, Kevin Chipman, Bruno De Meulenaer, Michael Dinovi, Wim Mennes, Josef Schlatter, Dieter Schrenk, Katleen Baert, Bruno Dujardin and Heather Wallace

3-MCPD

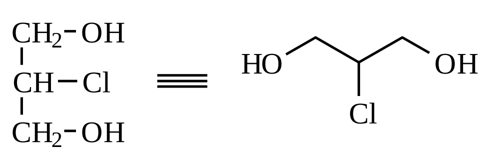


Chloropropanols and their esters

- Chloropropanols - processing / technological contaminants
  - 1978 *Velíšek J., Davídek J., Hajšlová J., Kubelka V., Janíček G., Mánková B.: Chlorohydrins in protein hydrolysates. Z. Lebensm. Unters. Forsch., 167, 241-244*
- Esters of chloropropanols with fatty acids
  - 1980 *Velíšek J., Davídek J., Kubelka V., Janíček G., Svobodová Z., Šimicová Z.: New chlorine-containing organic compounds in protein hydrolysates. J. Agric. Food Chem., 28, 1142* – 1144
- Toxicological assessment
  - potential carcinogens
  - mutagenic, chemosterile and nephrotoxic effects



3-chlorpropan-1,2-diol (3-MCPD)

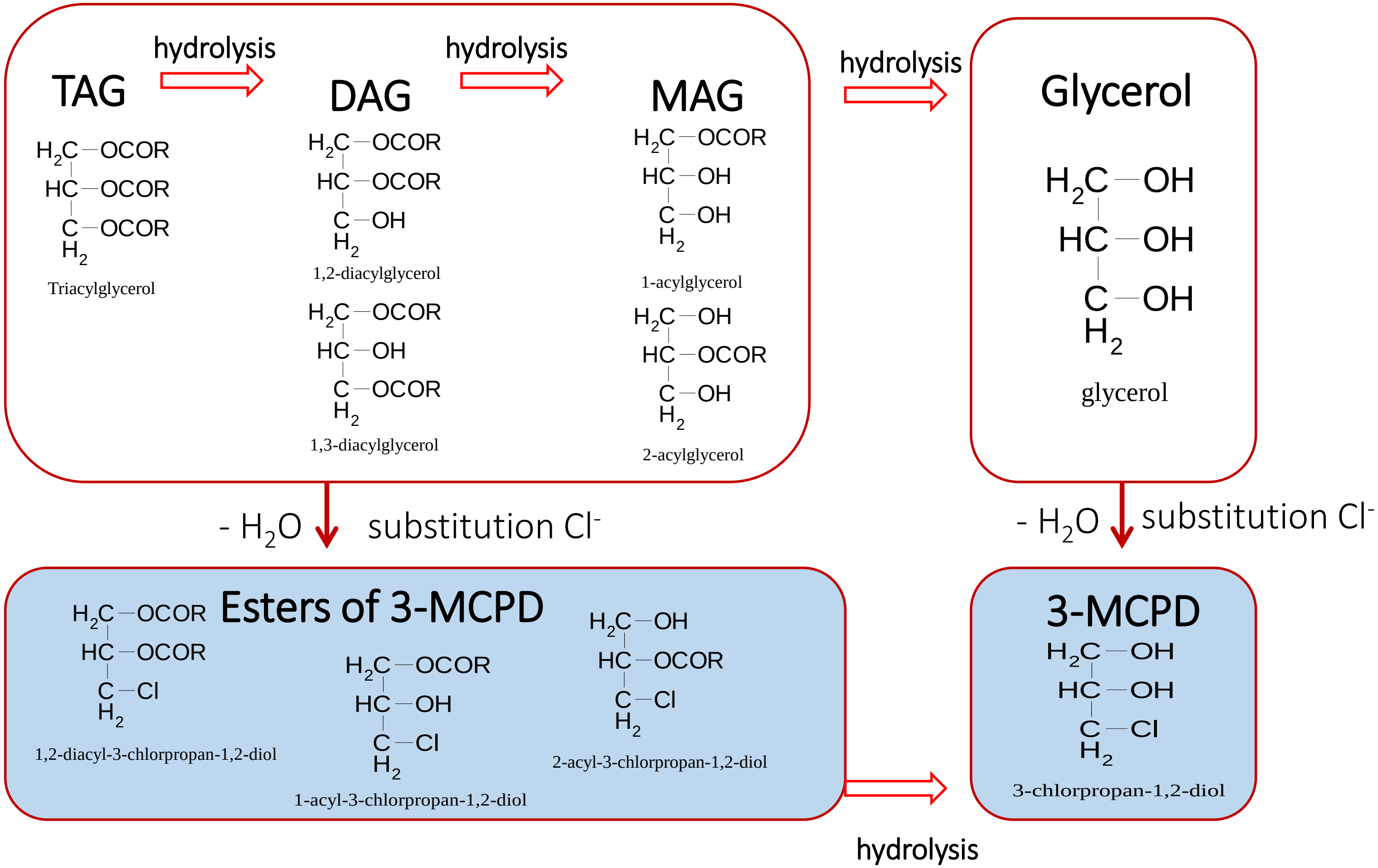


2-chlorpropan-1,3-diol (2-MCPD)

Formation of 3-MCPD in food

- naturally occurring levels in the raw materials
- storage of raw materials
- use of chlorinated water for washing purposes
- commercial processing treatments including baking, evaporation, fermentation, malting,
- pasteurization, roasting, smoking, spray drying, sterilization.
- migration from food contact materials
- storage of prepared products
- domestic preparation including baking, boiling, frying, grilling and toasting

Formation pathway of 3-MCPD



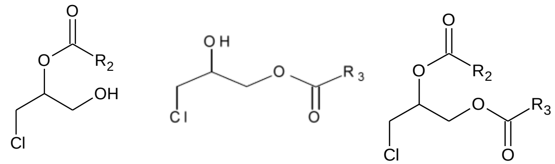
Chloropropanol precursors

- Precursors
  - lipids (triacylglycerol's, partial acylglycerol's, phospholipids), glycerol, allyl alcohol (garlic)
  - Additives derived from acylglycerols
  - salt (sodium chloride, chloride ions, chlorinated water)

Factors

- lipid content (glycerol)
- salt content
- water content (water activity)
- processing conditions (time, temperature, pH)
- substances causing decomposition
- lipase

3-MCPD esters

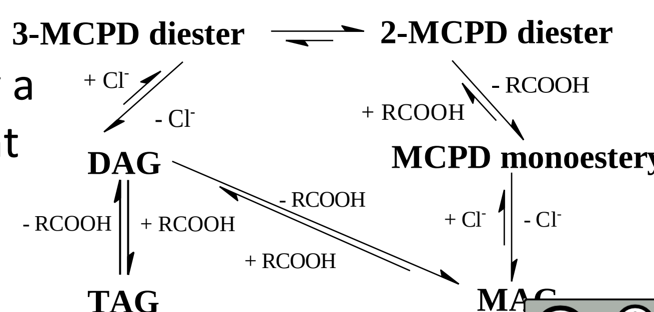


- **Formation:** refining of vegetable oil (180-250 °C)
  - Palm oil > 4000 µg/kg
  - rapeseed oil < 1500 µg/kg
- Highest exposure – usage of refined palm oil as a raw material for food production
- **Risk:** release of free 3-MPCD during gastrointestinal tract digestion
- **Precursors:** phospholipids, chloride ions, glycerol tri-, di- or monoacylglycerol's

Findings in different types of food (EFSA, 2013)

food	3-MCPD esthers (µg/kg)
margarine	< 150-7700
Breakfast cereals	40-888
Baby food	< 75-588
knäckebrot	420-580
French fries	35-397
Roasted coffee	< 100-390
Toast bread	60-160

→ The formation of 3-MCPD esters is accompanied by a process of their degradation during the heat treatment (isomerization, deacylation, dechlorination)



Glycidol and its esters

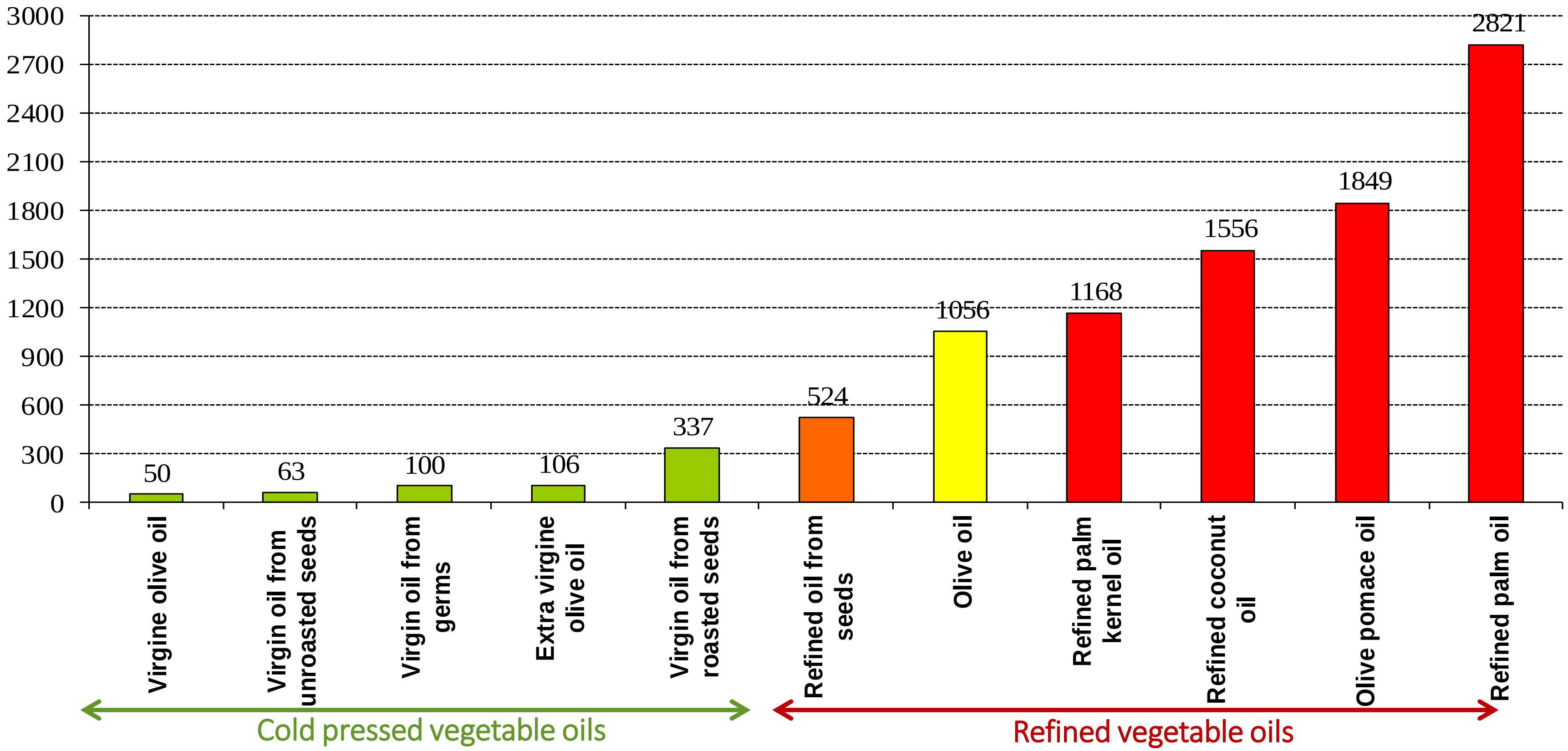
Glycidol (2,3-Epoxy-1-propanol)

- alcohol and epoxy functional groups
- probably human carcinogen group 2A (IARC, 2000)

Glycidol esters (GE)

- Formation: refining of vegetable oil (>200 °C) → deodorizing processes
- Precursors: DAG (MAG)
- Risk: release of free glycidol during gastrointestinal tract digestion

Esters of 3-MCPD in vegetable oils and fats



3-MCPD in food

Food Group	Number of Samples	3-MCPD fatty acid esters level (µg/kg), expressed as 3-MCPD	
		Mean*	Minimum – Maximum
Breakfast cereal	20	7	ND# - 43
Noodles	20	53	ND - 210
Biscuit	25	440	50-860
Meat, and its products	30	19	ND-280
Poultry, and its products	15	23	ND-160
Fish, and its products	15	77	ND-280
Nuts and seeds	15	5	ND for all samples
Fats and oils	20	390	ND - 2500
Condiments and sauces	15	75	ND - 490
Snacks	25	270	9 - 1000
Bakery wares	35	120	ND - 410
Chinese pastry	20	270	ND - 1200
Dairy products	15	17	ND - 230
Soup and non-alcoholic beverages	20	12	ND - 61
Infant formula	10	100	26 -290

3-MCPD in food

efsa European Food Safety Authority

Oils	Number of Samples	3-MCPD fatty acid esters level (μg/kg), expressed as 3-MCPD	
		Mean	Minimum – Maximum
Peanut oil	3	570	500 - 650
Canola oil	3	110	100 - 130
Corn oil	3	280	120 - 470
Olive oil	3	390	250 - 640
Grape seed oil	3	1180	390 - 2500
Extra virgin olive oil	1	10	ND

SCIENTIFIC OPINION

EFSA Journal

ADOPTED: 3 March 2016

doi: 10.2903/j.efsa.2016.4426

Risks for human health related to the presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food

EFSA Panel on Contaminants in the Food Chain (CONTAM)

Abstract

EFSA was asked to deliver a scientific opinion on free and esterified 3- and 2-monochloropropane-1,2-diol (MCPD) and glycidyl esters in food. Esters 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. 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. 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 (P95) 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, likely via a genotoxic mode of action. The Panel selected a $BMDL_{10}$ 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 T25 value of 10.2 mg/kg bw per day for neoplastic effects in rats. The margins of exposure (MoEs) were 11,300–102,000 and 4,900–51,000 across surveys and age groups at mean and P95 exposures, respectively. An exposure scenario for infants receiving formula only resulted in MoEs of 5,500 (mean) and 2,100 (P95). MoEs of 25,000 or higher were considered of low health concern.

efsa

European Food Safety Authority

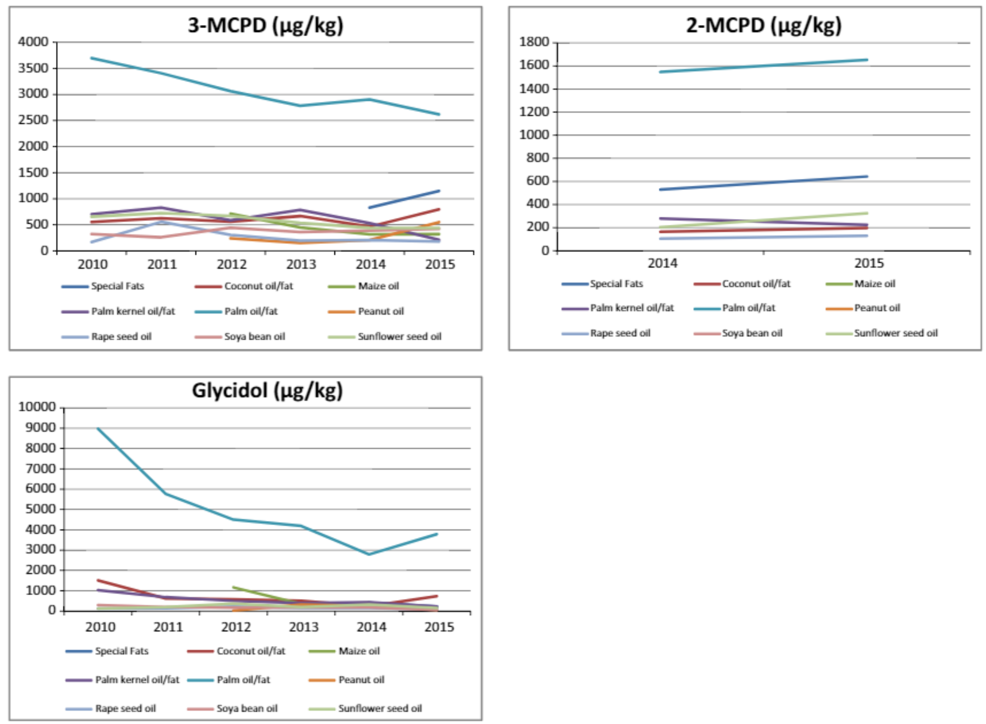


Figure 5: Graphs showing the evolution across the years 2010–2015 of the average level (μg/kg) of 3- and 2-monochloropropanediol (MCPD) from esters and glycidol from esters (all expressed as free moiety) in different types of oils and fats

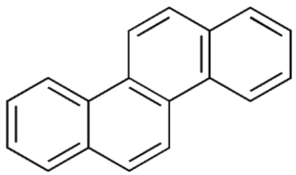
UCT PRAGUE

Polycyclic aromatic hydrocarbons (PAHs)

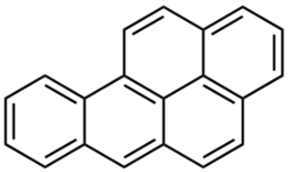
UCT PRAGUE

What are PAHs?

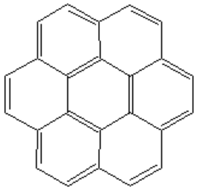
- Compounds composed of two or more aromatic rings



chrysene



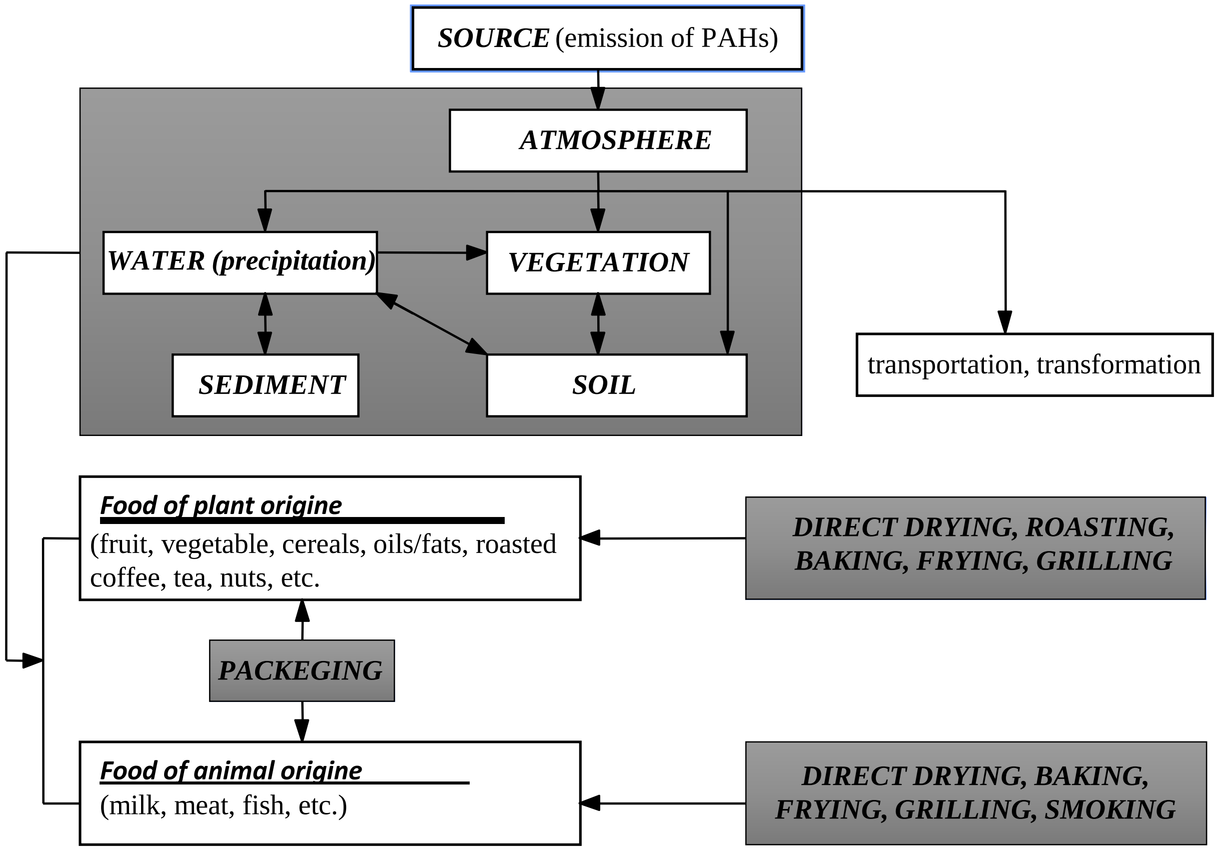
benzo[*a*]pyrene



coronen

- The most commonly observed: 2-6 aromatic rings
- Formed during incomplete combustion of organic matters
- Very stable - able to last for a long time in the environment
- **Sources:** forest fires, oil seeps, oil spills, vulcanic eruption, burning of fossil fuel, coal tar, garbage, municipal solid waste incineration, petroleum spills
- **Teratogenic, mutagenic and carcinogenic potential**

Mechanisms of food contamination by PAHs



Contamination of food by PAHs

- Atmospheric deposition
  - (transport and disposal from the environment)
- Cooking practices
  - Drying
  - Smoking
  - Grilling
  - Baking
  - Frying
  - Roasting

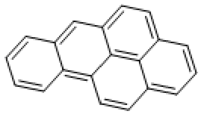
Tested food

- Smoked meat products
- Vegetable oils
- Smoked fishes
- Non-smoked fishes
- Sea food
- Baby / infant food

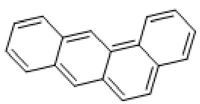
PAHs legislation

- **1984** – United States Environmental Protecting Agency (US EPA) – ***16 US EPA PAH***
- **2001** – European Food Safety Authority (EFSA) – ***BaP as a marker of carcinogenic PAHs***
- **2002** – SCIENTIFIC COMMISSION for food– ***16 EU PAHs***
- **2006** – COMMISSION REGULATION 1881/2006 ES – limits for the food commodities
- **2008** – ***PAH8, PAH4, PAH2***
- ***2012*** – COMMISSION REGULATION 835/2011 ES

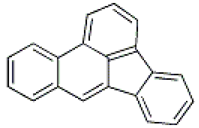
PAHs



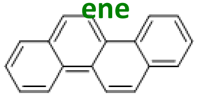
Benzo(a)pyrene



Benzo(a)antracene

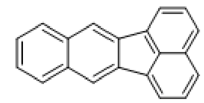


Benzo(b)fluoranthene

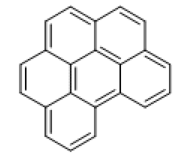


Chrysene

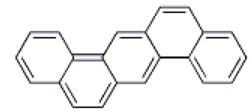
US EPA PAU (16 PAU)	EU PAU (16 PAU)
Acenaftene	5 - metylchrysene
Acenaftylene	Benzo(*c*)fluorene
Antracene	Benzo(*j*)fluorantene
Fluorene	Cyklopenta(*cd*)pyrene
Fluorantene	Dibenzo(*a,e*)pyrene
Naftalene	Dibenzo(*a,h*)pyrene
Pyrene	Dibenzo(*a,i*)pyrene
Fenantrene	Dibenzo(*a,l*)pyrene
Benzo(*a*)antracene	
Benzo(*a*)pyrene	
Benzo(*b*)fluorantene	
Benzo(*k*)fluorantene	
Benzo(*g,h,i*)perylene	
Chrysene	
Dibenzo(*a,h*)antracene	
Indeno(1,2,3-cd)pyrene	



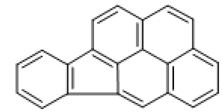
Benzo(k)fluorantene



Benzo(ghi)perylene



Dibenzo(ah)antracene



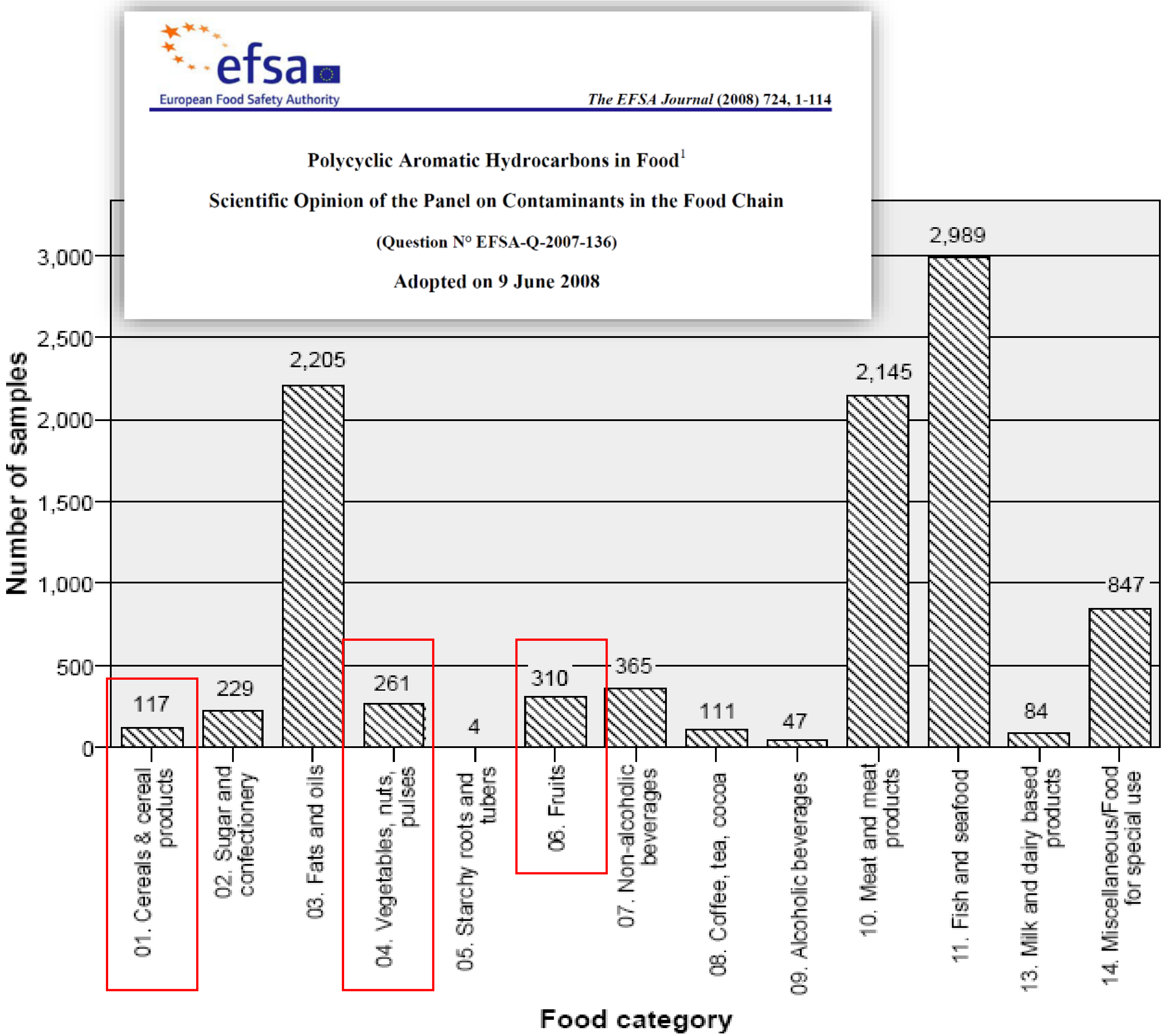
Indeno(1,2,3-cd)pyrene

PAHs toxicity

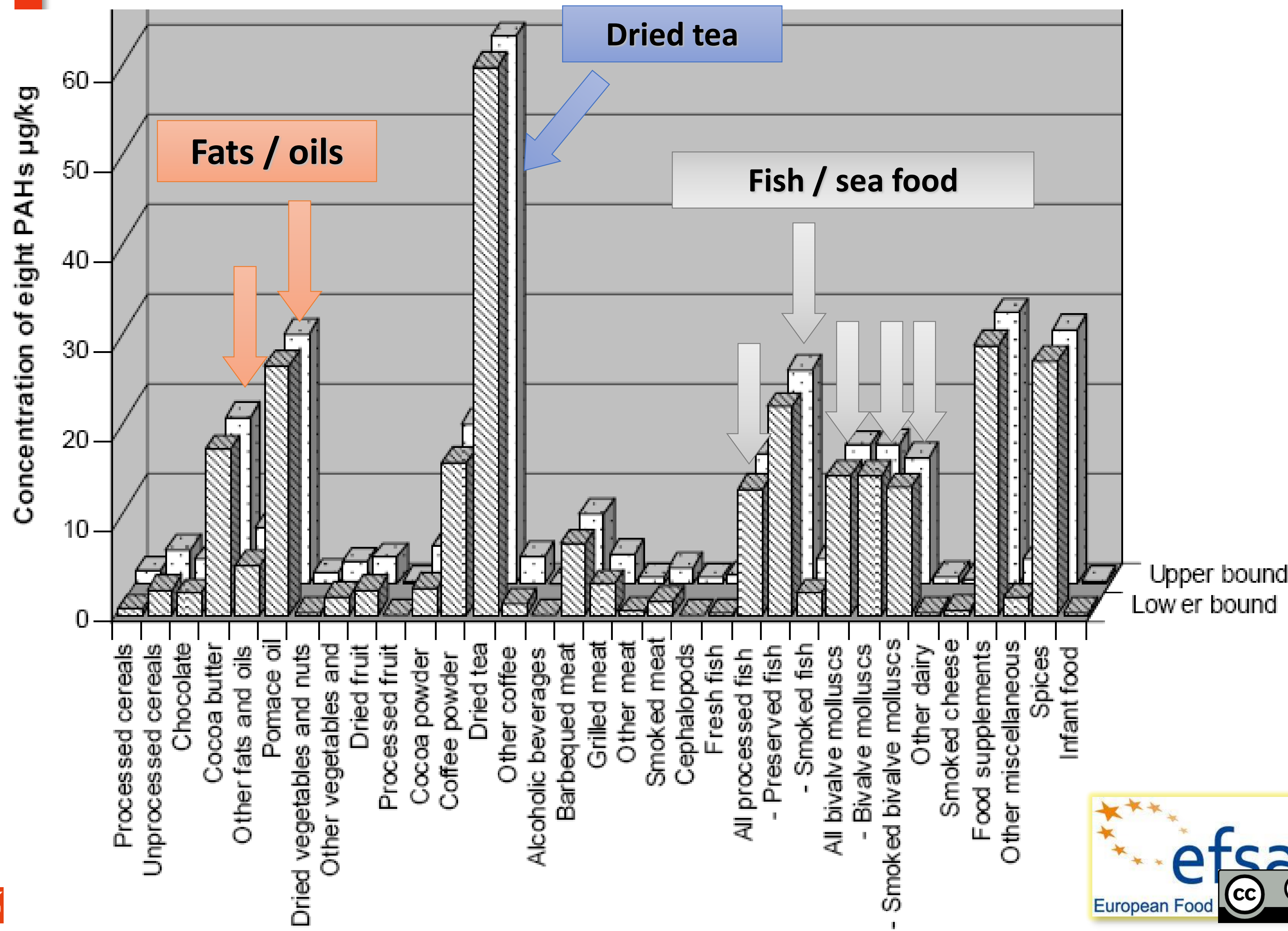
* European Commision (2002)
** IARC (1987)

PAH	# of rings	Genotoxicity*	Carcinogenity**
Phenanthrene	3	unknown	?
Anthracene	3	limited data	positive
Fluoranthene	4	unknown	positive?
Pyrene	4	negativ	?
Triphenylene	4	limited data	negative?
Benzo[b]fluorene	4	genotoxic	positive
Benz[a]anthracene	4	genotoxic	Positive
Benzo[c]phenanthrene	4	limited data	positive?
Chrysene	4	genotoxic	Positive
Benzo[b]fluoranthene	5	genotoxic	Positive
Benzo[j]fluoranthene	5	genotoxic	Positive
Benzo[k]fluoranthene	5	genotoxic	Positive
Benzo[a]pyrene	5	genotoxic	Positive
Benzo[e]pyrene	5	Unknown	?
Perylene	5	limited data	negative?
Dibenzo[a,h]pyrene	6	genotoxic	positive
Dibenzo[a,i]pyrene	6	genotoxic	positive
Dibenzo[a,l]pyrene	6	genotoxic	positive
Dibenzo[a,e]pyrene	6	genotoxic	positive

Number of analyzed samples



Mean concentrations of the sum of the eight PAHs in 4,065 samples split across 33 food categories/subcategories (EU market)



efsa
European Food

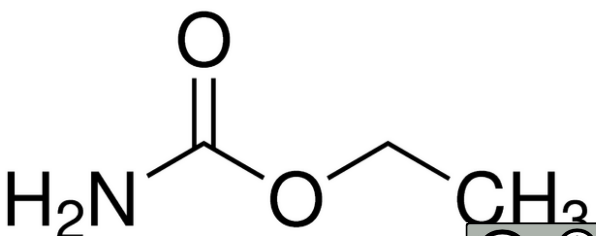
Consumer exposure to PAHs

efsa
European Food Safety Authority

Category	Consumption	Exposure			
	Median g/day	BaP ng/day	PAH2 ng/day	PAH4 ng/day	PAH8 ng/day
Cereals and cereal products	257	67	129	257	393
Sugar and sugar products including chocolate	43	5	13	25	39
Fats (vegetable and animal)	38	26	112	177	239
Vegetables, nuts and pulses	194	50	124	221	378
Fruits	153	5	40	75	87
Coffee, tea, cocoa (expressed as liquid)	601	21	55	106	156
Alcoholic beverages	413	4	12	25	74
Meat and meat products and substitutes	132	42	107	195	279
Seafood and seafood products	27	36	140	289	421
Fish and fishery products	41	21	84	170	210
Cheese	42	6	12	20	30

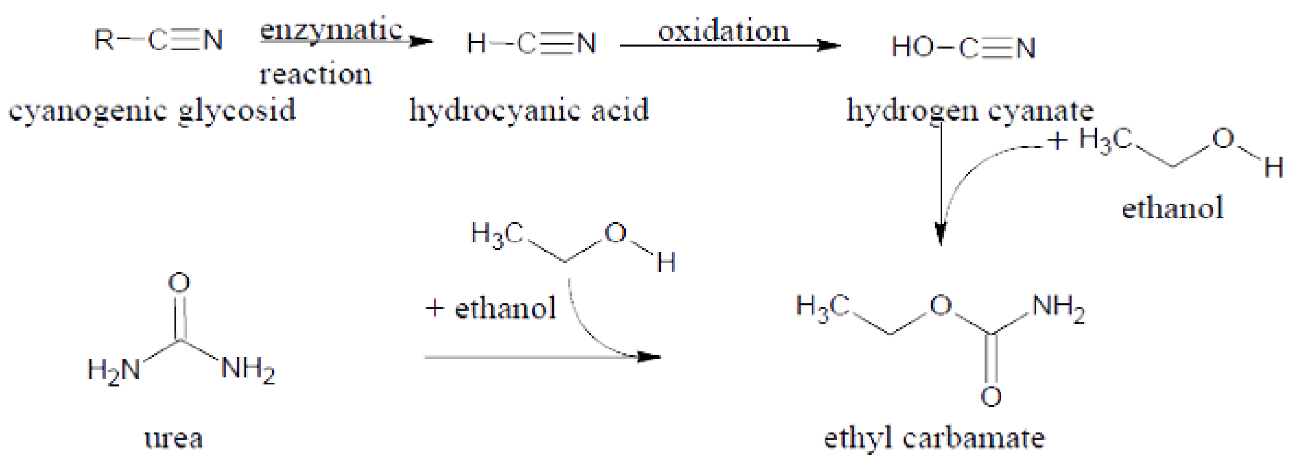
Ethyl carbamate (Urethane)

- Is a natural compound can be found in fermented foods and alcoholic beverages.
- It's the ethyl ester of carbamic acid.
- Is genotoxic and multisite carcinogen (especially for lung and stomach).
- The FAO / WHO has estimated that it takes 0.3 mg / kg b.w. per day to increase for 10% the incidence of lung neoplasms in mice.

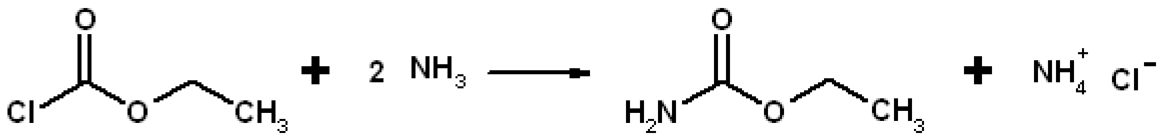


Formation of ethyl carbamate

- Through various precursors.
- In spirits cyanogenic glycosides reacts with ethanol and that leads to the formation of ethyl carbamate.



Ethyl carbamate (Urethane) in food



Food/ beverage group	No. of samples	EC concentration (µg/kg) Mean	Range
Fermented cereals and grains products	**25**	**2.01**	**ND – 8.6**
➢ Bread/ Rolls/Buns	15	2.63	ND – 8.6
• Chinese steamed bun	5	0.20	ND
• Bread and toasted bread	10	3.85	1.0 – 8.6
➢ Crackers	10	1.08	ND – 5.1
Legumes (fermented soy products)	**20**	**121**	**ND – 650**
• Fermented bean curd	6	80.7	11 – 130
• Fermented red bean curd	5	386	150 – 650
• Fermented black soy bean	5	2.22	ND – 7.0
• Stinky tofu	4	0.20	ND
Preserved /dried vegetables	**45**	**3.03**	**ND – 10**
Meat products (fermented pork products)	**5**	**18.0**	**12 – 29**
Fermented dairy products	**11**	**0.39**	**ND – 1.1**
• Cheese	5	0.44	ND – 1.1
• Yogurt	3	0.50	ND – 1.1
• Dairy-based fermented beverages	3	0.20	ND

Ethyl carbamate (Urethane) in food

Fermented fish products (salted fish)	**5**	**0.20**	**ND**
Condiments and sauces	**55**	**5.11**	**ND – 44**
• soy sauce	5	6.84	1.8 – 17
• oyster sauce	5	0.54	ND – 1.1
• vinegar	18	9.32	ND – 37
• condiment and savory sauces	27	2.84	ND – 44
Non-alcoholic beverages	**40**	**1.09**	**ND – 15**
➢ Vinegar drink (fruit vinegar)	5	1.54	0.4 – 3.0
➢ Tea (tea leaves)	35	1.03	ND – 15
• fully fermented tea (black tea)	5	3.26	ND – 15
• semi-fermented tea (Chinese tea)	30	0.65	ND – 5.1
Alcoholic beverages	**70**	**55.9**	**ND – 390**
➢ Beer/ale	15	1.13	ND – 5.8
➢ Wine or spirit made from cereals and grains	30	93.7	2.0 – 390
• Yellow wine	6	265	140 – 390
• Sorghum-based spirit	3	54.3	37 – 66
• Rice wine	21	50.4	2.0 – 330
- Chinese rice wine	12	32.1	3.3 – 62
- Sake	9	74.7	2.0 – 330
➢ Wine made from fruit			
• Grape wine	10	21.2	6.7 – 47
- Red wine	5	17.7	8.3 – 35
- White wine	5	24.7	6.7 – 47
• Plum wine	5	110	0.4 – 230
• Cider	5	6.90	ND – 31
➢ Compound alcoholic beverages	5	57.6	17 – 150
➢ Distilled spirits (Chinese distilled spirits)*	9	36.5	20 – 66

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

4. Natural toxic substances - the most important groups, legislative aspects

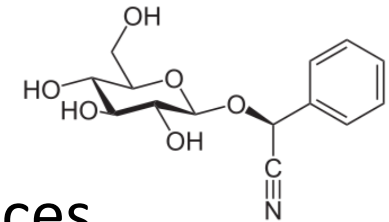
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

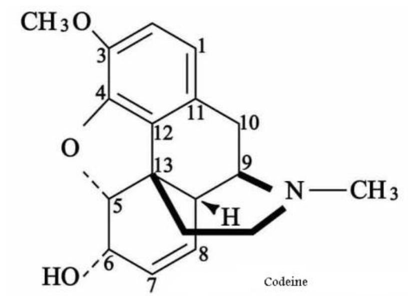
MINISTRY OF EDUCATION, YOUTH AND SPORTS

Natural Toxins

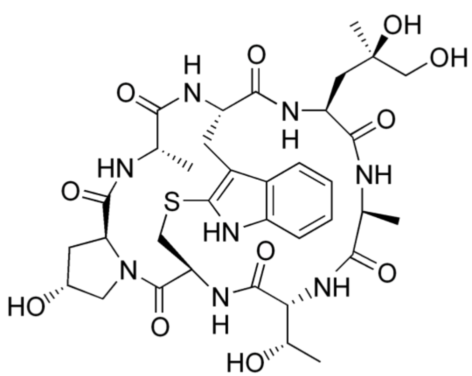
- Natural toxins are chemicals that are naturally produced by living organisms. These toxins are not harmful to the organisms themselves, but they may be toxic to other creatures, including humans, when eaten
- Usually, natural toxins are not acutely toxic, except in a few cases in animals
- Most of the natural toxins, particularly those occurring in plant-derived foods, induce adverse effects only after chronic ingestion or by allergic reactions.

Groups of Natural Toxins

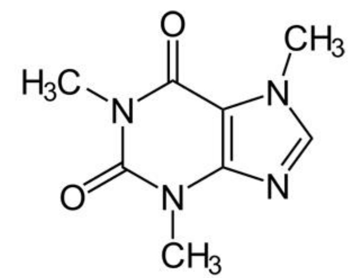




Natural Toxins



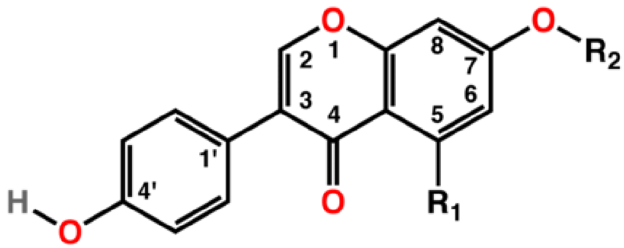
- Toxic phenolic substances (Phytoestrogens)
- Alkaloids
- Cyanogenic glycosides
- Saponins
- Glucosinolates
- Biogenic amines
- Bacterial toxins
- Fycotoxins
- Mushroom toxins
- Mycotoxin (Fusarium t., Aflatoxins)



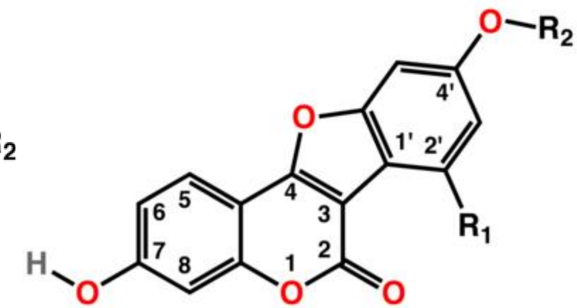
Phytoestrogens

- **Phytoestrogens are a group of plant-derived molecules that are named so because they posess an estrogen-like activity and they are similar like in human body.**
- When they are consumed, depending on the concentration in the diet and concentration of sex hormones in the body, they have estrogenic and anti-estrogenic effects.
- They include a group of chemicals such as **isoflavones, coumestans** and **lignans.**

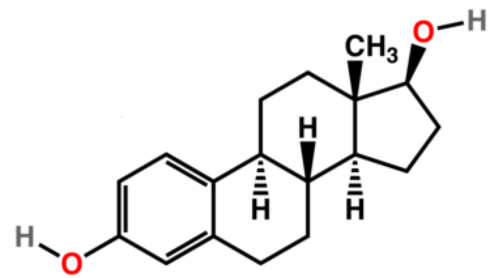
Chemical Structure



Isoflavones



Cumestran



Lignans

- Phytoestrogens are a diverse group of polyphenolic non-steroidal plant compounds that bind to human estrogen receptors.
- Isoflavones, cumestran and lignans are three of the most active in estrogenic effects in this class.
- The best studied of these compounds are **isoflavones**, phytoestrogens present in **soy** and **red clover.**

Sources of Phytoestrogens

- More than 300 foods have been shown to contain phytoestrogens

Most food Phytoestrogens

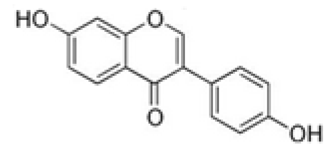
isoflavonoids	lignans	coumestans
Found in beans of legume family with soyabeans as major dietary source	Found in high fiber foods such as cereal brans and flaxseeds	Various beans such as split peas, long beans and red clover sprouts

Effects of phytoestrogens in humans

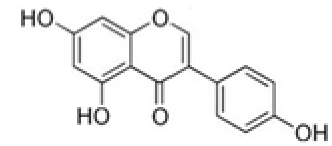
Phytoestrogens → Mainly: Women → Postmenopausal: Hot flushes; Uterus; Breast; Bones

- The effects are mostly from postmenopausal women, in particular hot flushes.
- Very little is known about the effects of these compounds on the bone, uterus and breast.
- This information is urgently required to allow evaluation for prevention of osteoporosis.
- Very little is known about the therapeutic potential of phytoestrogen in men.

Isoflavonoids

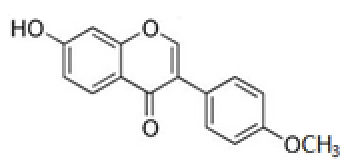


Daidzein

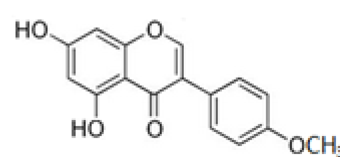


Genistein

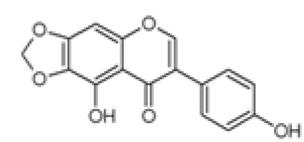
- Produced almost exclusively by the members of the *Fabaceae* (i.e., *Leguminosae*, or bean) family
- Some are termed antioxidants because of their ability to trap singlet oxygen
- Isoflavones (and closely related phytoestrogens) have grown popular as dietary supplements
- Soybeans are the most common source of isoflavones in human food; the major isoflavones in soybean are genistein and daidzein



Formononetin



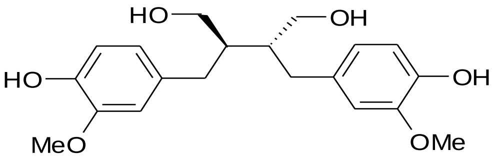
Biochanin A



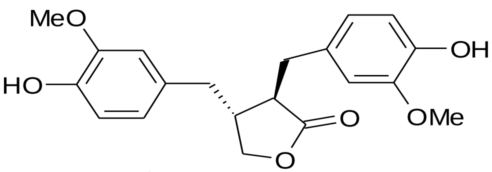
Irilone

Lignans

- phytoestrogens - biological active compounds
- structurally characterized by coupling of two phenylpropanoid units
- identified in woody tissues of trees already in the 19th century
- beneficial health effects - antitumor, antioxidant, both estrogenic and antiestrogenic activity, the protection against coronary heart disease
- the richest dietary source of lignans are flaxseeds



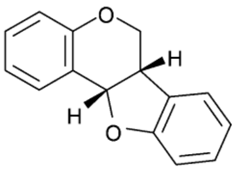
SECO



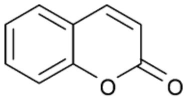
MAT

- **secoisolariciresinol (SECO)**
- **matairesinol (MAT)**

Coumestans

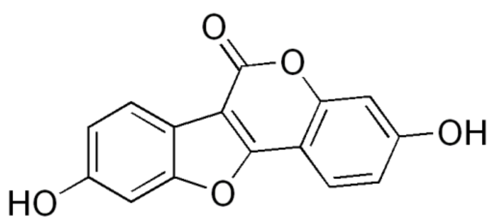


Pterocarpan

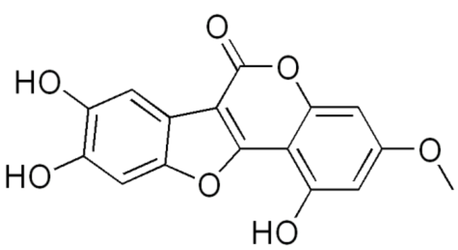


Coumarin

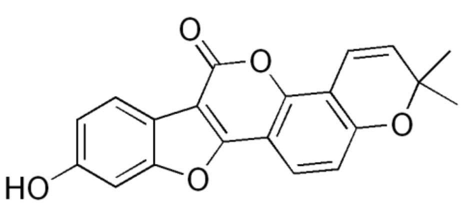
- Oxidation products of pterocarpan that are similar to coumarin
- Food sources high in coumestans include split peas, pinto beans, lima beans, and especially alfalfa and cloversprouts



coumestrol

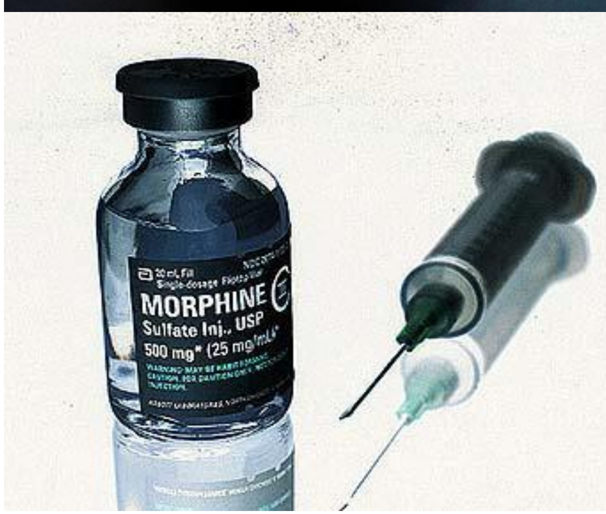


Wedelolactone



Plicadin

Alkaloids



Alkaloids

- Alkaloids have a large variety in their botanical & biochemical origin, in chemical structure and pharmaceutical action
- Families rich in Alkaloids: Apocynaceae, Rubiaceae, Solanaceae and Papaveracea.

Apocynaceae

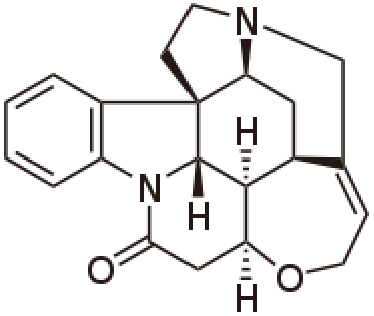
Rubiaceae

Solanaceae

Papaveracea

Alkaloids

- They may act as **protective** against insects and herbivores due to their bitterness and toxicity.
- They are, in certain cases, the final **products of detoxification** (**waste products)**.
- They, sometimes, act as **growth regulators** in certain metabolic systems
- Alkaloids are decomposed by heat, except **Strychnine** and **caffeine** (**sublimable**).



Strychnos nux-vomica

Alkaloids

- Within the plant, the amount of alkaloids can vary widely from part to part – some parts may contain no alkaloids.
- **<u>Distribution in Plant:</u>**
  - All Parts e.g. Datura.
  - Barks e.g. Cinchona
  - Roots e.g. Aconite
  - Fruits e.g. Black pepper
  - Leaves e.g. Tobacco
  - Latex e.g. Opium

Cinchona

Datura

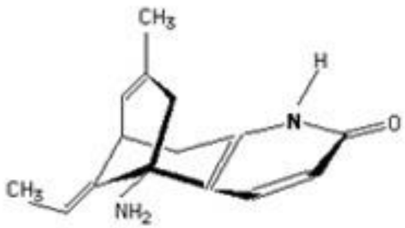
Black pepper

Aconite

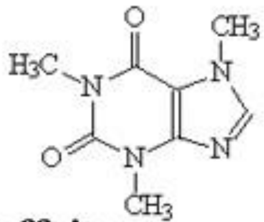
Opium

Tobacco

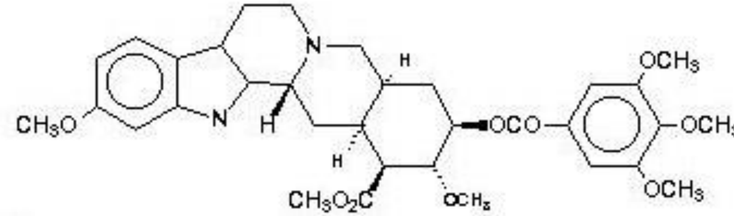
An Assortment of Alkaloids



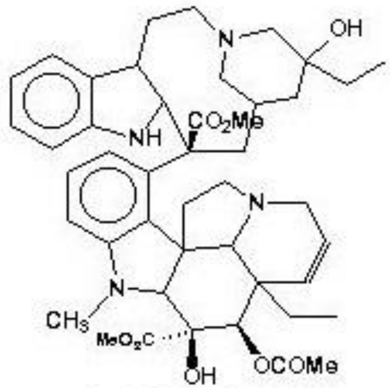
huperzine A
Chinese herbal medicine
nootropic



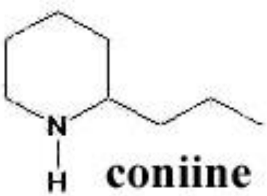
caffeine
Coffea arabica
study



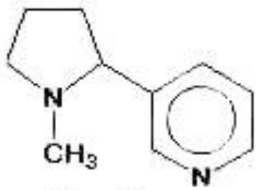
reserpine
Indian herbal medicine
antipsychotic



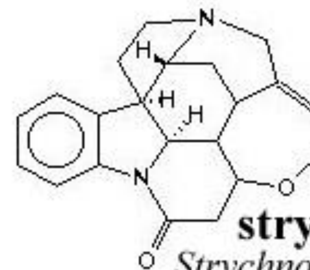
vinblastine
Madagascar periwinkle
antileukemic



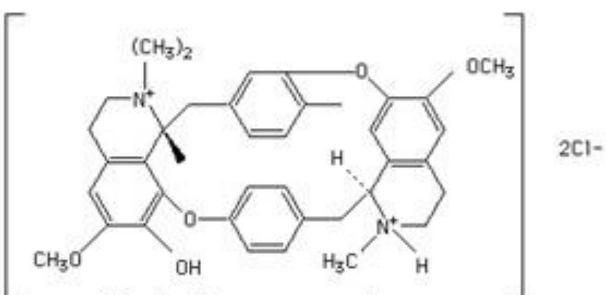
coniine
hemlock
ants, Socrates



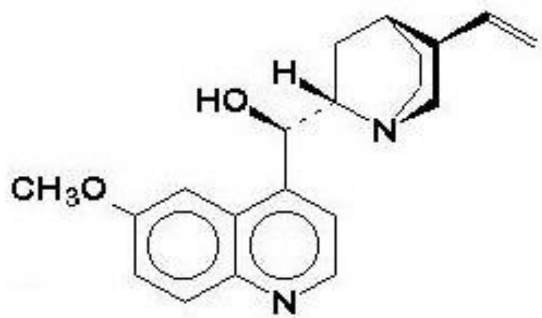
nicotine
tobacco
Black Leaf 40
insecticide



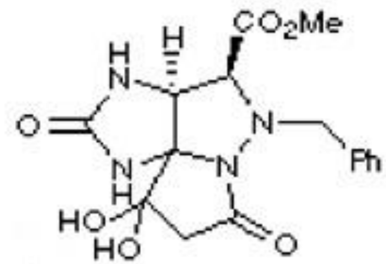
strychnine
Strychnos nux-vomica
rodenticide



D-tubocurarine
arrow poison, muscle relaxant for surgery

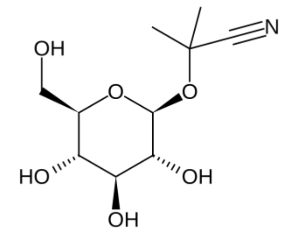


quinine
Cinchona tree, antimalarial



saxitoxin
deadly algal toxin
chemical warfare agent
CIA suicide pill

Cyanogenic glycosides




Cassava

- We know more than 50 cyanogenic glucosides
- They are bitter and primarily act as repellents
- Sources: plants (manioc, almond, apricot, peach..)
- Lethal intakes by humans: 0.5-3.5 mg/kg body weight
- Beans: 200-300 mg/100g → selected breeding of low-cyanide varieties
- Cassava: 1-60 mg/100 g → fermented cassava

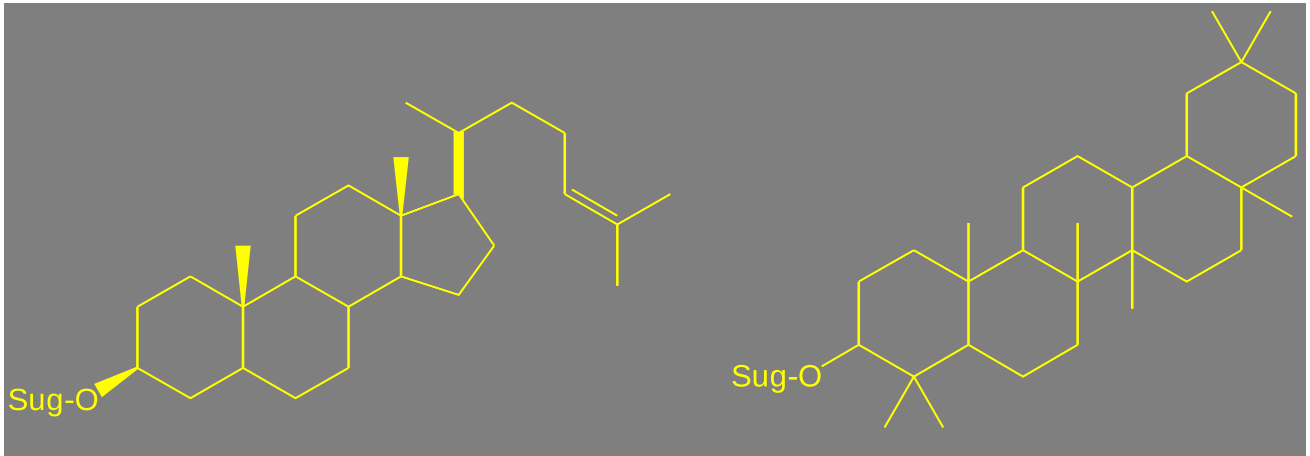

Almon

Most known cyanogenic glycosides

Glucoside	**Plants**	**HCN (mg/kg) content in fresh flesh**
Linamarin	Manioc, white clover, cultivated flax	Manioc-bitter type -peel of bulbs 840 -pulp of bulbs 330
Faseolunatin	Sugar bean	100-4000
Lotaustralin	Bird´s-food trefoil, white clover, manioc	
Linustatin Neolinustatin	Cultivated flax	-seeds 200-380
Prunasin	Plum tree	
Sambunigrin	Elder – Sambucus nigra	
Amygdalin	Plum tree, kernels of stone-fruits: bitter almonds, apricot, peach	Kernels of these plants approximately 3 %
Vicianin	Bob, vetch	
Taxifyllin	Common yew, bamboo	
Dhurrin	Sorghum	

Saponins

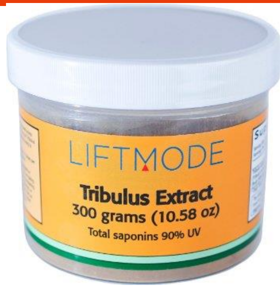
- Group of organic compounds that form persistent froth when shaken with water
- According to the nature of the aglycone saponins are classified into Steroidal and Triterpenoidal saponins



Steroidal Saponins

Triterpenoidal Saponins

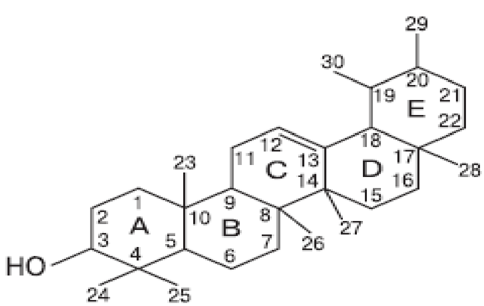
Steroidal saponins



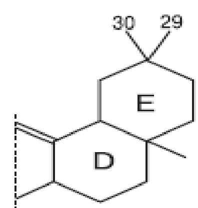
- In plants of such families as: **Liliaceae, Amaryllidaceae, Dioscoreaceae, Schrophulariaceae, Zygophyllaceae, etc.**
- Steroidal saponins - **great pharmaceutical importance** - relationship to compounds such as the sex hormones, cortisone, diuretic steroids, vitamin D and the cardiac glycosides.
- Some are used as starting materials for the synthesis of these compounds

Triterpenoid saponins

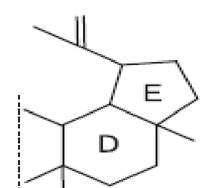
- In many triterpenoid saponins **oleanolic acid is sapogenin**.
- They are abundant in many dicotyledonous families, particularly the **Caryophyllaceae, Sapindaceae, Polygalaceae and Sapotaceae, Ranunculaceae, Papaveraceae, Araliaceae, Rubiaceae and Compositeae.**
- Altogether some 70 families are involved



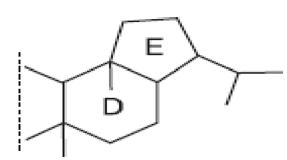
α-amyrin



α-amyrin



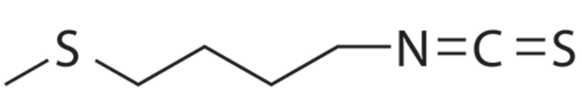
lupeol



hopan

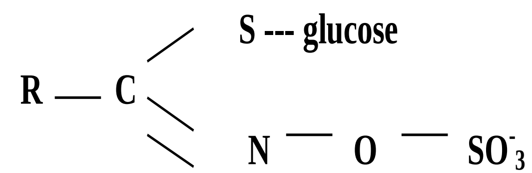
Glucosinolates

- Substances that can be considered as natural toxins, but also as antinutritives
- About 120 different glucosinolates are known to occur naturally in plants.
- Glycoalkaloids are thermostable, so you cannot destroy them by cooking, frying or drying. They bear temperatures higher than 300°C.
- Source: Found mainly in Brassicaceae, Resedaceae and Capparaceae families.

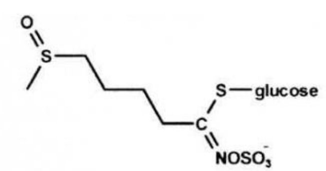


Erucin

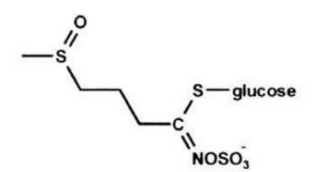
Glucosinolates



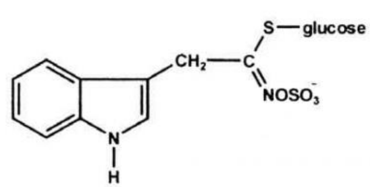
- Vegetables as cabbage, turnips, radish, mustard seed contain them in high concentration
- Some most important of them : erucin, glucobrassicin, glucosinalbin, glucoerucin, sinigrin, progoitrin
- They are of acrid taste and these characteristics are necessary in mustard and horseradish, but not in other species
- Toxicity: cytotoxic and mutagenic.



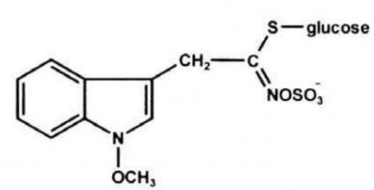
Glucoraphanin



Glucoiberin



Glucobrassicin



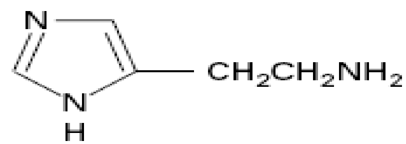
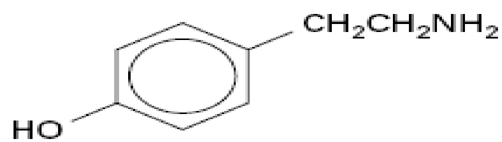
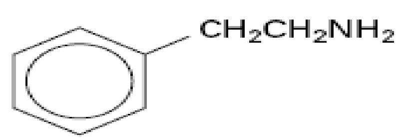
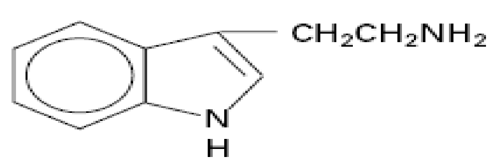
Neoglucobrassicin

Biogenic amines

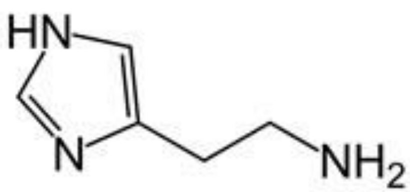
- Low molecular weight organic bases, which pose biological activity.
- The main producers of biogenic amines in foods are Enterobacteriaceae and Enterococci. (Enterobacteriaceae → cadaverine formation, lactobacilli → tyramine formation)
- Naturally present in animals, plants and microorganisms.
- Sources: fermented products, particularly wine, cheese, fish, and meat, fruits, vegetable
- Prevention : Pasteurization of cheese milk, good hygienic practice, and selection of starters with low decarboxylase activity

Biogenic amines

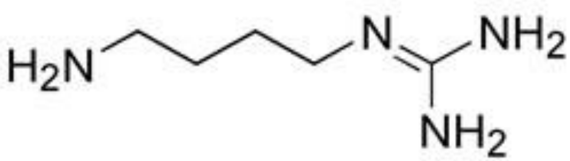



Amine	*Formula*	*Precursor*
Ethylamine C_2H_7N	$CH_3CH_2NH_2$	Alanine
Putrescine $C_4H_{12}N_2$	$H_2N\ (CH_2)_4\ NH_2$	Ornithine
Histamine $C_5H_9N_3$		Histidine
Cadaverine $C_5H_{14}N_2$	$H_2N\ (CH_2)_5\ NH_2$	Lysine
Tyramine $C_8H_{11}NO$		Tyrosine
Phenylethylamine $C_8H_{11}N$		Phenylalanine
Tryptamine $C_{10}H_{12}N_2$		Tryptophan

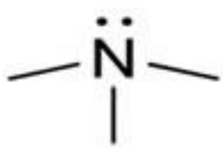
Biogenic amines



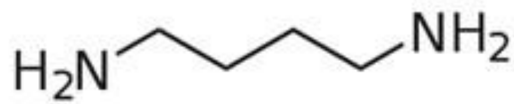
Histamine



Agamtine

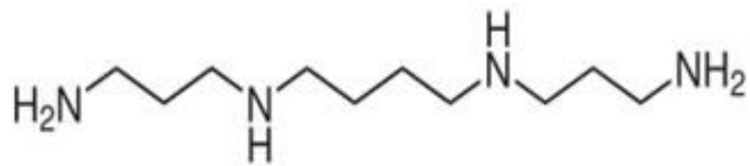


Trimethylamine

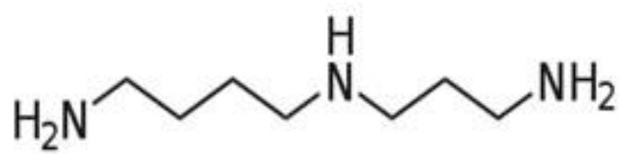


Putrescine

Cadaverine



Spermidine



Sperimine

Biogenic amines

Table 2.3 Biogenic amine content of some fruits and vegetables (mg per 100 g fresh weight)

Amines	Avocado	Banana pulp	Eggplant	Orange	Red plum	Tomato (ripe)	Potato
Dopamine	0.4–0.5	66–70		0.1			
Epinephrine		<.25					
Norepinephrine		10.8					0.01–0.02
Serotonin	1.0	2.5–8.0	0.2		1.0	1.2	
Tyramine	2.3	6.5–9.4	0.3	1.0	0.6	0.4	0.1

				Pineapple			Plantain		
	Date	Fig	Pawpaw	Green	Ripe	Juice	Green	Ripe	Cooked
Dopamine	<0.08	<0.02	0.1–0.2						
Epinephrine	<0.08	<0.02							
Norepinephrine	<0.08	<0.02					0.2	0.25	
Serotonin	0.9	1.3	0.1–0.2	5.0–6.0	2.0	2.5–3.5	2.0–6.0	4.0–10	4.7

Jansenn, Put & Nout (1997)

Biogenic amines

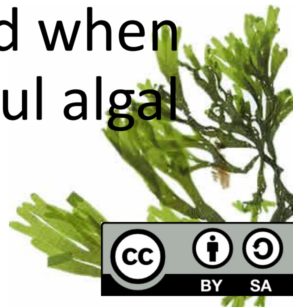
- *Toxicity and symptoms.* The symptoms of intoxication, persisting for several hours, include burning throat, headache, nausea, hypertension, numbness and tingling of the lips, and vomiting.
- 1000 mg/kg amine (based on histamine intoxication & amine concentration in food) is dangerous for human health.
- The toxicity dose of BA depends on the individual sensitivity and characteristic

Phycotoxins

- About 70 million tons of seafood each year
- Postharvest contamination with infectious organisms, toxins of bacteria origin or algae
- Contamination of seafood with potent neurotoxins that are naturally produced by marine algae

  - Microalgae: Dinoflagellates and diatoms produced some very strong natural toxins

  - Algae : Under certain condition produce blooms and when these blooms cause health issues, we call it : Harmful algal blooms or **HABs**

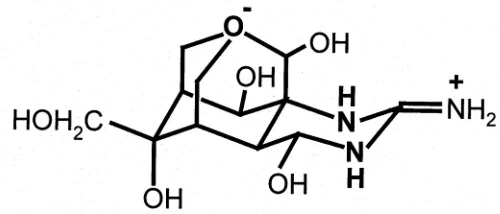


UCT PRAGUE

Why are they so dangerous?

- Because of the natural processes occurring in seafood (such as filtration…) the HABs may accumulate in a variety of marine organisms
- Odorless and tasteless
- Not destroyed by cooking or by food preservation processes (Drying, freezing…)
- Refractory to the action of human digestives enzymes
- No antidotes for their biological activity

Tetrodotoxin



Tetrodotoxin

- **Source:**
  - Gonads, liver, intestines, and skin of about 80 species of puffer fish, blowfish or fugu
  - Also found in the California newt, parrotfish, frogs (*Atelopus* genus), blue-ringed octopus, starfish, octopus, and xanthid crabs
- **Range:**
  - Primarily the Indo-Pacific Ocean
  - Other cases and deaths have occurred from puffer fish from the Atlantic Ocean, Gulf of Mexico, and Gulf of California

Tetrodotoxin

- **Onset:** 20 minutes to 3 hours
- **Initial symptoms:** numbness of the lips and tongue
- **Secondary symptoms:** prickling of the face and extremities, a sensation of lightness or floating, headache, epigastric pain, nausea, diarrhea and/or vomiting
- **Tertiary symptoms:** increasing paralysis and death within 4-6 hours
- **Control:** Mouse bioassay, HPLC method

Do not eat puffer fish or avoid improperly prepared

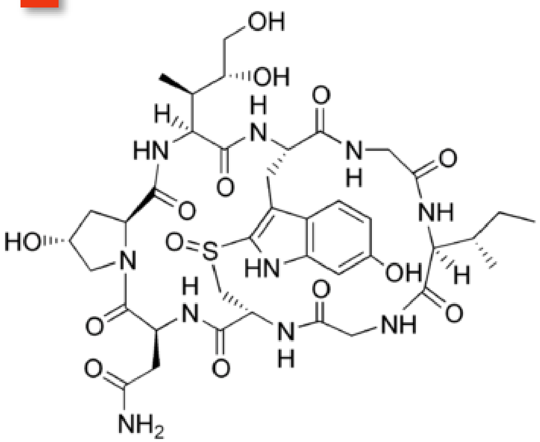
Mushroom Toxins

- Most dangerous mushrooms are the “death cap” (Amanita phalloides) or the “death angel” (Amanita ocreata).
- Most susceptible are children less than 10 years of age
- Initial symptoms are nausea, vomiting, diarrhea and irregular heart rate
- Amatoxin, damages the liver cells causing liver and kidney failure and possibly death
- Amatoxin is very potent: only 0.1 to 0.3 mg/kg of body weight results in death

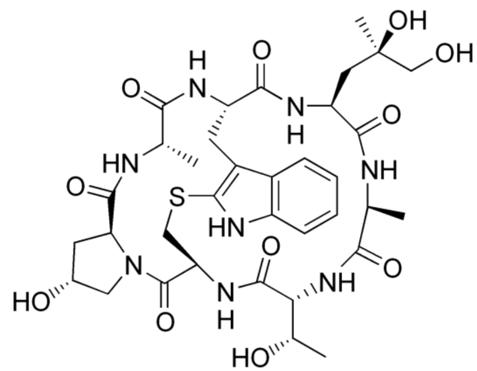
Mushroom Toxins

- **There are four categories of mushroom toxins:**
  - **Neurotoxins:** Cause neurological symptoms such as profuse sweating, hallucinations, depression, spastic colon, excitement, convulsions, and coma.
  - **Protoplasmic poisons:** Cause generalized destruction of cells, which is followed by organ failure.
  - **Gastrointestinal irritants:** Produce rapid, transient nausea, abdominal cramping, vomiting, and diarrhea.
  - **Disulfram-like toxins:** Disulfram-like toxins are usually nontoxic and produce no symptoms. However, if alcohol is consumed within 72 hours after eating them, they may produce vomiting, nausea, headache, flushing, and cardiovascular disturbances.

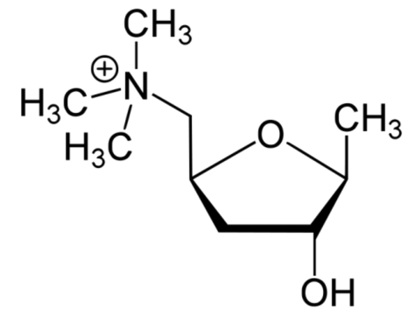
Mushroom Toxins



amanitin



phalloidin

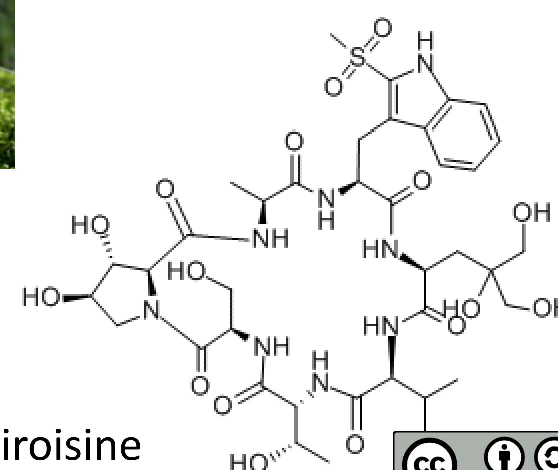


muscarine

Amanita ocreata

Amanita muscaria

Amanita falloides



viroisine

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

5. Mycotoxins and bacterial toxins

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Mycotoxins



- Toxic compounds produced by different types of fungi, belonging mainly to the *Aspergillus*, *Penicillium* and *Fusarium* genera
- Under favourable environmental conditions, when temperature and moisture are conducive, these fungi proliferate and may produce mycotoxins.
- They commonly enter the food chain through contaminated food and feed crops, mainly cereals.
- The presence of mycotoxins in food and feed may affect human and animal health as they may cause many different adverse health effects – cancer, mutagenicity, estrogenic, gastrointestinal and kidney disorders.

Brief History of Mycotoxins

- Mycotoxin contamination has affected humans for thousands of years.
- In 7th and 8th century, festival for Roman God Robigus, protector of grain and trees was celebrated to stave off rust and mold.
- Middle Ages had outbreaks of ergotism.
- Only in last 30-40 years have scientists been able to isolate specific toxins from their fungal source.
- Research ideas and methodologies in this field change frequently, and data from 20 years ago are considered questionable.

Mycotoxin Statistics

- 300-400 mycotoxins presently identified, with more becoming evident as new isolation techniques are used.
- Most frequent toxins present are aflatoxin, DON, ZEN, fumonisin, and T-2 toxin, to name a few.

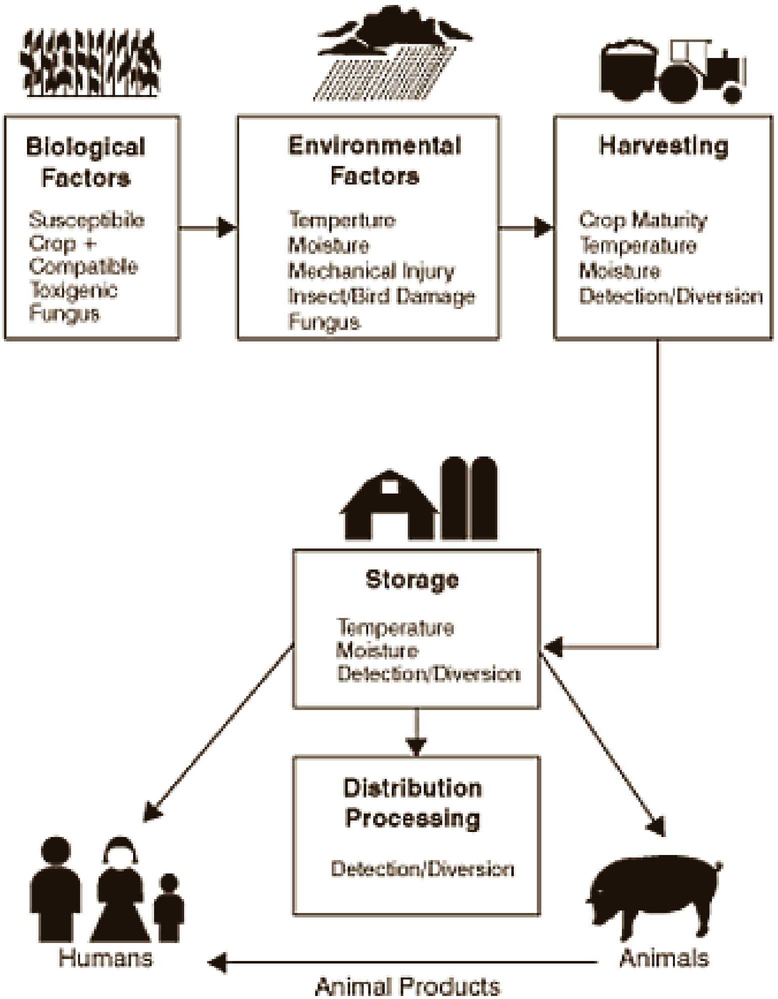
Fungal Infection

- Can occur at any stage in crop production.
- While in the field.
- During harvesting.
- While in silage and storage.
- Spores can lay dormant for months to years, waiting for positive conditions for germination.

Conditions to Encourage Fungal Growth

- Relative humidity over 70%.
- Temperatures over 30 degrees Celsius for a period of a few days to a week.
- Stress to the affected plant, such as drought, flood, or insect infestation.
- High moisture content of crop (20% or higher).
- Must occur in conjunction, or fungal growth cycle will cease.

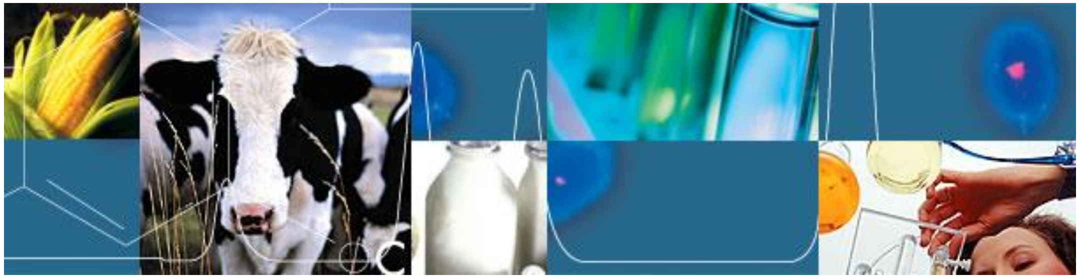
Mycotoxin Chain of Events



http://www.foodtech-international.com/papers/images/mycotoxins/figure1.gif

Mycotoxin Health Hazards

- Generally lower risk in well developed countries due to improved standards of living.
- High intake of affected product, usually in conjunction with limited amounts of other food sources.
- Greatest threat comes from long term exposure due to eating spoiled food or meat from animals fed contaminated feed.

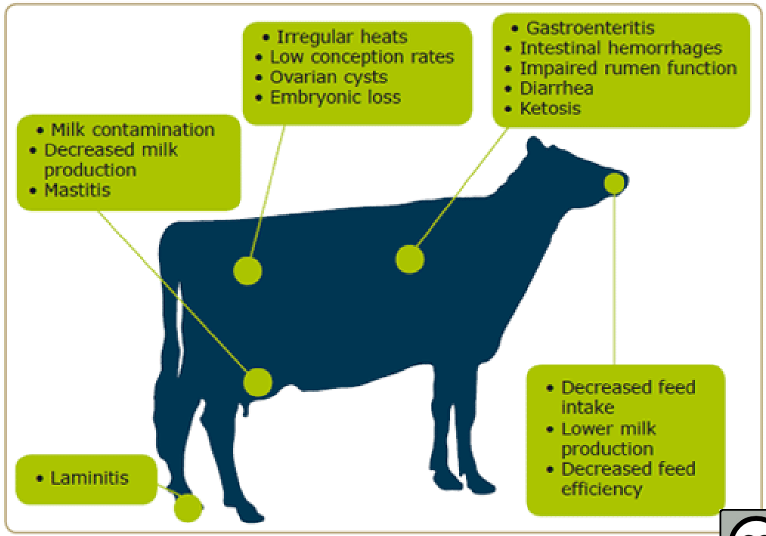


Mycotoxin Effects on Humans

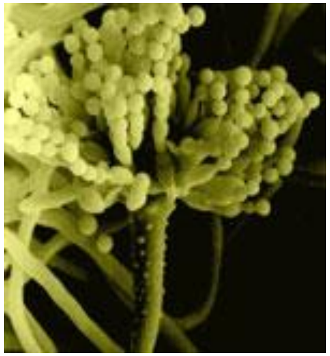
- Economic loss due to impaired health of stock animals.
- Illness: symptoms can include cold/flu-like symptoms, sore throats, headaches, nose bleeds, fatigue, diarrhea, dermatitis, and immune suppression, and vary by species.
- Death.

Mycotoxin Effects on Animals

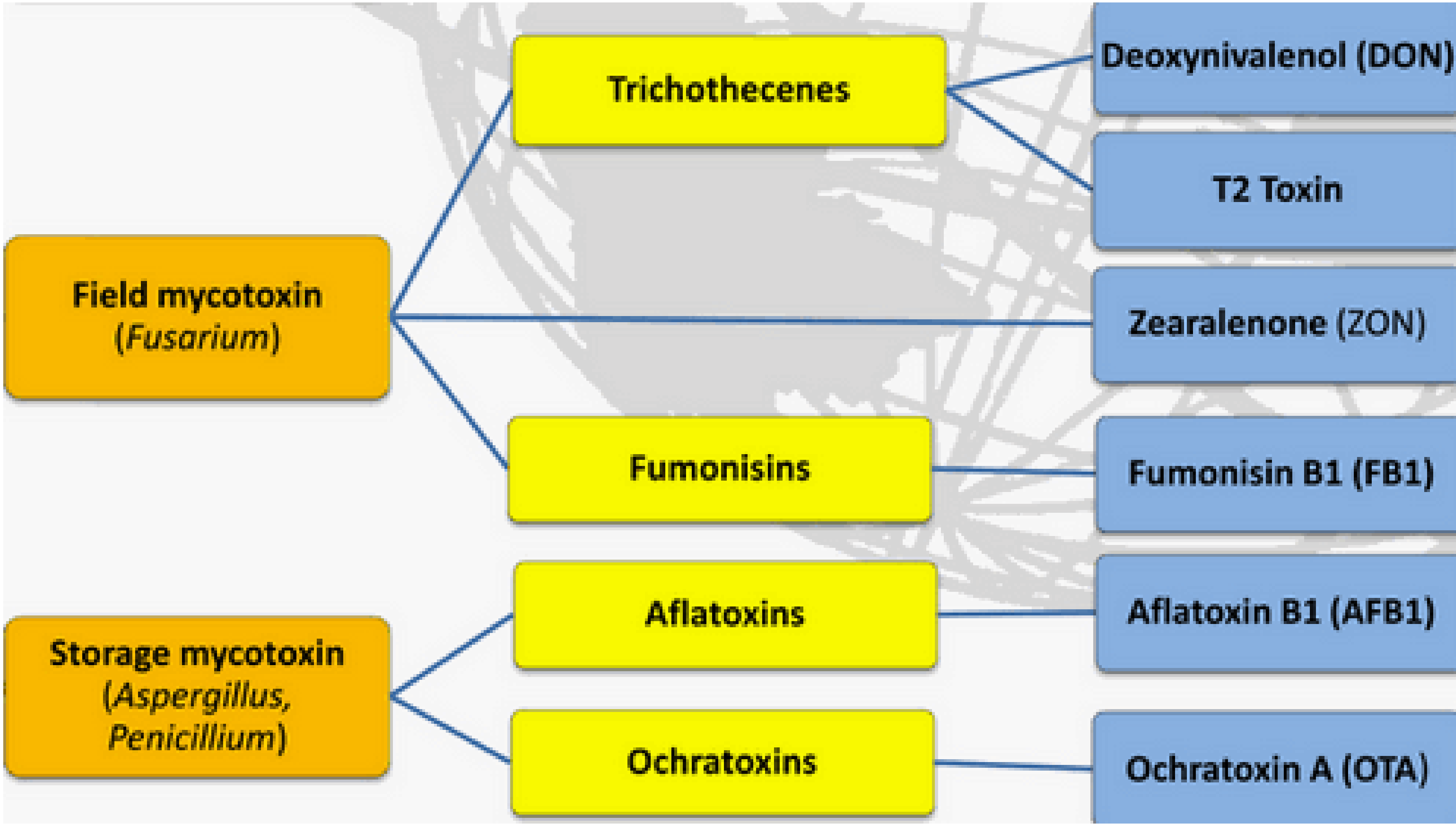
- Feed refusal
- Impaired animal health, resulting in reduced production of eggs, milk, weight gain, etc.
- Metabolites are passed through the milk in cheese, dry milk, and yogurt.
- Disease.
- Death in animals.



Mycotoxins

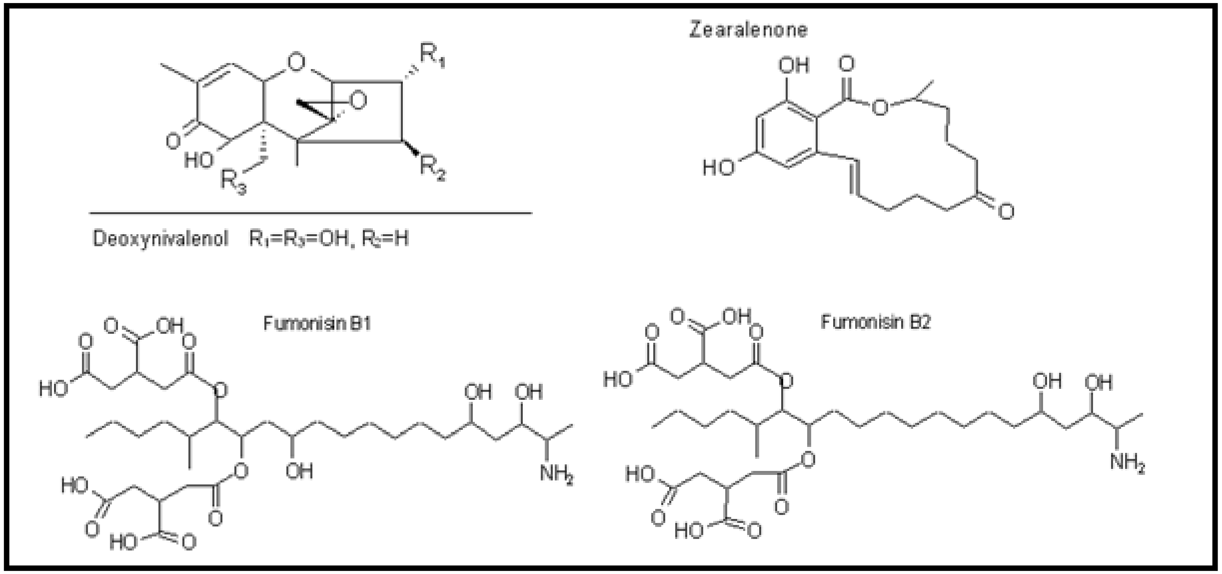
***Aspergillus* sp.**	***Fusarium* sp.**	***Aspergillus ochraceus***	***Penicillium expansum***	***Claviceps purpurea***
Aflatoxins B1, B2, G1, G2, M1	**Deoxynivalenol Zearalenone T-2 , HT-2 toxin Fumonisins**	**Ochratoxin A**	**Patulin**	**Ergot alkaloids**
maize, peanuts, nuts, spices, milk	**cereals, soybeans oil seeds, bananas, mango**	**cereals, rice, peanuts, green coffee, residue in pork**	**apples and apple products, cereals**	**cereals, grass**



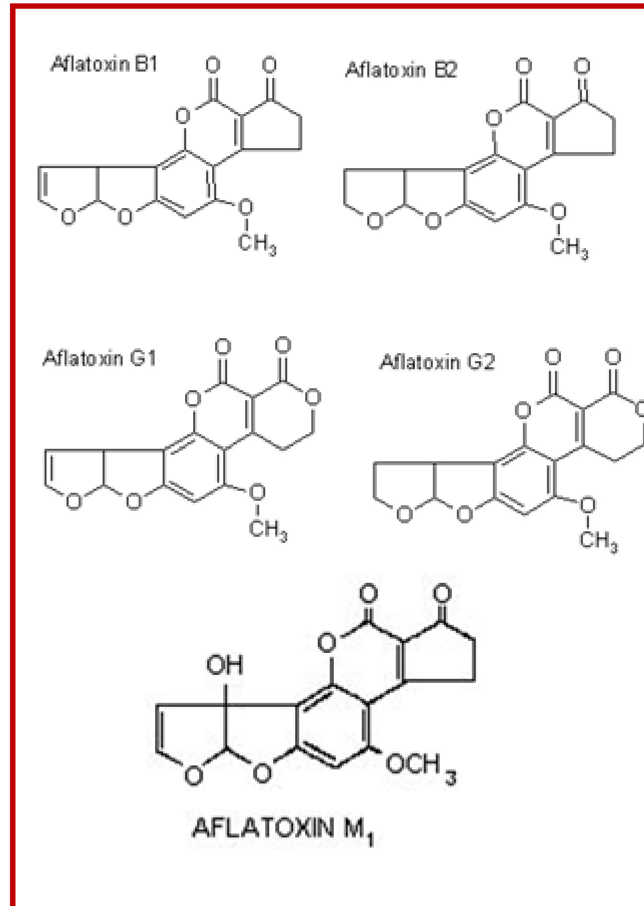
Field mycotoxin (*Fusarium*)
Storage mycotoxin (*Aspergillus*, *Penicillium*)
Trichothecenes
Fumonisins
Aflatoxins
Ochratoxins
Deoxynivalenol (DON)
T2 Toxin
Zearalenone (ZON)
Fumonisin B1 (FB1)
Aflatoxin B1 (AFB1)
Ochratoxin A (OTA)

Mycotoxins in food - regulated

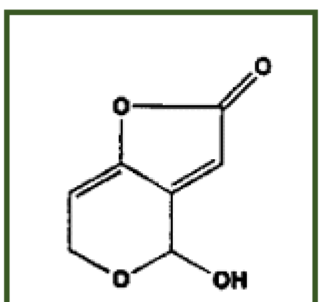
Commission regulation (EC) No 1881/2006 amended by Regulation (EC) No 1126/2007



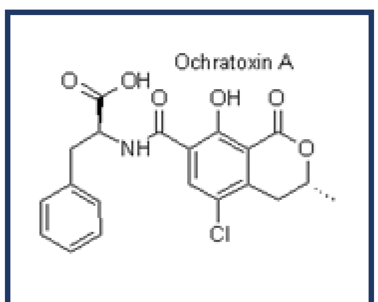
Fusarium mycotoxins



Aflatoxins

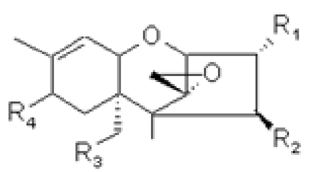


Patulin

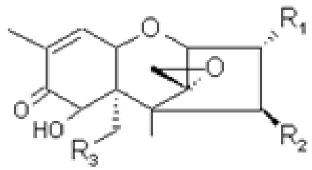


Ochratoxin A

Mycotoxins in food

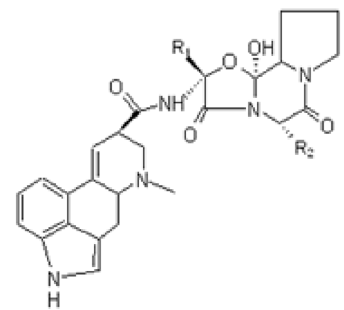


Verrucarol $R_1=R_4=H$, $R_2=R_3=OH$
Neosolaniol $R_1=OH$, $R_2=R_3=R_4=OAc$
Diacetoxyscirpenol $R_1=OH$, $R_2=R_3=OAc$, $R_4=H$
HT_2 toxin $R_1=R_2=OH$, $R_3=OAc$, $R_4=OCOi\text{-}Bu$
T_2 toxin $R_1=OH$, $R_2=R_3=OAc$, $R_4=OCOi\text{-}Bu$

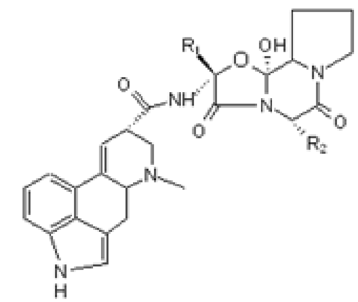


Deoxynivalenol $R_1=R_3=OH$, $R_2=H$
Nivalenol $R_1=R_2=R_3=OH$
Fusarenon-X $R_1=R_3=OH$, $R_2=OAc$
3-Acetyldeoxynivalenol $R_1=OAc$, $R_2=H$, $R_3=OH$
15-Acetyldeoxynivalenol $R_1=OH$, $R_2=H$, $R_3=OAc$

Other trichothecenes

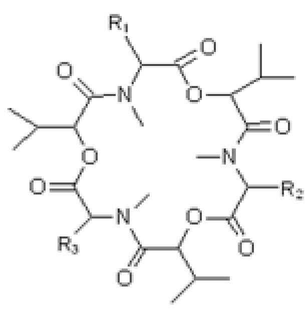


Ergosine $R_1=CH_3$, $R_2=CH_2CH(CH_3)_2$
Ergotamin $R_1=CH_3$, $R_2=CH_2C_6H_5$
Ergocornin $R_1=CH(CH_3)_2$, $R_2=CH(CH_3)_2$
Ergocristin $R_1=CH(CH_3)_2$, $R_2=CH_2C_6H_5$



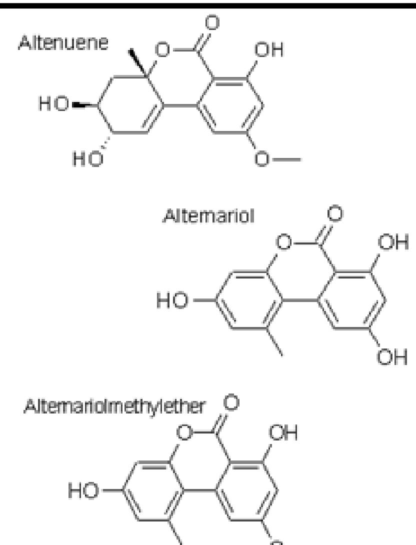
Ergosinine $R_1=CH_3$, $R_2=CH_2CH(CH_3)_2$
Ergotaminine $R_1=CH_3$, $R_2=CH_2C_6H_5$
Ergocorninine $R_1=CH(CH_3)_2$, $R_2=CH(CH_3)_2$
Ergocristinine $R_1=CH(CH_3)_2$, $R_2=CH_2C_6H_5$

Ergot alkaloids



Enniatin A $R_1=R_2=R_3=CH_2C_6H_5$
Enniatin A_1 $R_1=R_2=R_3=CH(CH_3)CH_2CH_3$
Enniatin B $R_1=CH(CH_3)CH_2CH_3$, $R_2=R_3=CH(CH_3)_2$
Enniatin B_1 $R_1=R_2=R_3=CH(CH_3)_2$

Enniatins



Alternaria mycotoxins

European Food Safety Authority

EFSA calls in 2010

EXTENDING THE NUMBER OF MYCOTOXINS HAVING MAXIMUM LEGISLATIVE LIMITS

Mycotoxins - legislation

EFSA call 2010!

LEGISLATION

EC 1881/2006

EC 1126/2007

EFSA LIST

European Food Safety Authority

DEOXYNIVALENOL

zearalenon

aflatoxins

fumonisins

ochratoxin A

patulin

T-2 toxin, HT-2 toxin

nivalenol

diacetoxyscirpenol

moniliformin

beauvericin, enniatins

sterigmatocystin

citrinin

alternaria toxins

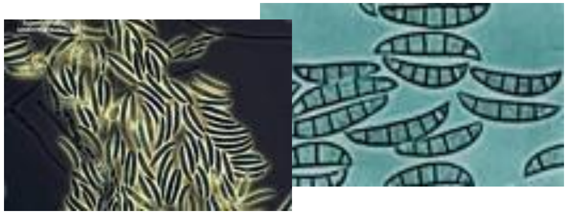
ergot alkaloids

Fusarium mycotoxins

Microscopic fillamentary fungi genus *Fusarium*

F. graminearum, F. culmorum

F. moniliformis, F. proliferatum



Occurrence in cereals

good stability during technological processing

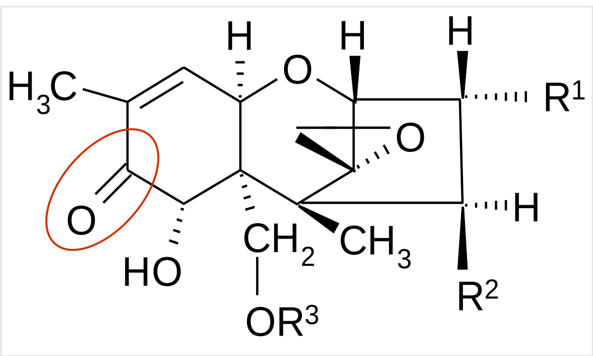
Transfer to cereal based products

Fusarium mycotoxins

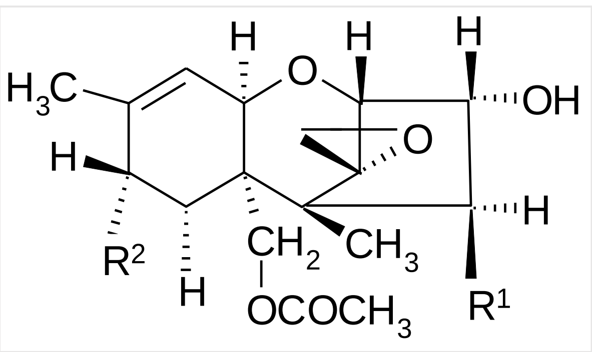
MAIN TOXIC SECONDARY METABOLITES PRODUCED BY *FUSARIUM* GENUS IN CROPS - WIDE RANGE OF POLARITIES

Trichothecenes and zearalenone

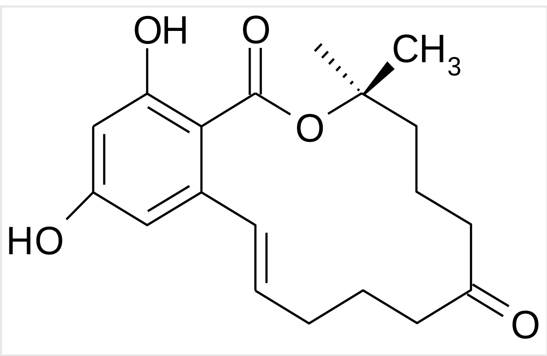
Trichothecenes type B



Trichothecenes type A



Zearalenon (ZON)



Nivalenol (NIV)

4-Deoxynivalenol (DON)

Fusarenon-X (FUS-X)

3-Acetyldeoxynivalenol (3ADON)

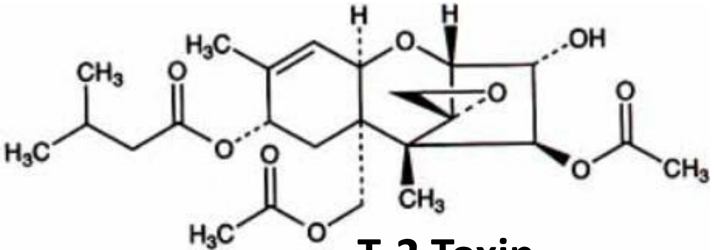
15-Acetyldeoxynivalenol (15ADON)

marker of mycotoxin contamination

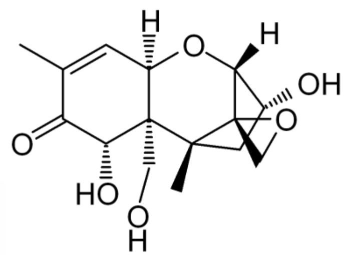
Deoxynivalenol (DON), T-2 toxin

DON and T-2 Toxin *(produced by F. graminearum)*

- These are tricothecenes of wheat (DON), grain, and barley.
- They cause necrosis and hemorrhage of the digestive tract, decreased blood production in the bone and spleen, and changes to reproductive systems.
- In poultry, causes reduced egg production, beak lesions, and abnormal feathering
- Advisory level of DON is 1 ppm.



T-2 Toxin

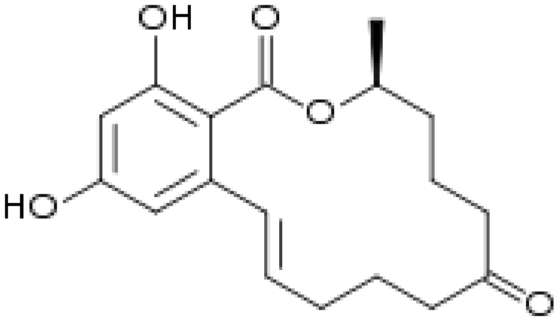


DON

Zearalenone

Zearalenone *(produced by F. graminearum)*

- A tricothecene.
- Mimics the body's production of estrogen.
- Causes feminization of male animals.
- Disrupts conception, ovulation, and fetal development in female animals.
- Pigs are especially sensitive, poultry and cows show little sensitivity.



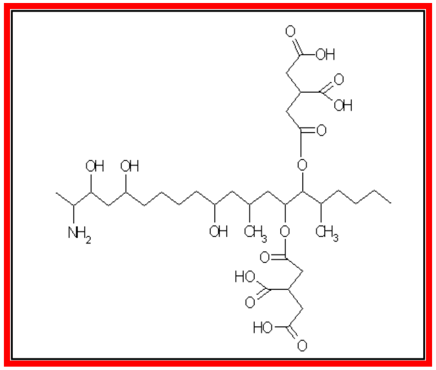
Zearalenone

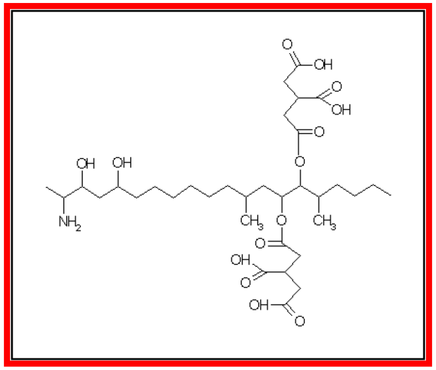
Fusarium mycotoxins

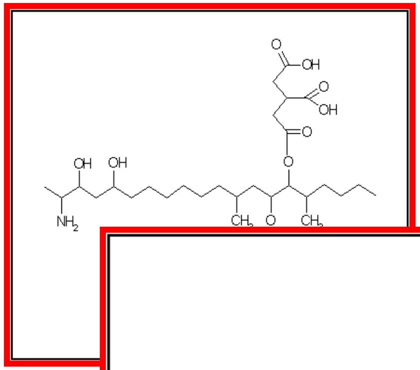
Fumonisins **B1, B2 a B3**

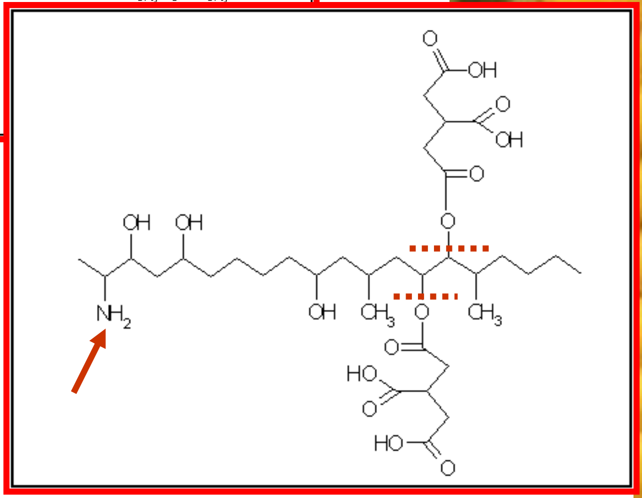
Toxicity: probably carcinogenic for humans (IARC – class 2B)

Chemical properties: polar compounds, pKA ~ 3,5









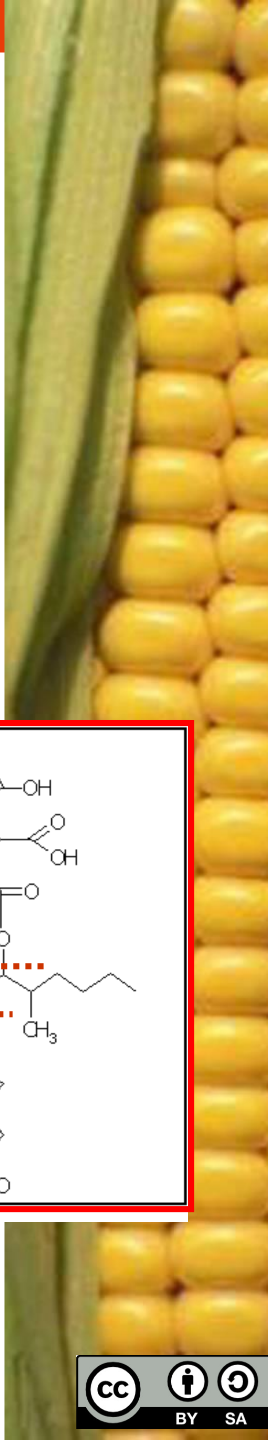
Hydrolyzed fumonisins

Cleaving of tricarballylic acid

Conjugated fumonisins

Produkts of reaction with reduction sugars

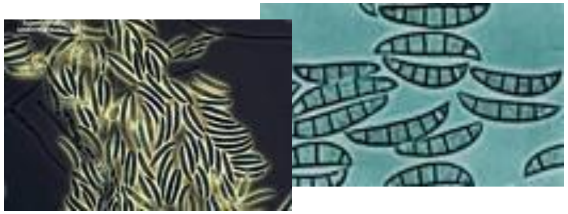
Minor fumonisins type A, C, P



Aflatoxins

Microscopic fillamentary fungi genus *Aspergillus*

A. flavus, A. parasiticus



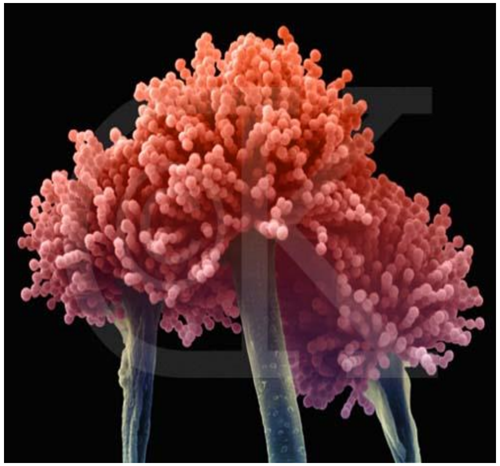
Occurrence in maize, peanuts, nuts, spices

Transfer to food and products

Aflatoxins

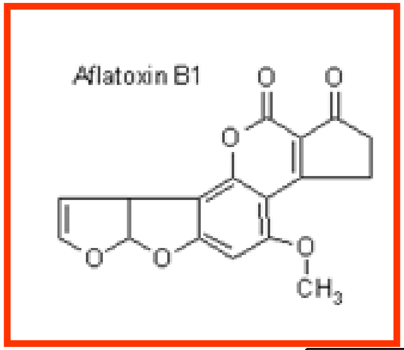
MAIN TOXIC SECONDARY METABOLITES PRODUCED BY *ASPERGILUS* GENUS (by Aspergillus flavus and Aspergillus parasiticus)

Aflatoxins are recognized as the most important mycotoxins



They can colonize and contaminate grain before harvest or during storage.

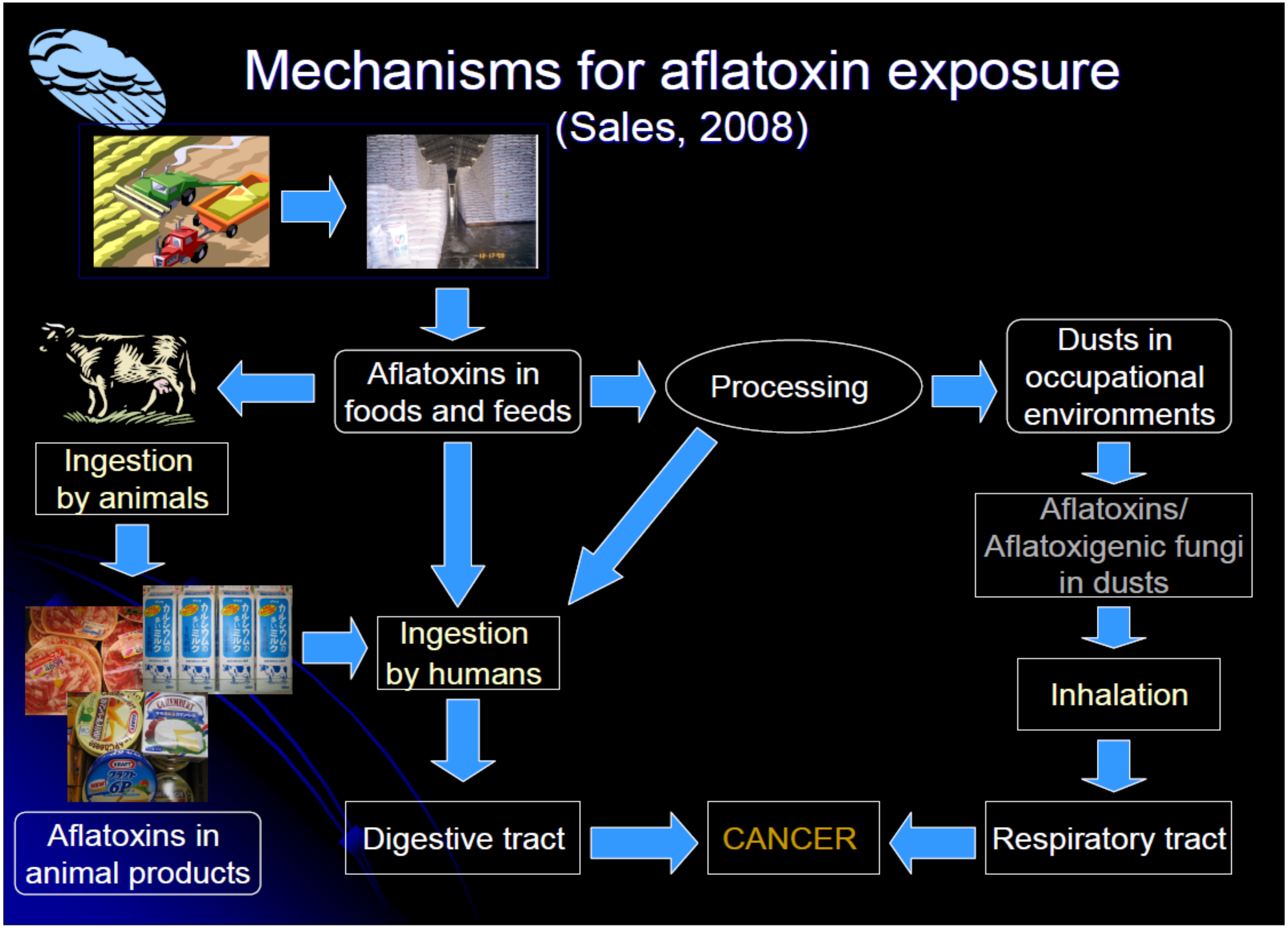
Aflatoxin B_1 is considered the most toxic and is produced by both *Aspergillus flavus* and *Aspergillus parasiticus*



Aflatoxin G_1 and G_2 are produced exclusively by *A. parasiticus*

Aflatoxins M_1, M_2 were originally discovered in the milk of cows

Mechanisms of aflatoxins exposure



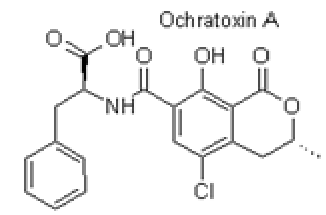
Toxicity

- carcinogenic-(cause hepatocellular carcinoma)
- teratogenic
- mutagenic
- Immunosuppressive - (suppresses the immune system).
- The aflatoxins display potency of toxicity, carcinogenicity, mutagenicity in the order of AFB1 > AFG1 > AFB2 > AFG2.

Carcinogenicity

- Aflatoxins are *known to be human carcinogens* (hepatocellular carcinoma, or primary liver-cell cancer).
- The risk of liver cancer increased significantly with increasing aflatoxin consumption.
- **Biomarkers** for aflatoxin exposure (aflatoxin metabolites in the urine and aflatoxin albumin adducts in the blood)

Ochratoxins



Ochratoxin A

- Is a mycotoxin produced by ***Penicillium*** and ***Aspergillus*** species.
- They are weak organic acids consisting of isocoumarin derivatives coupled to phenylalanine.
- The family of ochratoxins consists of three members, A, B, and C.
- **Ochratoxin A** is the most abundant , the most commonly detected and the most toxic one.
- It is a potent toxin affecting mainly the kidney.
- **Ochratoxin A** is found mainly in cereal and cereal products, coffee, spices, dried fruits, grape juice

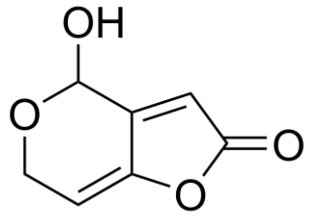
Ochratoxin A

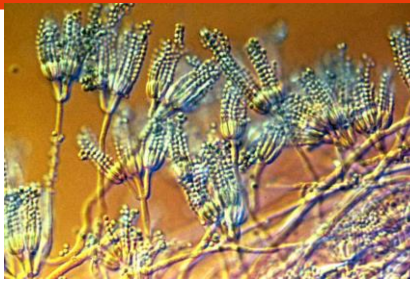
- Ochratoxin A is a toxic carcinogenic fungal toxin
- Ochratoxin A is absorbed from the gastrointestinal tract.
- The absorbed ochratoxin A is distributed via blood, mainly to the kidneys, and at lower concentrations to the liver, muscle and fat.
- Levels of ochratoxin A in human can be measured by detection of ochratoxin A in human blood and breast milk.

Toxicity of Ochratoxin A

- Ochratoxin A has been shown to be nephrotoxic, hepatotoxic, teratogenic and immunotoxic to several species of animals and carcinogenic in mice and rats causing tumours of the kidney and liver.
- The acute toxicity of ochratoxin A is relatively low.
- At present, there are no documented cases of acute toxicity reported in humans

Patulin

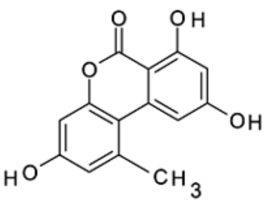




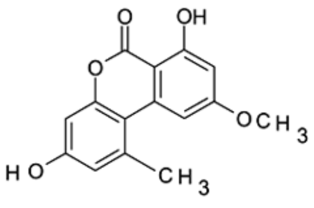
- Patulin is produced by *Penicillium clariform, P. expansum, P. patulum* and by *Aspergillus* spp.
- Bread, sausage, fruits (apricots, grapes, peaches, pears, and apples), and apple juice are the major source for this toxin.
- Patulin is needed in high dosage to show pathogenesis. It is a carcinogenic toxin and is reported to be responsible for subcutaneous sarcoma.
- The allowable daily intake limit is 0.4 mg/kg body weight.

Alternaria Toxins

- Infects the plant in the field, such as wheat, sorghum, and barley.
- Also fruits and vegetables that can cause spoilage in refrigeration.
- Toxins include: alternariol, alternariol monomethyl ether, altenuene, tenuazonic acid, and altertoxins.
- Little is know of these toxins; but, toxic effects are seen in rats, chicks, ducklings, and turkeys



ALTERNARIOL

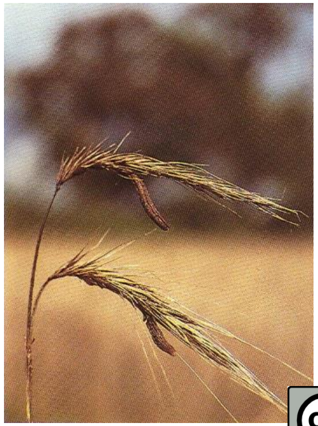


ALTERNARIOL MONOMETHYL ETHER

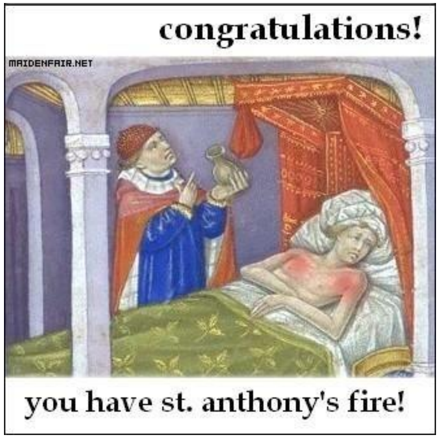
Claviceps Toxins – Ergot alkaloids

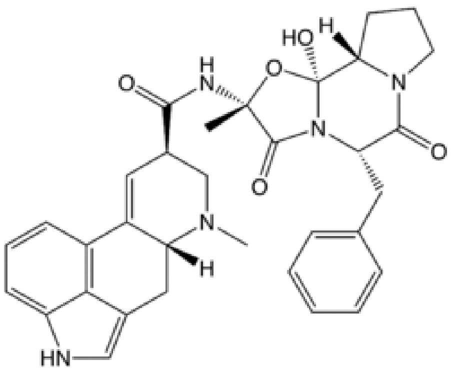
- Earliest recognized mycotoxicosis caused by C. purpurea, with ergot mold.
- Outbreaks have been reported since 857 A.D.
- The Middle Ages had near epidemic proportions.
- Humans consumed bread baked with grain containing ergot spores, which produced lysergic acid diethylamide (LSD) symptoms and hallucinations.

Ergot of rye



Ergot Poisoning (St. Anthony's Fire)





ergotamine

- Disease of rye, barley, oats and wheat.
- Grains are replaced by ergot sclerotia that contain toxins.
- Main toxin is called ergotamine.
- Named for the belief that a pilgrimage to the shrine of St. Anthony would alleviate the symptoms.

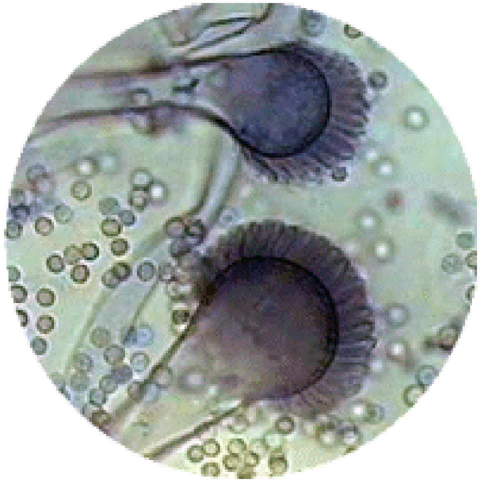
Ergot Poisoning (Cont.)

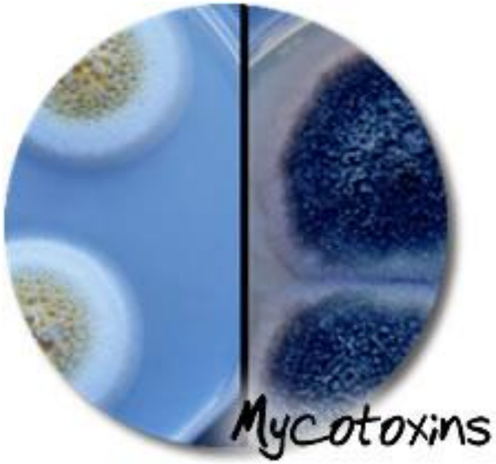
- Animal symptoms: dry gangrene, internal bleeding, vomiting, constipation, diarrhea, and in pigs: abortion of fetuses.
- Human symptoms: gastrointestinal stress; convulsions; fetal abortion; extreme burning and cold sensations in fingers, hands, and feet; gangrene of the extremities.
- Other outbreaks: Russia in 1926, Ireland in 1929, France in 1953, India in 1958, and Ethiopia in 1973.


alcoholic beverages
corn
wheat
barley
sugar cane
sugar beets
cottonseed
peanuts
11 Foods HIGHEST in Mycotoxins
www.ExhibitHealth.com
rye
sorghum
hard cheeses

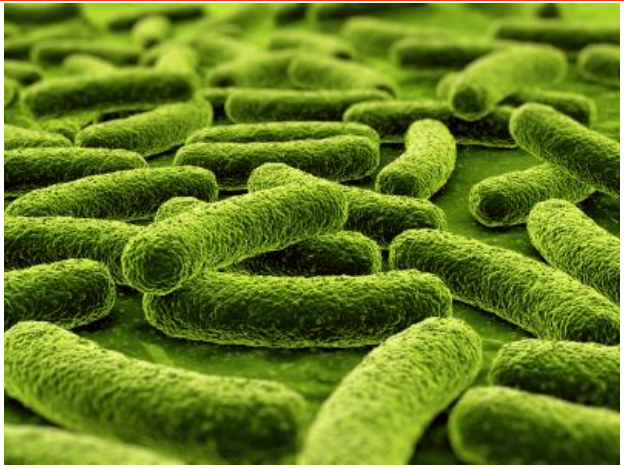
Preventing Mycotoxins

- Use “clean” procedures
- Prevent contamination
- Inhibit mold growth
  - Drying
  - Refrigeration
  - Mold inhibitors





Bacterial toxins



Toxin

Exotoxin

a toxin that is released by bacteria into the environment

Endotoxin

a toxin kept "within" the bacterial cell and to be released only after destruction of the bacterial cell wall

Groups of bacterial foodborne pathogens

- **Group I** contains bacteria that do not produce typical toxins, and the diseases they cause are a result of their outgrowth within a host organism. (ex. *Salmonella, Shigella, Listeria monocytogenes*)

- **Group II** includes bacteria that produce toxins responsible for the course of disease during gastrointestinal invasion. (ex. *Aeromonas* sp., *E. Coli, Bacillus cereus*)

- **Group III** comprises bacteria that produce toxins in food outside the host organisms.(ex. *Clostridium botulinum*, *Staphylococcus aureus*)

Most significant of food toxi

Group III: *Clostridium botulinum*

- **G^+, rod-shaped, anaerobic spore-former**
- Based on the serological properties of neurotoxins produced by various strains of *C. botulinum*, the following serovars were identified: A, B,C1, C2, D, E, F, G.
- **Type I** (so-called ‘proteolytic’): produces A, B, and F neurotoxins, harmful for humans; min. t^o for growth 12°C
- **Type II** (so-called ‘non-proteolytic’): produces B, E, and F neurotoxins, harmful for humans, min. t^o for growth 3,3°C
- **Type III** produces C and D toxins; dangerous for birds, minks, and calves, do not affect humans, min. t^o for growth 15°C
- **Type IV** produces G toxin, harmful for humans, min. t^o for growth 12°C

Botulin toxins

- *C. botulinum* toxins belong to the AB group of toxins, which also includes diphtheria toxin, pseudomonas exotoxin A, anthrax toxin, Shiga(like) toxin, cholera toxin, pertussis toxin, and plant toxins, e.g., ricin.
- **Affecting vesicular membrane and fusion apparatus** (7 types of BoNT’s , 1 type of TeNT)
- **Affecting actin cytoskeleton assembly** (C2, C3, D, C3 exoenzyme)
- **Affecting membrane permeability**(hemolysins from *Staphylococcus*, tetanolysin from *C. tetani*, botulysin

  from *C. botulinum*, and perfringolysin from *C. perfringens*)
- **Botulin toxin is the most toxic of all known poisons!!!**

Clostridium botulinium in Food

- **<u>Main sources:</u>**

Infants: Honey, home-canned vegetables and fruits, corn syrup

Children and adults: Home-canned foods with a low acid content, improperly canned commercial foods, home-canned or fermented fish, herb-infused oils, baked potatoes in aluminum foil, cheese sauce, bottled garlic, foods held warm for extended periods of time

- **<u>What can prevent spore germination?</u>**

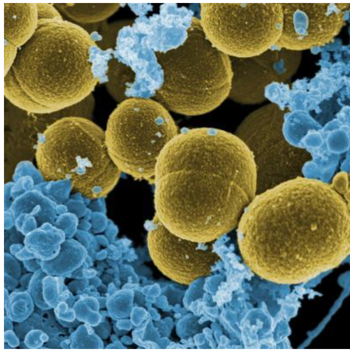
  low pH, lack of particular AA, potential bacteriocin activity of lactobacilli

- The outgrowth of *C. botulinum* requires a suitable medium, temperature, atmosphere, pH, Eh potential, and water activity. Toxin is usually only produced in optimal or close-to-optimal conditions.

Detection of botulin toxins

- Biological methods (mice testing)
- Genetic methods (PCR and its variants)
- Microbiological methods

Group III: Staphylococcus aureus



- **G^+, coccal bacterium, "golden staph"**
- Known for its ability to produce a variety of toxins and many disease syndromes
- Frequently present on tonsils of healthy carriers
- A majority of food isolates belongs to *S. aureus* and its toxins are the main cause of food poisonings.
- Humans are the main reservoir of staphylococci
- Bacteria being frequently found in noses, throats and on skin of human carriers

Staphylococcal toxins

- **6 biotypes**
- Most frequent: biotype A, biotype C, biotype E
- Enterotoxin groups named from A to H (SEA, SEB, SEC, etc.)
- 95% of staphylococcal food poisoning caused by types from SEA to SEE
- **Resistant to low a_w**
- SE's are single polypeptides (26 to 28 kDa) displaying high heterogeneity in isoelectric focusing
- **SE's are not destroyed by heating at $100^o C$ for 30 mins** – most important aspect of potential occurrence in food

Enterotoxins in food

<u>Main sources:</u>

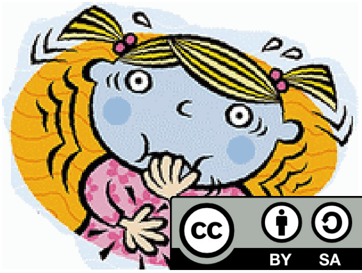
- Foods that are made with hand contact and require no additional cooking, such as: Salads, such as ham, egg, tuna, chicken, potato, and macaroni
- Bakery products, such as cream-filled pastries, cream pies, and chocolate éclairs
- Sandwiches
- Other sources include milk and dairy products, as well as meat, poultry, eggs, and related products.

Staphylococcal food poisoning

- The most frequently observed symptoms include : vomiting (82%), nausea (74%), abdominal cramps (64%), diarrhea (64%), and also headaches and muscular cramping

- Symptoms usually starts after 6 to 10 hours after food ingestion, however they may be reported earlier

- Lethal cases are rare and occur among infants and elderly people



Detection of Staphylococcal toxins

- Biological methods (cell cultures; in past were testing on cats)
- Immunological methods (ELISA technique)
- Molecular biology methods (PCR and its variants)

The published materials are intended for students of the University of Chemistry and Technology, Prague as a study material. Some text and image data contained herein are taken from public sources. In the case of insufficient quotations, the author's intention was not to intentionally infringe the possible author(s) rights to the original work.

If you have any reservations, please contact the author(s) of the specific teaching material in order to remedy the situation.

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

6. "New" risky groups of chemical compounds, the global protection of the food chain

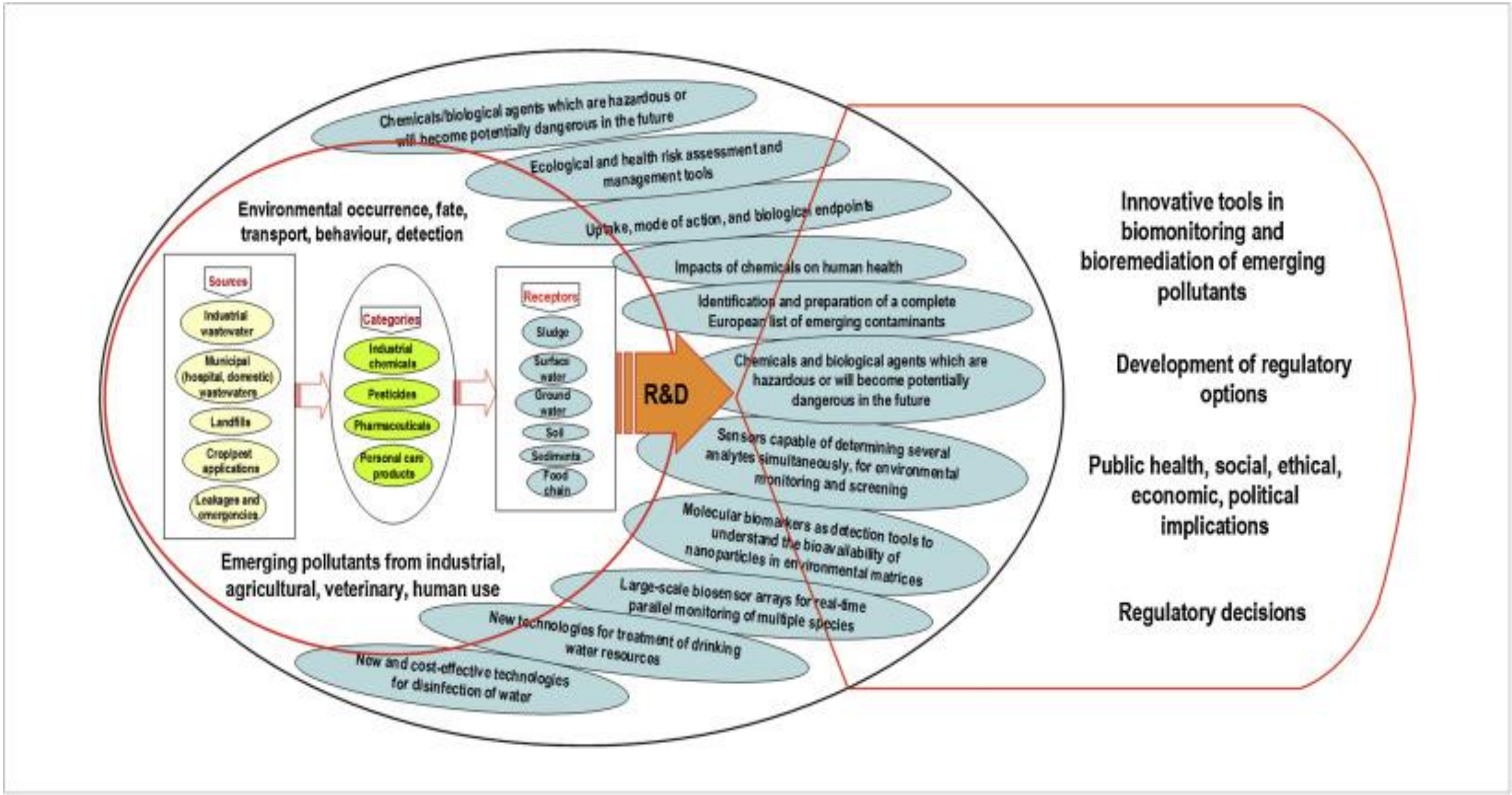
EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Stockholm Convention on persistent organic pollutants (POPs)

Emerging contaminants

- Non-regulated chemicals, naturally occurring or synthetic, that have become recognized as occurring in the environment and may potentially pose a risk to human health or the environment.
- Improvements in analytical methods has increased our ability to detect the occurrence of chemicals in very little quantities.
- Very little is known about the health impact of these chemicals, but they are widespread, persistent in the environment and tend to bioaccummulate.
- Effects of a mixture of these chemicals unknown

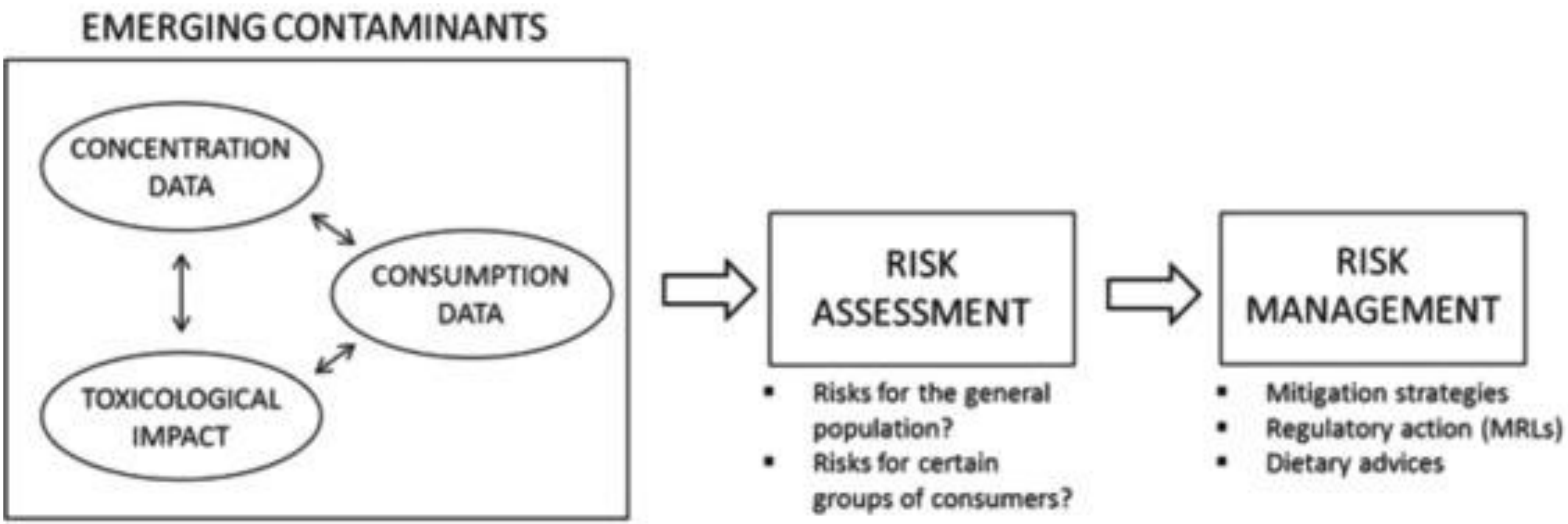

Chemicals/biological agents which are hazardous or will become potentially dangerous in the future
Ecological and health risk assessment and management tools
Environmental occurrence, fate, transport, behaviour, detection
Uptake, mode of action, and biological endpoints
Impacts of chemicals on human health
Identification and preparation of a complete European list of emerging contaminants
Sources
Industrial wastewater
Municipal (hospital, domestic) wastewaters
Landfills
Crop/pest applications
Leakages and emergencies
Categories
Industrial chemicals
Pesticides
Pharmaceuticals
Personal care products
Receptors
Sludge
Surface water
Ground water
Soil
Sediments
Food chain
R&D
Chemicals and biological agents which are hazardous or will become potentially dangerous in the future
Sensors capable of determining several analytes simultaneously, for environmental monitoring and screening
Molecular biomarkers as detection tools to understand the bioavailability of nanoparticles in environmental matrices
Emerging pollutants from industrial, agricultural, veterinary, human use
Large-scale biosensor arrays for real-time parallel monitoring of multiple species
New technologies for treatment of drinking water resources
New and cost-effective technologies for disinfection of water
Innovative tools in biomonitoring and bioremediation of emerging pollutants
Development of regulatory options
Public health, social, ethical, economic, political implications
Regulatory decisions

Emerging Contaminants vs Conventional Contaminants

- Most emerging contaminants are not acute toxic for people and wildlife at their average environmental concentrations. However, most of them are chronic and their long-term effects on human health are unknown
- Very low concentration: Super-trace level in the aquatic environment (ng/L to ug/L level, ever lower)
- Regulation missing due to lacking information and knowledge of emerging contaminants on presence, fate, and effects in the environment

- What kinds of emerging contaminants are occurring in the environment?
- What are the sources of emerging contaminants? Where do they come from?
- What are environmental fate and effect of these emerging contaminants?
- What are the pollution prevention strategies to minimize the loading of emerging contaminants into the environment?
- What are treatment techniques for removal of emerging contaminants in contaminated environment?

Emerging contaminants



Contaminants of emerging concern

	TIER ASSIGNMENTS	MANAGEMENT	MONITORING
TIER 4 HIGH CONCERN	No CECs currently in this tier	303(d) listing TMDL or alternative management plan. Aggressive control actions for all controllable sources	Studies to support TMDL or an alternative management plan
TIER 3 MODERATE CONCERN	PFOS Fipronil Nonylphenol and nonylphenol ethoxylates PBDEs	Action plan or strategy Aggressive pollution prevention Low-cost control actions	Consider including in Status and Trends Monitoring Special studies of fate, effects, and sources, pathways, and loadings
TIER 2 LOW CONCERN	HBCD Pyrethroids Pharmaceuticals and personal care products PBDDs and PBDFs	Low-cost source identification and control Low-level pollution prevention Track product use and market trends	Discontinue screening, or periodically screen in water, sediment, or biota Periodic screening in wastewater effluent or urban runoff to track trends
TIER 1 POSSIBLE CONCERN	Alternative flame retardants Pesticides Plasticizers Many, many others	Identify and prioritize contaminants of potential concern, track international efforts Develop targeted and non-targeted analytical methods	Screening in water, sediment, biota, wastewater effluent, urban runoff

Emerging risk definition (EFSA, 2007)

efsa

European Food Safety Authority

Committed *since 2002* to ensuring that Europe's food is safe

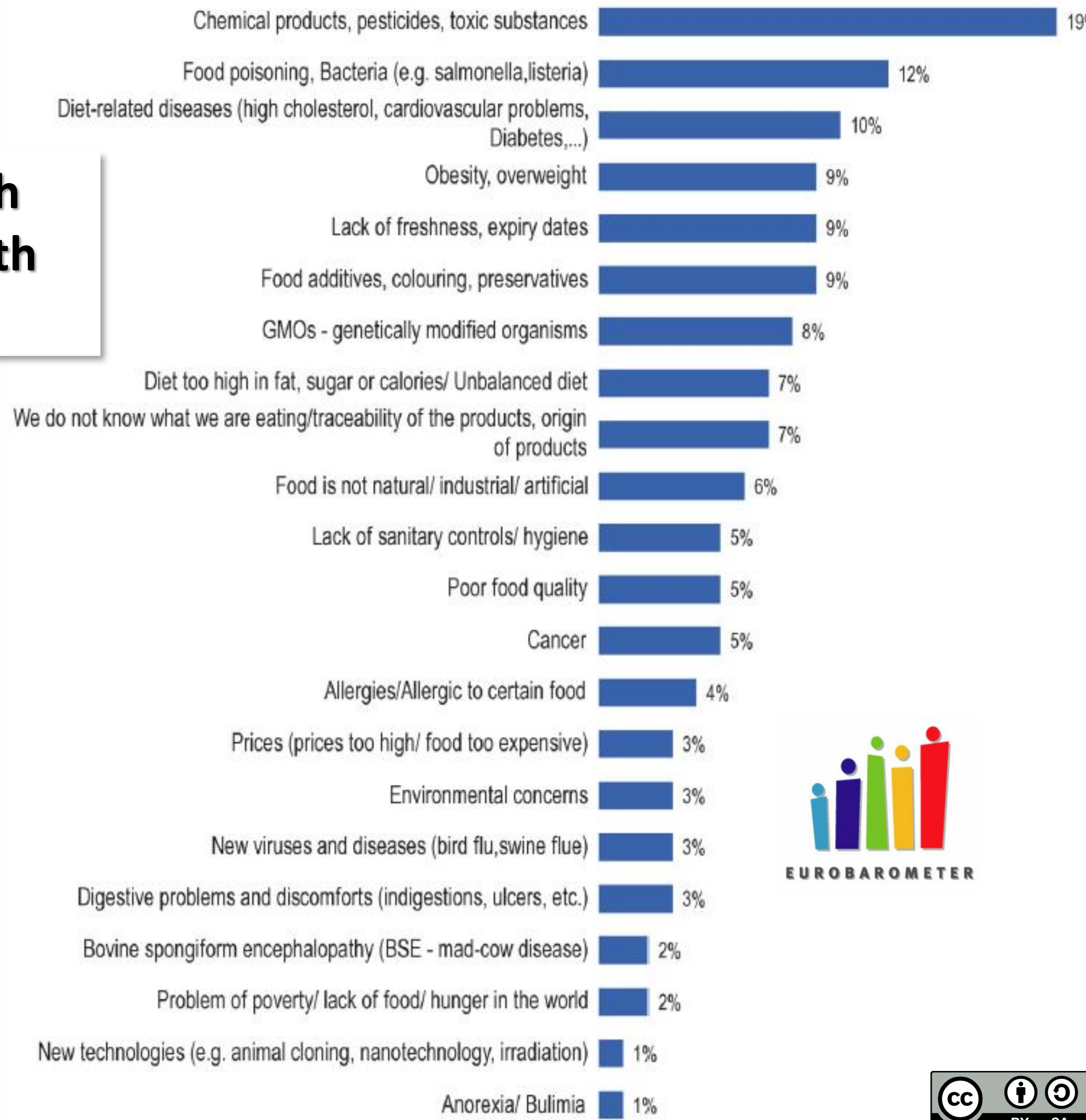
(i) New hazard + High exposure

(ii) Known hazard + Newly identified high exposure

(iii) Known hazard + Increased sensitivity + High exposure

´NEW´ RISK

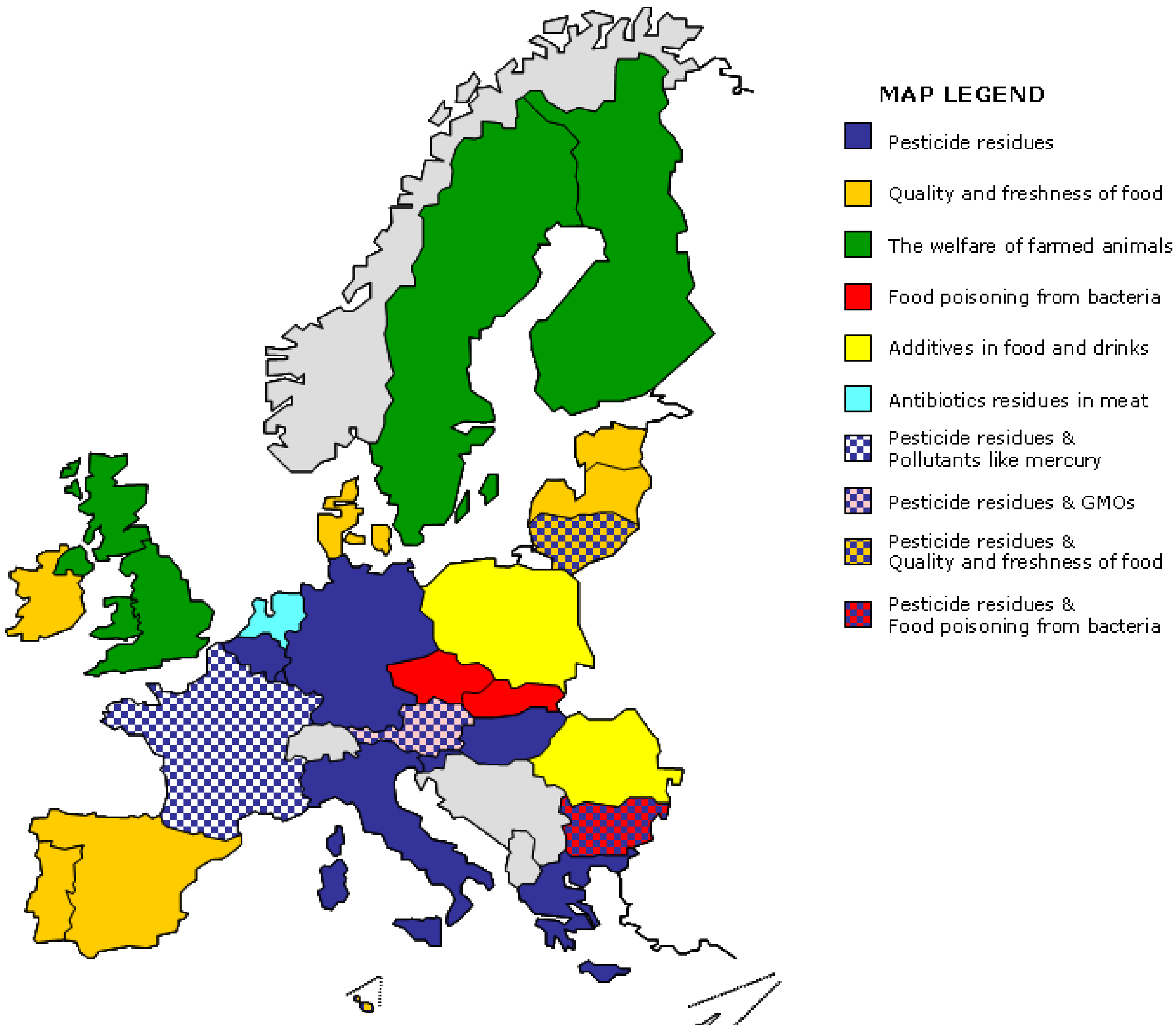
Perception of health risks associated with foods:



European Commission

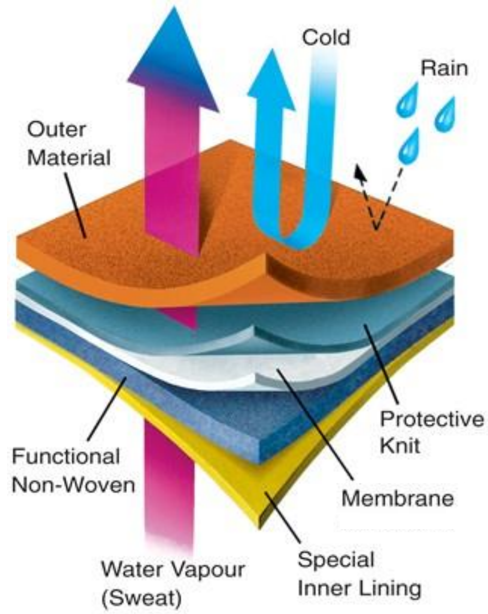
EUROBAROMETER

Food associated health risks - perception in EU member states



Issues of concern

- **Industrial organic pollutants:**
  - Perfluoroalkylated substances (PFAS)
  - Brominated flame retardants (BFRs)
  - “New” pesticides
  - Nanomaterials
- **Pharmaceutical & personal care products (PPCPs)**
- **Biotoxins:**
  - Mycotoxins



Perfluoroalkylated substances (PFAS): ´emerging´ environmental / food contaminants

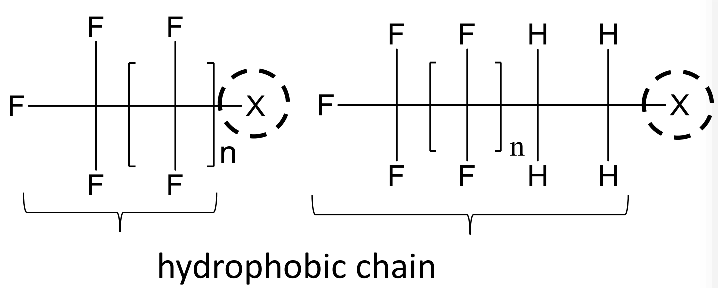
Perfluoroalkylated substances (PFASs)

- hydrophobic alkyl chain and a hydrophilic end group
- **thermal and chemical stability**
- cleaning agents, impregnation agents for textiles, carpets, paper, packaging, furniture, paint and varnish, fire-extinguishing liquids, wax, floor polishing agents

General structure

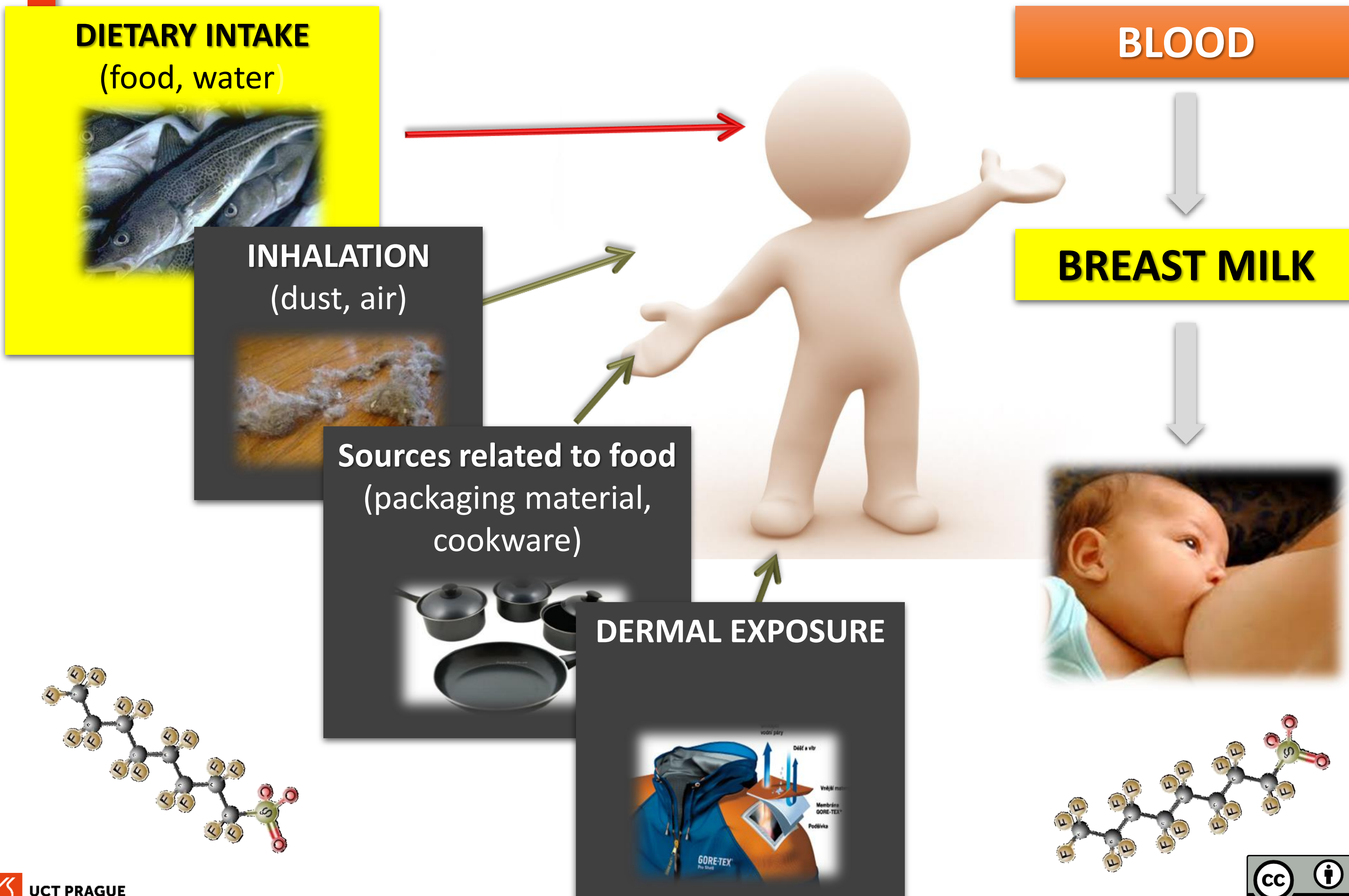
X hydrophilic group

n usually 3 - 15



- several PFASs have been recognized as generally persistent in the environment and are associated with a broad spectrum of **health effects**

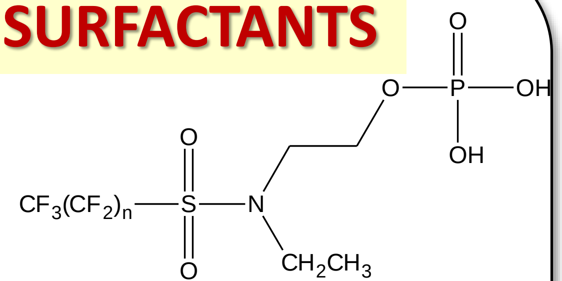
Sources of human exposure to PFASs



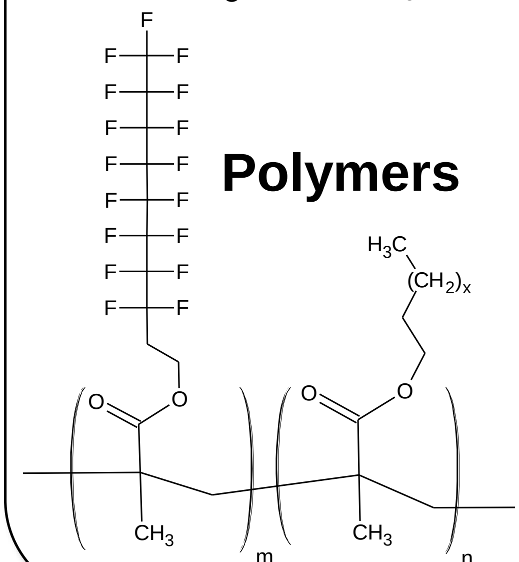
Sources of PFAS in the human environment

PFCs are released from industrial sources and from ‘in use’ consumer products.

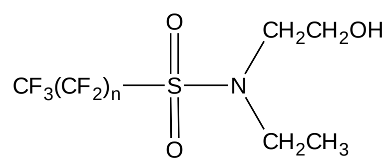
SURFACTANTS



Polymers



Reactive Intermediates

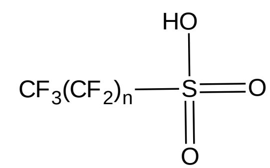


FOSEs

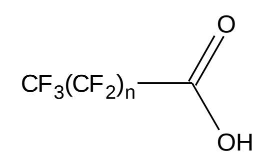
$CF_3(CF_2)_nCH_2CH_2OH$

FTOHs

DEGRADATION PRODUCTS

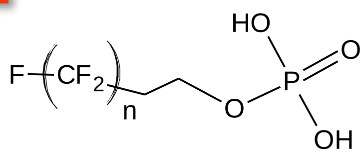


PFSAs

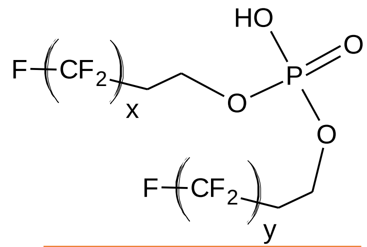


PFCAs

Structures of selected PFAS

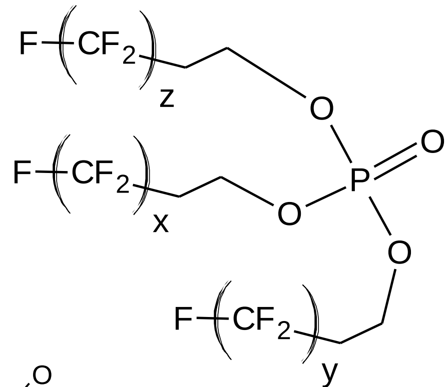


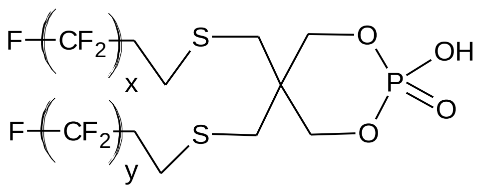
monoPAPS



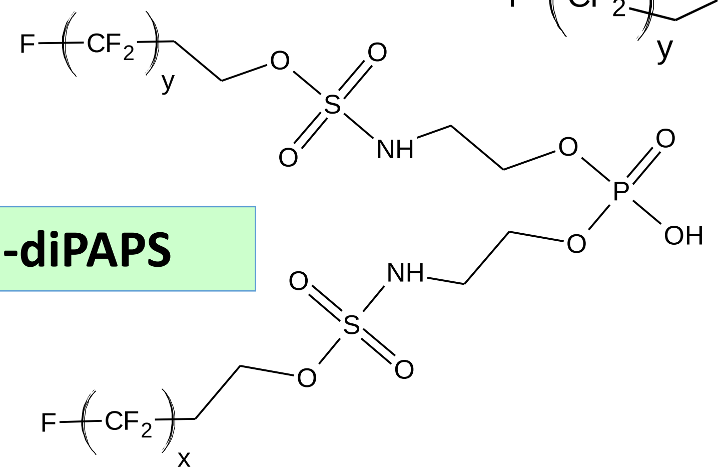
diPAPS

triPAPS

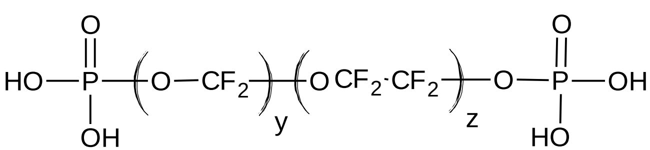




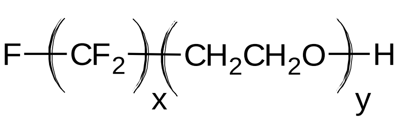
S-diPAPS



SN-diPAPS



Polyfluoropolyethers (PFPE)



Fluoroalkoxylates

Brominated flame retardants: another group of “emerging“ contaminants

Brominated flame retardants

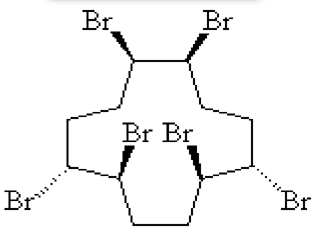
- Brominated Flame Retardants (BFRs) are produced from 60s of 20th century.
- Due to their lipophilicity, these substances may be accumulated in various parts of the environment as well as in food chain.

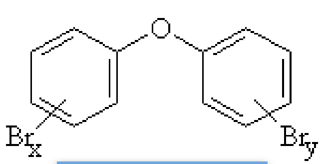
European Food Safety Authority

- **December 2009:**

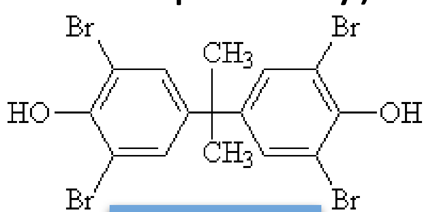
  EFSA released a call for more data concerning, except for routinely determined polybrominated diphenyl ethers (PBDEs), also polybrominated biphenyls (PBB), **hexabromocyclododecane (HBCD)**, **tetrabromobisphenol A (TBBPA)** and **other brominated phenols** as well as for other emerging BFRs as decabromodiphenyl ethane (DBDPE) and bis(2,4,6-tribromphenoxy)ethane (BTBPE).

HBCD



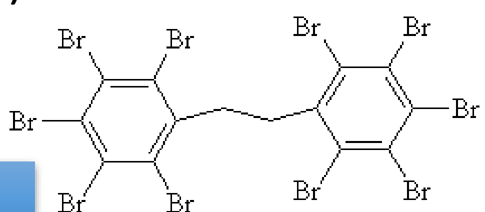


PBDE



TBBPA

DBDPE



Categorization of the brominated flame retardants (BFR)

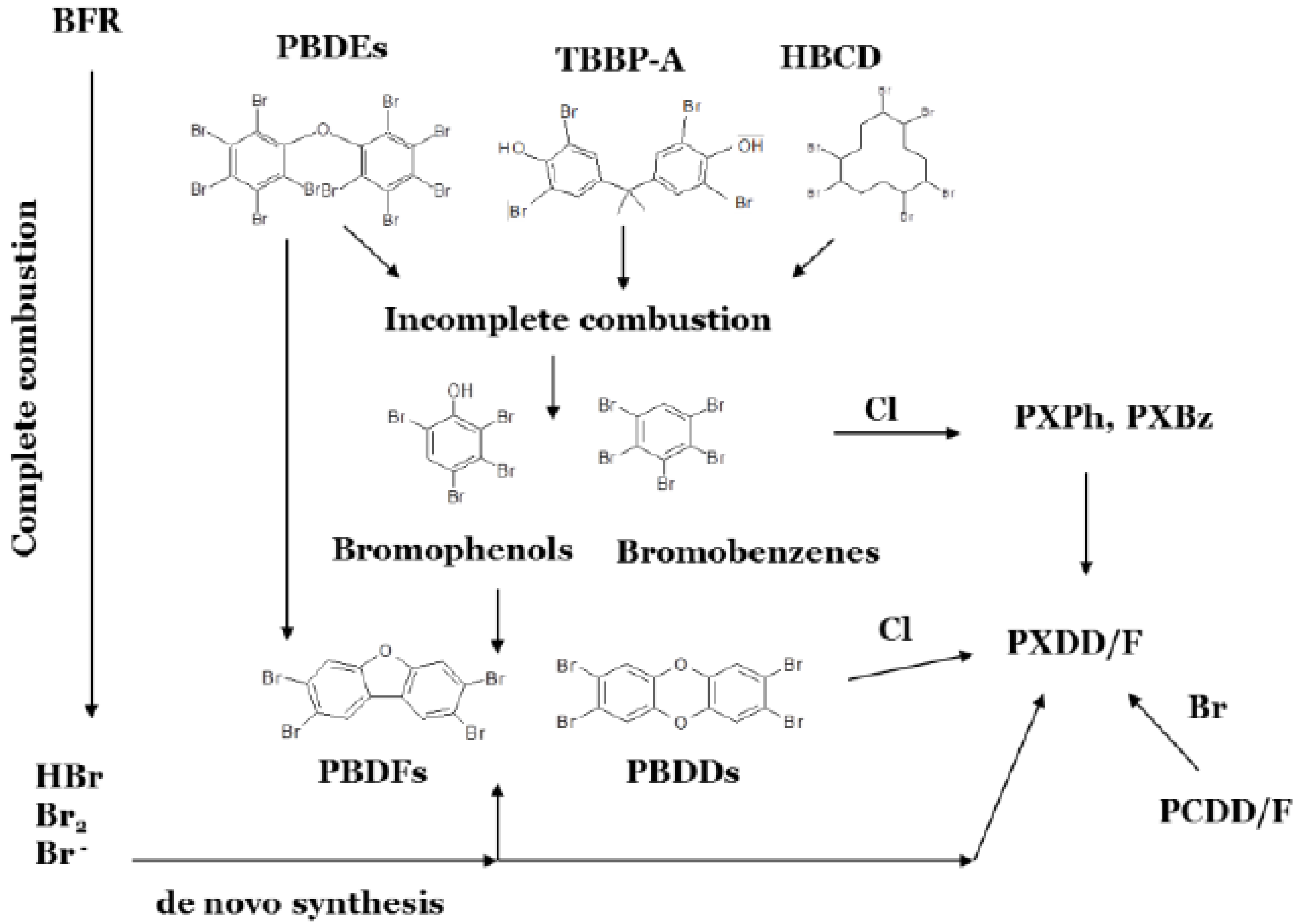
European Food Safety Authority

Established BFRs:	**There are extensive data sets describing each one of the chemical, or chemical groups, as BFRs (i.e. incl. data on their chemistry, fate, exposure, ecotoxicity and toxicity)**
Novel BFRs:	BFRs only reported to occur in material, goods/articles or in products. No data available on environmental occurrence or presence in biota.
Emerging BFRs:	BFRs reported to occur in the abiotic environment or in biota, incl. humans, but for which the data sets are limited and/or incomplete
Potential BFRs:	Chemicals that are proposed (patented) for applications as BFRs

There are currently around 20 BFRs in use, worldwide. For these substances there are many important data gaps, in particularly for the emerging BFRs. For example, data on production, use and ecotoxicology are missing.

Growing demand for data, regulation needs

Pyrolysis and combustion of BFRs

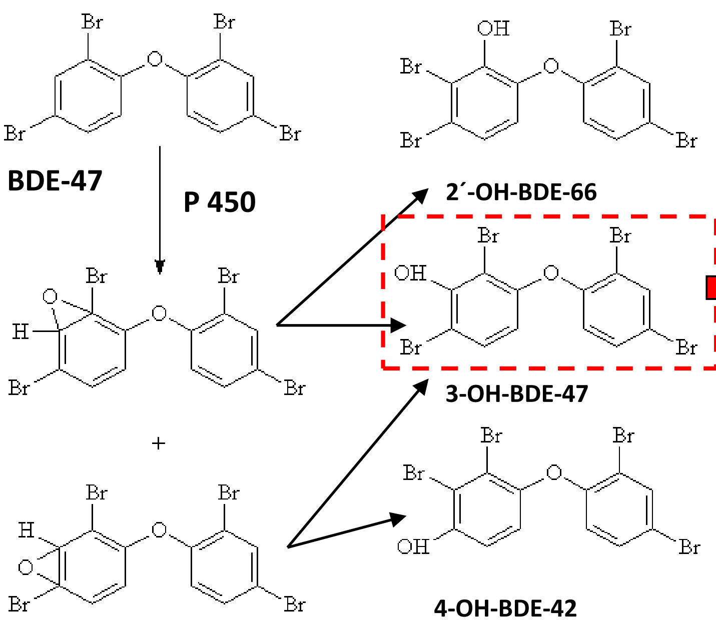


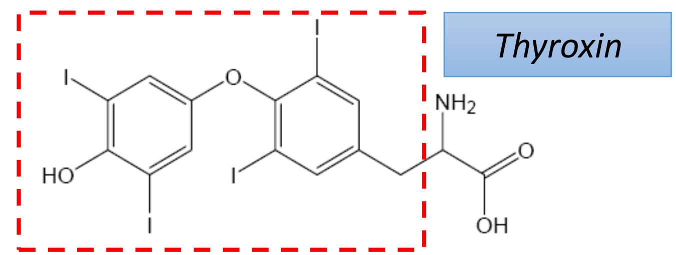
Metabolites of PBDE

Methoxy and hydroxy PBDE derivatives (OH-PBDE a MeO-PBDE)

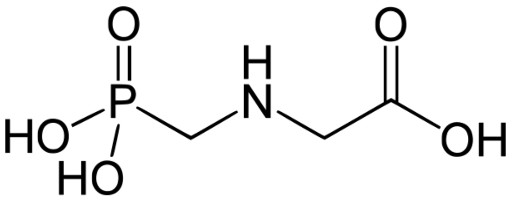
- **Origin of PBDE derivatives**
  - Natural synthesis (inferior marine organisms)
  - Metabolism of PBDEs by organisms

Hydroxylation pathway of BDE-47 in mice:

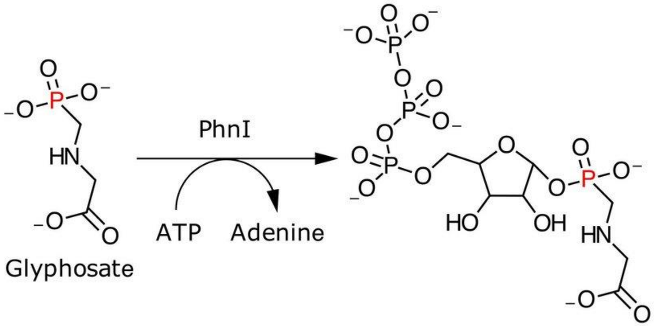




Hydroxylated PBDEs are supposed to interfere with thyroid hormones!



“NEW“ pesticides

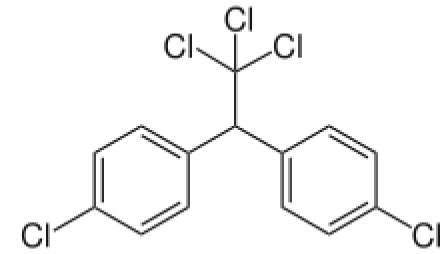


UCT PRAGUE

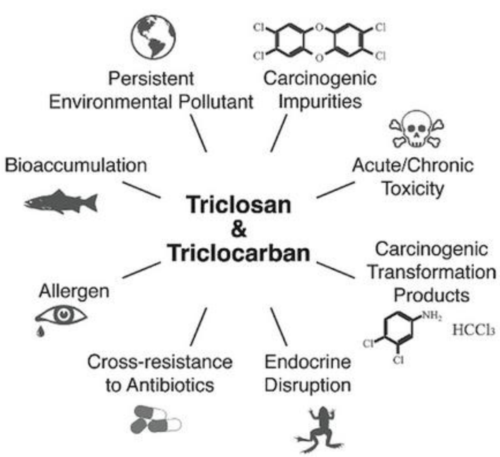
“New“ pesticides

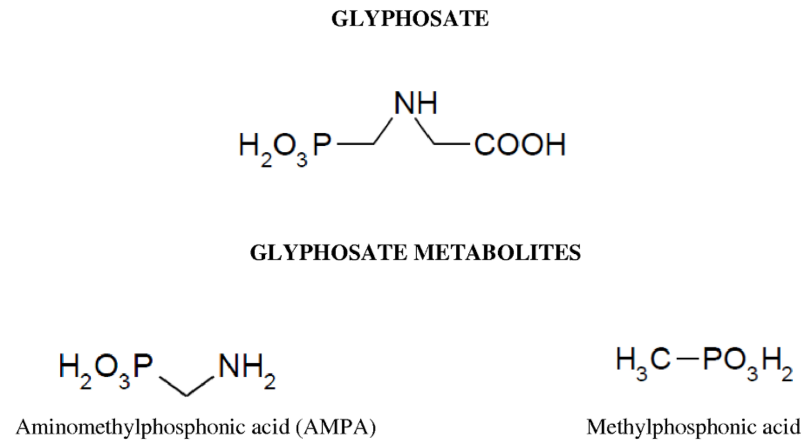
- Pesticides are used in agriculture related to crop growth, storage, and transport; in food marketing; in wood and wood products in industries; in livestock for the control of insects, arachnids, and other pests; in gardening; and in household maintenance.
- Use of banned, unauthorized and counterfeit pesticides
- Consumers protection: monitoring of pesticide residues in food and follow up
- Environmental protection: Monitoring of pesticide contamination in water indicators

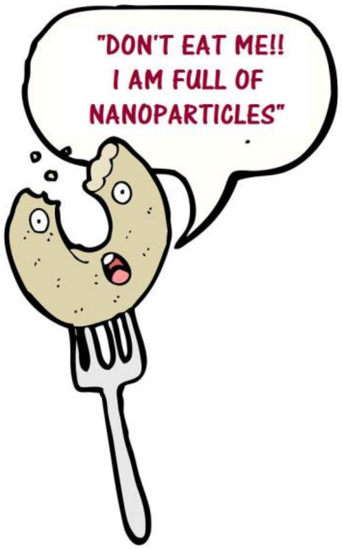
Pesticides of Emerging concern

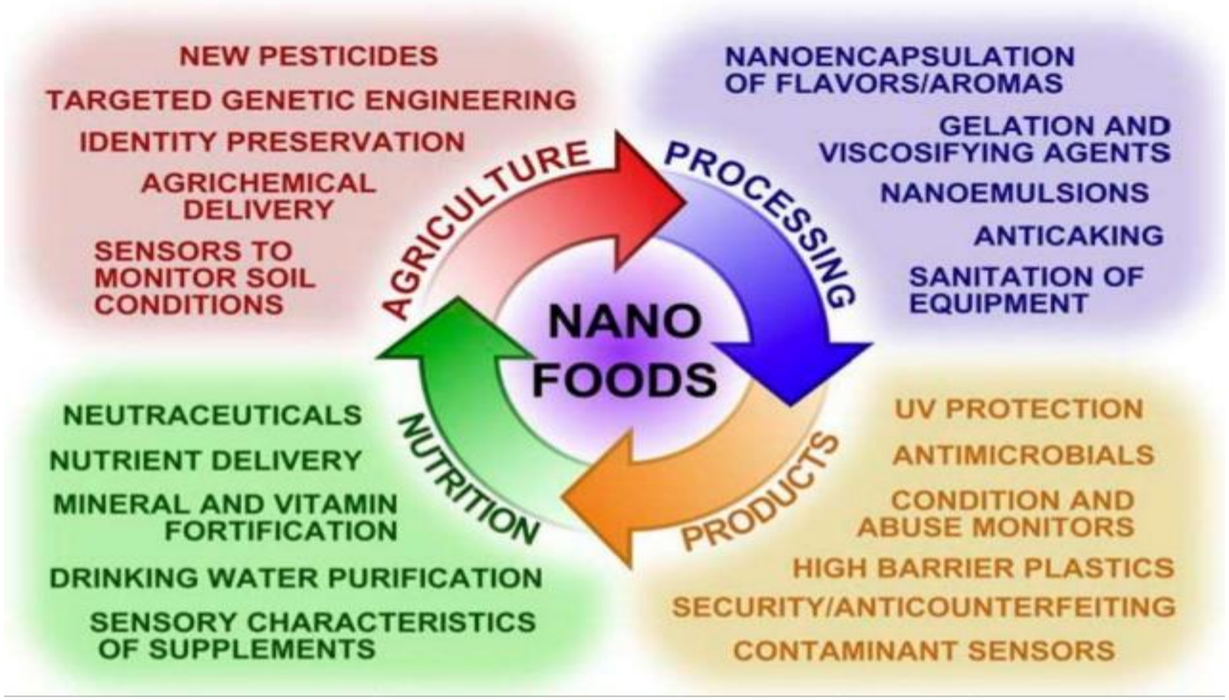


- DDT and organochlorine pesticides
- Glyphosate
- Transformation products (metabolites) of pesticides
- Triclosan
- And many more…..

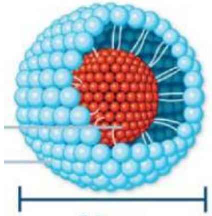








Nanoparticles in food

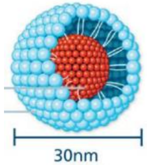


Nanomaterials

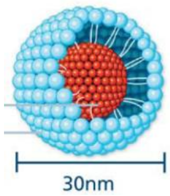
- Definition of nanomaterials:
  one dimension < 100 nm (300 nm)
- Increase of surface area
- Higher reactivity
- Behaviour different from bulk material
- Extraordinary properties have led to applications in various areas: semi-conductors, lacquers/ paints, drug delivery, ...
- Nanotechnology is a fast growing industry

Nanoparticles and food: a reality

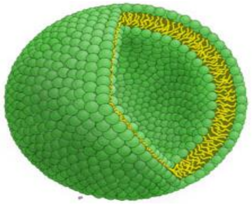
- Naturally occurring nanoparticles
  - milk: casein micelles (~ 100 nm), whey proteins (~ 3 nm)
- Conventionally produced food
  - Mayonnaise, Sauce Béarnaise: nano-sized droplets
- Engineered nanoparticles
  - nanoparticles in PET bottles (e.g. titanium nitride, nano-clay)
  - nano-silver in food containers
  - nano-encapsulated ingredients/preservatives
  - and, and, and...

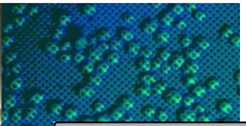


Main application areas



- Food packaging
  - **Sales packaging:** nano-particles incorporated in polymer matrix:clay, TiN, nylon, TiO_2, ZnO
  - **Active packaging:** nano-silver incorporated/coated: antimicrobial activity
  - **Preservation of quality, extension of shelf life**
- Food ingredients/supplements/auxiliaries
  - Nano-SiO_2 as anti-caking agent (
  - Nano-encapsulates (preservatives, vitamins, lycopene)
  - Nano-formulated ingredients (micelles)





Nano – Food: Risk assessment

The European Food Safety Authority (EFSA):

- Specific uncertainties apply to the **difficulty to characterize, detect and measure ENMs in food/feed** and biological matrices
- Limited information available on **toxicokinetics and toxicology**.
- Limited knowledge of current **usage levels and exposure** from possible applications and products in the food and feed area.

(Scientific Opinion of the Scientific Committee on a request from the European Commission on the Potential Risks Arising from Nanoscience and Nanotechnologies on Food and Feed Safety. The EFSA Journal (2009) 958, 1-39)

Pharmaceuticals & personal care products (PPCPs)

Pharmaceuticals & personal care products (PPCPs)

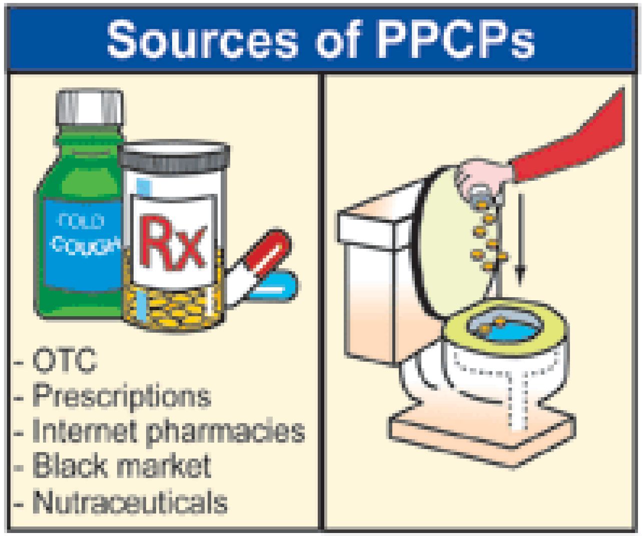
- Currently, pharmaceuticals and personal care products termed PPCPs are receiving great public attentions as emerging contaminants.
- PPCPs have been frequently detected in the lake, river, and stream in the US because they are widely used in human and veterinary clinical practices
- Compared with the "conventional" pollutants, little is known about PPCPs with regard to potential environmental effects.
- Some PPCPs show very highly acute toxicity to aquatic species.
- Long-term effects on human health are unknown (maybe chronic)???

Pharmaceuticals and Personal Care Products as Pollutants

- PPCPs comprise a diverse collection of thousand of chemical substances including:
  - Therapeutic drugs
  - Veterinary drugs
  - Fragrances
  - Cosmetics
  - Sun-screen products
  - Diagnostic agents
  - Nutraceuticals

PPCPs enter the Environment Through use and disposal

- Probably presented in the environment for as long as humans have been using them
- Contamination of the environment through:
  - Excretion
  - Bathing
  - Disposal of unwanted medication to sewers and trash



Pharmaceuticals and Personal Care Products as Pollutants

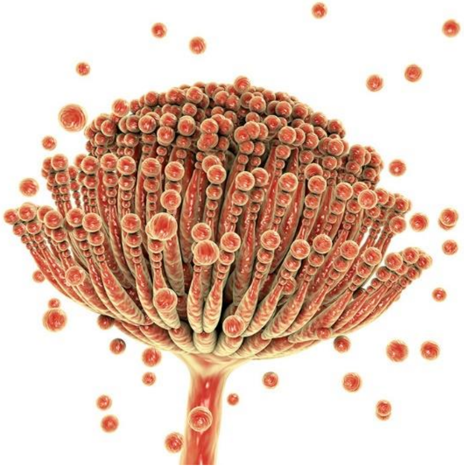
- The drugs that we take may be excreted in a biologically active form into wastewater and ultimately released into lakes and rivers

- Advances in technology have improved our ability to detect and quantify these chemicals

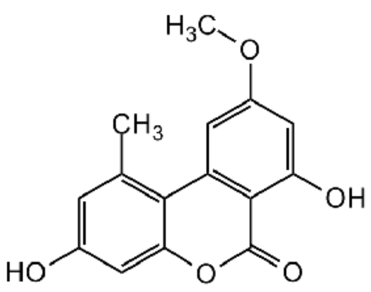
- Their effect on the environment is now recognized as an important area of research.

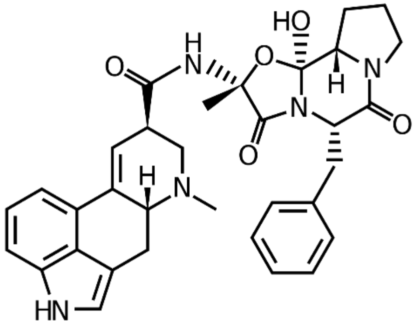
PPCPs are present in our waterbodies

- The most often detected chemicals (found in more than half of the streams:
  - Coprostanol (fecal steroid)
  - Cholesterol (plant and animal steroid)
  - N,N-diethyltoluamide (insect repellent)
  - Caffeine (stimulant)
  - Triclosan (antimicrobial disinfectant)
  - Tri (2-chloroethyl)phosphate (fire retardant)
  - 4-nonylphenol (nonionic detergent metabolite)
- Steroids, nonprescription drugs, and insect repellent were the chemical groups most frequently detected
- Detergent metabolites, steroids, and plasticizers generally were measured at the highest concentrations



Mycotoxins





Emerging Mycotoxins

New/unexpected occurrence data

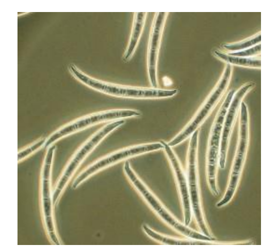
Advanced LC-MS methods

Climate change

Plant breeding

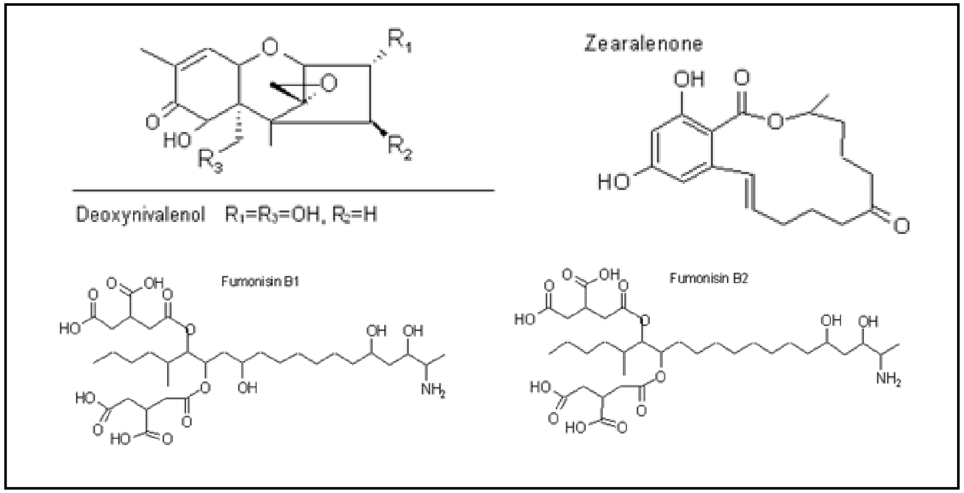
New findings (e.g. masked toxins)

Fusaproliferin, Beauvericin, Enniatins, Moniliformin, 3-AcDON, Ergot alkaloids, … ?

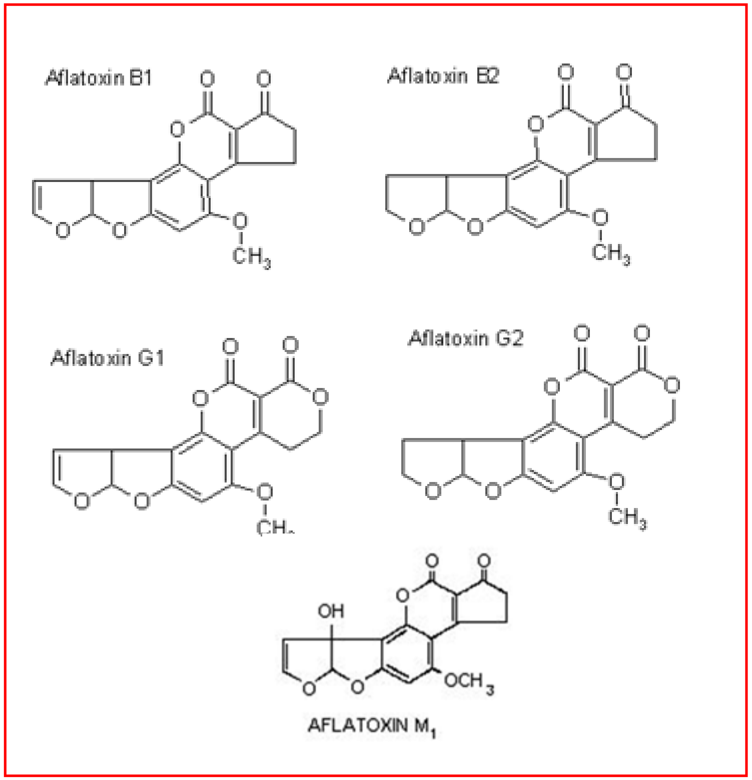


MYCOTOXINS IN FOOD - REGULATED

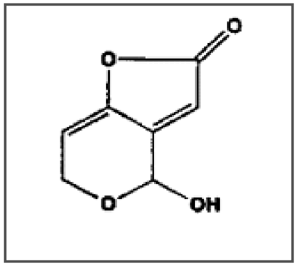
Commission regulation (EC) No 1881/2006 amended by Regulation (EC) No 1126/2007



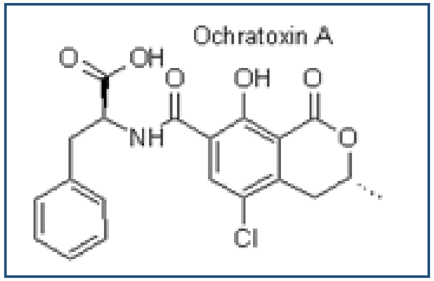
Fusarium mycotoxins



Aflatoxins



Patulin



Ochratoxin A

MYCOTOXINS IN FOOD – CONSIDERED FOR REGULATION

European Food Safety Authority

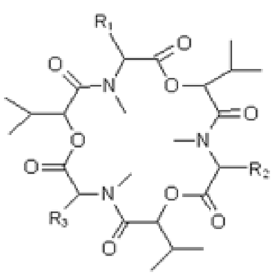
Verrucarol R_1=R_4=H, R_2=R_3=OH
Neosolaniol R_1=OH, R_2=R_3=R_4=OAc
Diacetoxyscirpenol R_1=OH, R_2=R_3=OAc, R_4=H
HT_2 toxin R_1=R_2=OH, R_3=OAc, R_4=OCOi-Bu
T_2 toxin R_1=OH, R_2=R_3=OAc, R_4=OCOi-Bu

Deoxynivalenol R_1=R_3=OH, R_2=H
Nivalenol R_1=R_2=R_3=OH
Fusarenon-X R_1=R_3=OH, R_2=OAc
3-Acetyldeoxynivalenol R_1=OAc, R_2=H, R_3=OH
15-Acetyldeoxynivalenol R_1=OH, R_2=H, R_3=OAc

Other trichothecenes

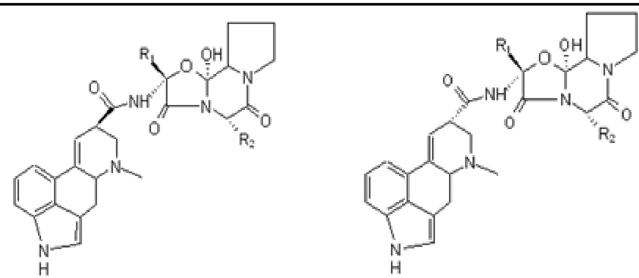
EFSA calls in 2010, 2011, 2012

EXTENDING THE NUMBER OF MYCOTOXINS HAVING MAXIMUM LEGISLATIVE LIMITS



Enniatin A R_1=R_2=R_3=$CH_2C_6H_5$
Enniatin A_1 R_1=R_2=R_3=$CH(CH_3)CH_2CH_3$
Enniatin B R_1=$CH(CH_3)CH_2CH_3$, R_2=R_3=$CH(CH_3)_2$
Enniatin B_1 R_1=R_2=R_3=$CH(CH_3)_2$

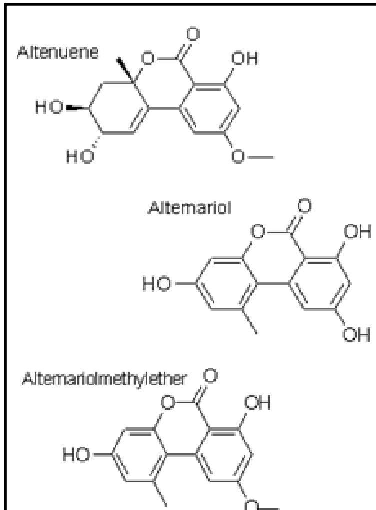
Enniatins



Ergosine R_1=CH_3, R_2=$CH_2CH(CH_3)_2$
Ergotamin R_1=CH_3, R_2=$CH_2C_6H_5$
Ergocornin R_1=$CH(CH_3)_2$, R_2=$CH(CH_3)_2$
Ergocristin R_1=$CH(CH_3)_2$, R_2=$CH_2C_6H_5$

Ergosinine R_1=CH_3, R_2=$CH_2CH(CH_3)_2$
Ergotaminine R_1=CH_3, R_2=$CH_2C_6H_5$
Ergocorninine R_1=$CH(CH_3)_2$, R_2=$CH(CH_3)_2$
Ergocristinine R_1=$CH(CH_3)_2$, R_2=$CH_2C_6H_5$

Ergot alkaloids



Alternaria mycotoxins

Emerging mycotoxins

- High contamination levels in Europe;
- Enniatins, Beauvericin, Alternaria Toxins,…
- Possible synergies with other mycotoxins;
- Toxicological role not completed understood/investigated;
- No maximum limits setting

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

7. Characterization of properties of exogenous contaminants, penetration into food chains

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Food contaminants

- **Unintentionally entry to 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

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**

Perception of health risks associated with food

Order	Scientist	General public
1	biological hazards	pesticides residua
2	natural toxins	industrial contaminants
3	industrial contaminants	additives
4	veterinary drug residua	veterinary drug residua
5	pesticides residua	biological hazards
6	additives	natural toxins

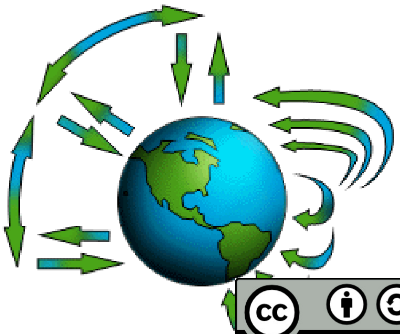
Contamination sources

- agriculture production
- use of pesticides
- fertilization
- emission
- water for irrigation
- use of surface water for irrigation
- attack by microorganisms, especially by mould
- veterinary treatment
- storage and processing
- • post harvest application of pesticides
- • formation from relatively nontoxic
- pesticides
- • attack by microorganisms
- • technological and cooking arrangement
- • penetration of additives from plastic materials

Classification of pollutants

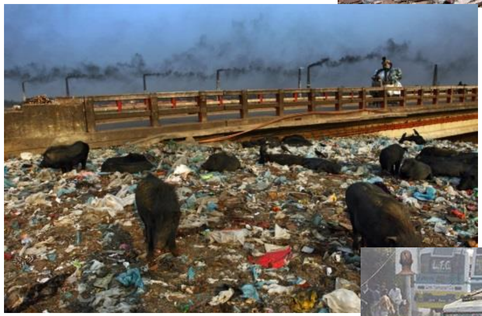
Pollutants may be classified by various criteria:

- **Origin**: whether they are natural or man-made (synthetic).
- **Effect**: on an organ, specie, or an entire ecosystem.
- **Properties**: mobility, persistence, toxicity.
- **Controllability**: easy or difficult removal.



Types of Pollution

- **Air pollution**
- **Water pollution**
- **Soil pollution (Land pollution)**
- Noise pollution
- Radioactive pollution
- Thermal pollution
- Light Pollution
- Visual Pollution



Sources of pollutants

Air pollution

- Vehicle or manufacturing exhaust
- Forest fires, volcanic eruptions, dry soil erosion, and other natural sources
- Building construction or demolition

- **Major pollutants produced by human activity include:** sulphur oxides (SO_x), nitrogen oxides (NO_x) - especially nitrogen dioxide, carbon monoxide (CO), volatile organic compounds (VOCs), lead, mercury, chlorofluorocarbons (CFCs), radioactive pollutants

Sources of pollutants

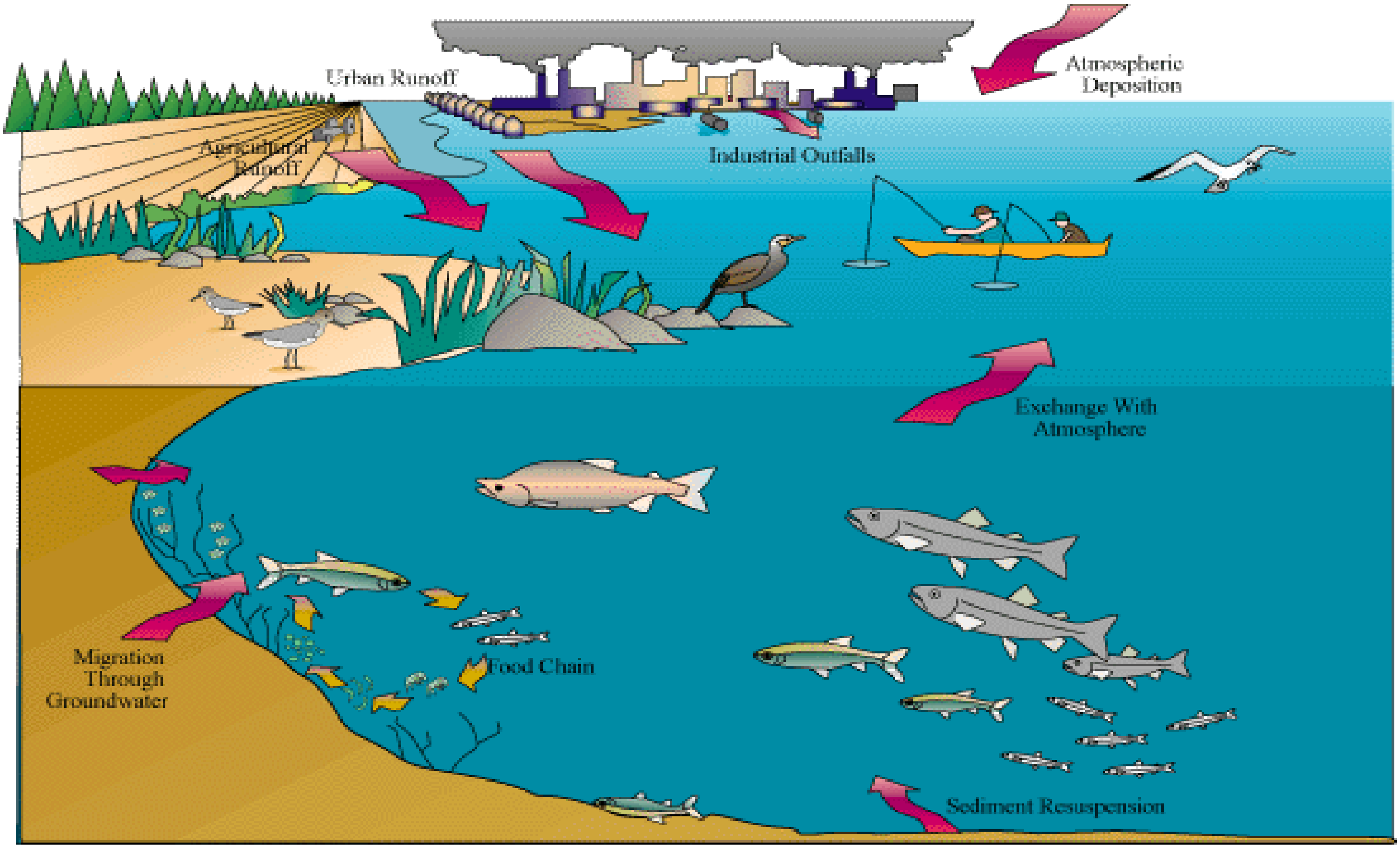
- **Water pollution**
  - Increased sediment from soil erosion
  - Improper waste disposal and littering
  - Leaching of soil pollution into water supplies
  - Organic material decay in water supplies

- **Water pollutants include:**

detergents, residues of pesticides, solvents, PCBs, heavy metals, fertilizers (nitrates and phosphates), compounds found in personal hygiene and cosmetic products

Sources of pollutants

- **Water pollution**



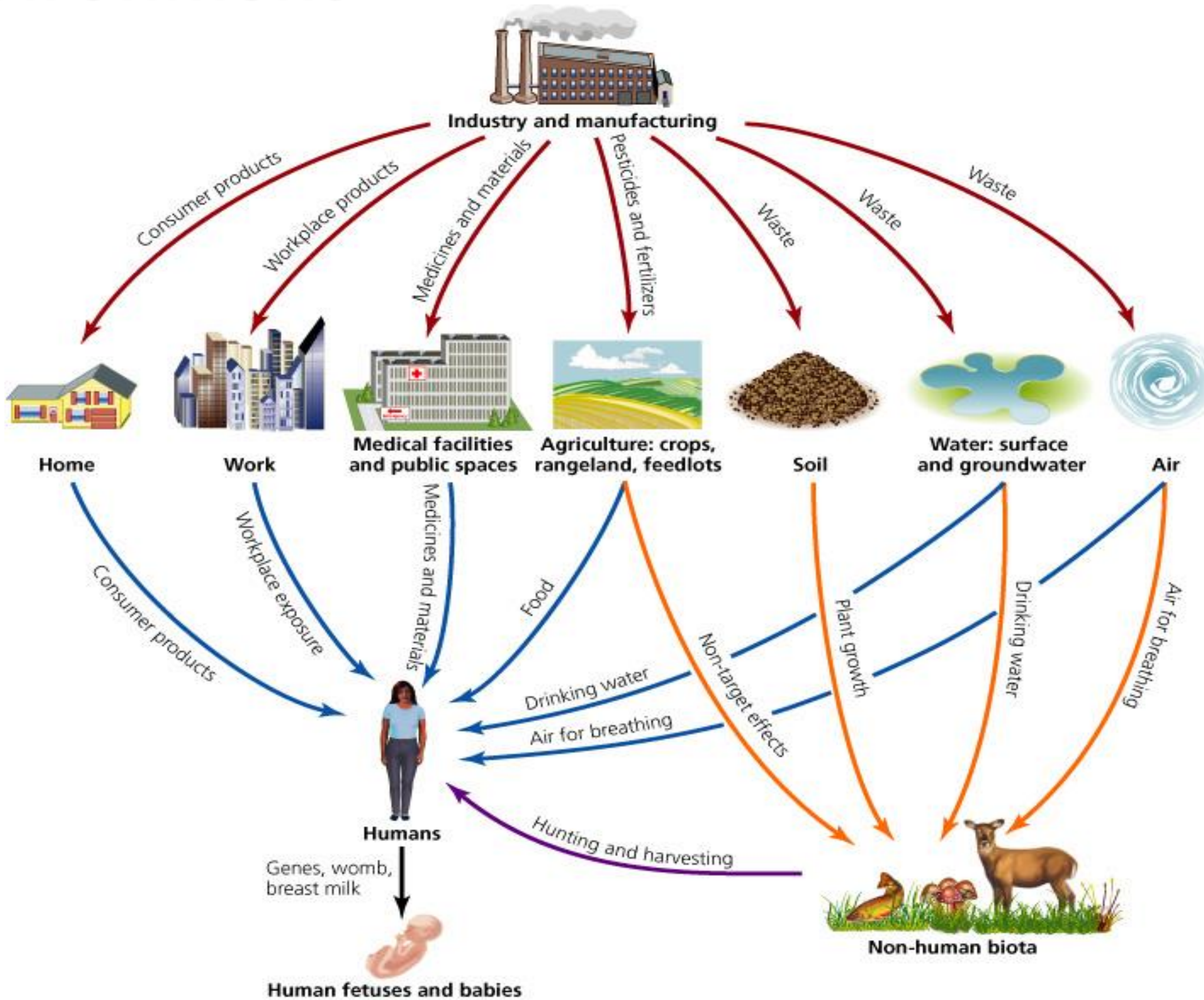
Sources of pollutants

Soil pollution

- Hazardous waste and sewage spills
- Non-sustainable farming practices, such as the heavy use of pesticides
- Strip mining, deforestation, and other destructive practices
- Household dumping and littering

- **The most common chemicals:**
  petroleum hydrocarbons, solvents, pesticid ad, and other heavy metals

Toxicants take many routes through the environment

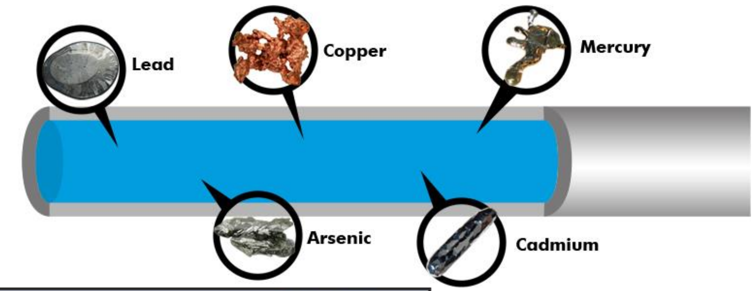


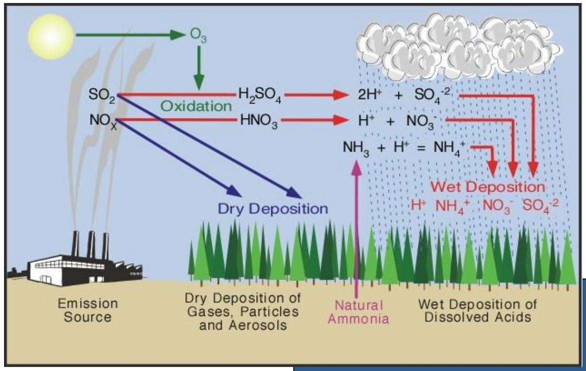
Sources of potential toxicants in food

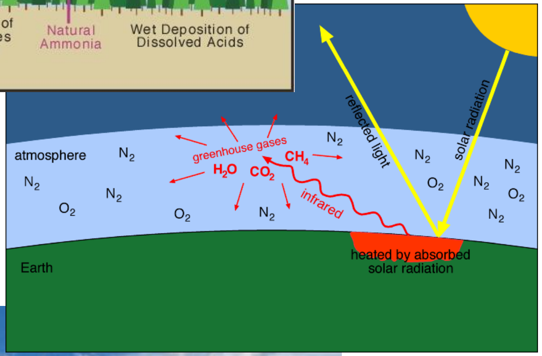
- Naturally occurring toxicants
  - intrinsic and exogenous (e.g. mycotoxins)
- Added intentionally and purposefully
  - food additives, nutritional supplements
- Present purposefully but not intentionally
  - pesticide residues, veterinary drug residues
- Present without purpose and unintentionally
  - environmental contaminants in the food chain (both anthropogenic and natural/geological)
- Produced during cooking/processing

Inorganic pollutants

- **Heavy metals**
  - Hg, Pb, Cd, As, Cu
- **Acids**
  - Acid rain
- **Greenhouse gasses**
  - Carbon dioxide (CO_2)
  - Nitrous oxide (N_2O)
- **Radionuclides**
  - ^{90}Sr, ^{134}Cs, ^{137}Cs , ^{241}Am
- Nanoparticles







Organic contaminants

- Volatile organic compounds (VOCs)
- **Persistent organic pollutants (POPs)**
  - Polychlorinated biphenyls (PCBs)
  - Polychlorinated dibenzodioxins/furans (PCDDs/Fs)
  - Organochlorine pesticides (OCPs)
  - Brominated flame retardants (BFRs)
  - Perfluorinated compounds (PFCs)
- **Polycyclic aromatic hydrocarbons (PAHs)**
- **Pesticides**
- “Musk“ compounds, Phthalates, Alkylphenols

Persistent organic pollutants (POPs)

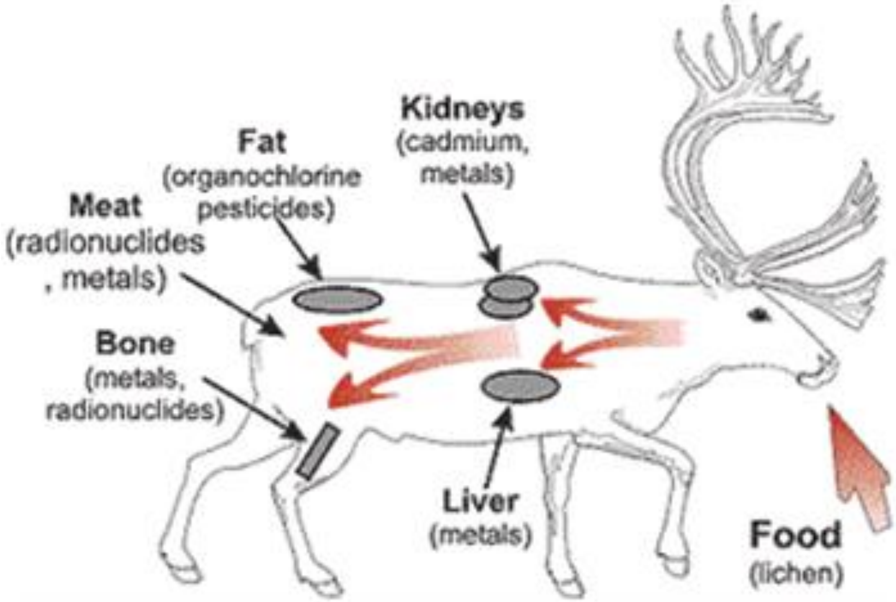
- **Intentionally formed compounds**
  - Hexachlorobutadiene, PCBs,
  - Polyflourinated compounds (PFOS)
  - Brominated flame retardants
  - Pesticides: DDT, aldrin, chlordane, dieldrin, endrine, HCH, heptachlor, HCB, mirex, toxaphene
- **Unintentionally formed compounds**
  - Dioxins
  - PAHs
  - Hexachlorobenzene
  - Brominated dioxins

Persistent organic pollutants (POPs)

- Resistant to biological and chemical degradation
- Semi-volatile: spread globally through the atmosphere
- Long-range transport leads to global pollution
- Lipophilic: accumulation in fatty tissues
- Able to bioaccumulate and biomagnify
- Ubiquitous
- Toxic – carcinogens, teratogens, endocrine disruptors

Bioaccumulation

- The process by which a contaminant accumulates in tissues of an individual organism
- E.g. certain chemicals in food eaten by a fish tend to accumulate in its liver and other tissues – the chemicals are taken in faster than the individual can get rid of them

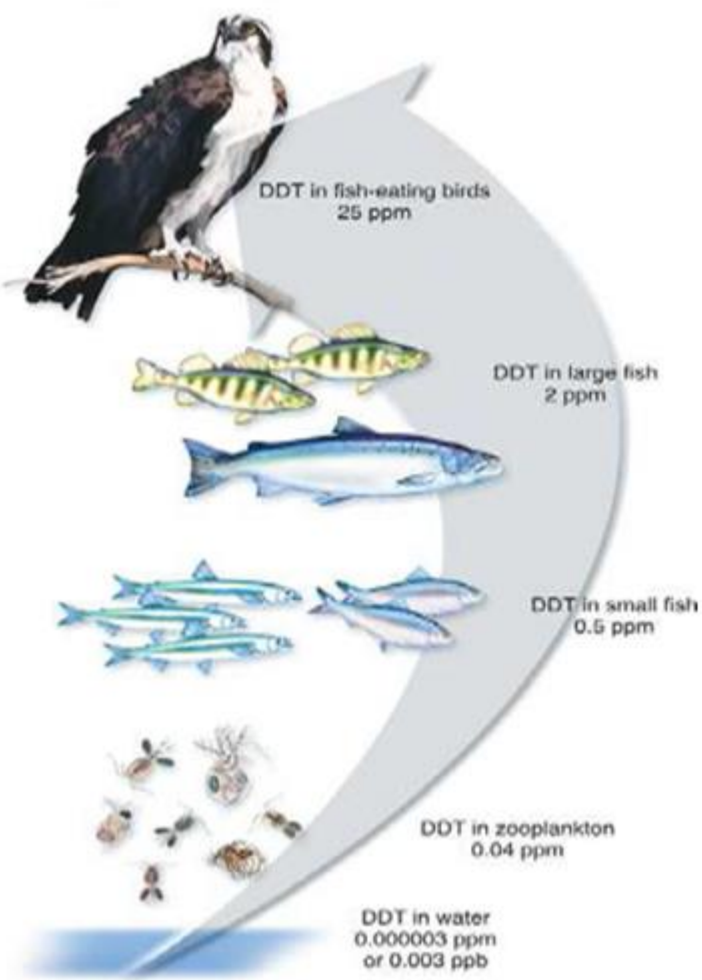


Biomagnification

- Increase in concentration of certain stable chemicals (heavy metals or fat-soluble pesticides) in successively higher trophic levels of a food chain or web.

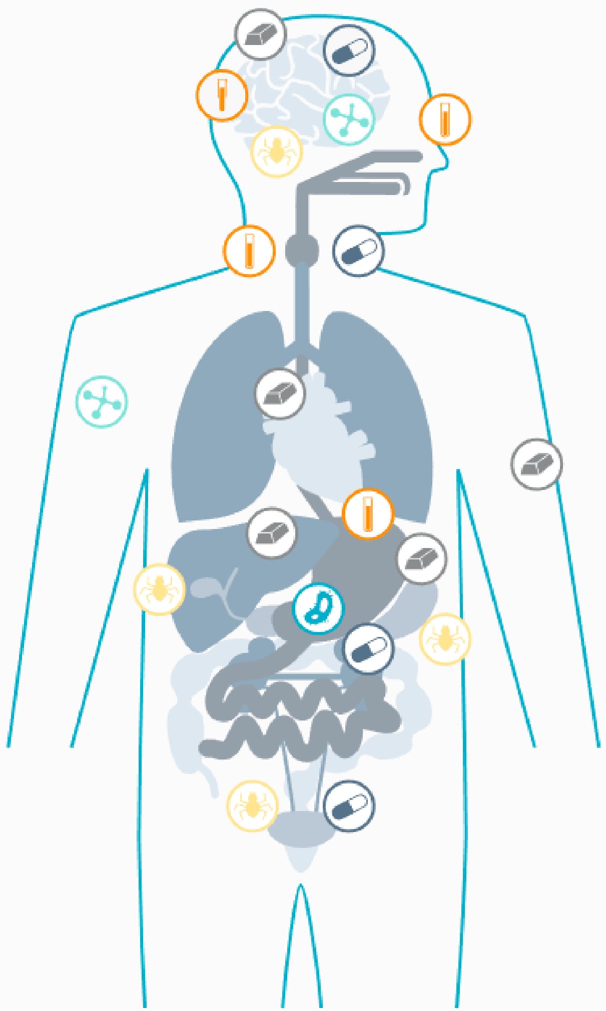
- E.g. mercury, PCBs, pesticides, dioxins

Note: Not all contaminants biomagnify



Bioaccumulation = Bioconcentration + Biomagnification

Effects of contaminants on human health



MICROBIAL

Gastro-enteric diseases

HEAVY METALS

Liver, kidney, circulatory system disorders, Skin, nervous system, Gastro-enteric diseases

CHEMICAL

Eye/nose irritation, stomach discomfort, Varied, including brain and thyroid disorders, Cancer, leukemia, anemia

TRIHALOMETHANES

Muscle, nervous system damage

PESTICIDES

Cancer, Reproductive damage, Liver, Kidney, nervous system damage

EMERGING CONTAMINANTS

Endocrine disruptor, reproductive and neurodevelopmental disorders

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

8. Persistent organic pollutants

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

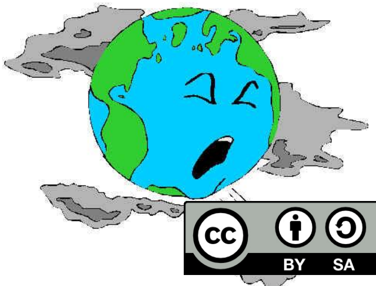
MINISTRY OF EDUCATION, YOUTH AND SPORTS

What is a pollutant?

In general, substance or energy introduced into the environment that has undesired effects, or adversely affects the usefulness of a resource.

A pollutant may cause long- or short-term damage by changing the growth rate of plant or animal species, or by interfering with human amenities, comfort, health, or property values.

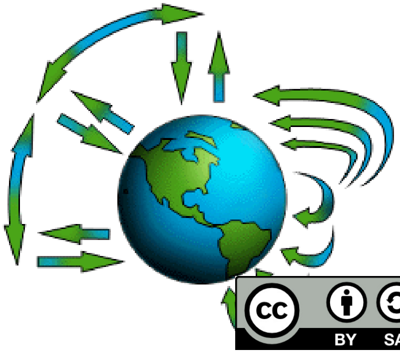
Pollutants can be in the form of solid particles, liquid droplets, or gases.



Classification of the pollutants

Pollutants may be classified by various criteria:

- **Origin**: whether they are natural or man-made (synthetic).
- **Effect**: on an organ, specie, or an entire ecosystem.
- **Properties**: mobility, persistence, toxicity.
- **Controllability**: easy or difficult removal.



Persistent organic pollutants (POPs)

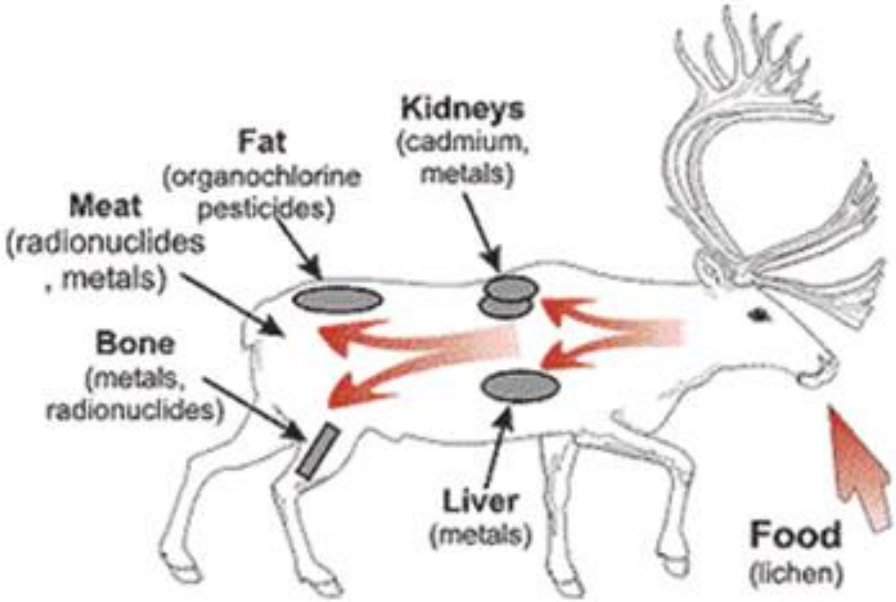
- **Intentionally formed compounds**
  - Hexachlorobutadiene, PCBs,
  - Polyflourinated compounds (PFOS)
  - Brominated flame retardants
  - Pesticides: DDT, aldrin, chlordane, dieldrin, endrine, HCH, heptachlor, HCB, mirex, toxaphene
- **Unintentionally formed compounds**
  - Dioxins
  - PAHs
  - Hexachlorobenzene
  - Brominated dioxins

Persistent organic pollutants (POPs)

- Resistant to biological and chemical degradation
- Semi-volatile: spread globally through the atmosphere
- Long-range transport leads to global pollution
- Lipophilic: accumulation in fatty tissues
- Able to bioaccumulate and biomagnify
- Ubiquitous
- Toxic – carcinogens, teratogens, endocrine disruptors

Bioaccumulation

- The process by which a contaminant accumulates in tissues of an individual organism
- E.g. certain chemicals in food eaten by a fish tend to accumulate in its liver and other tissues – the chemicals are taken in faster than the individual can get rid of them

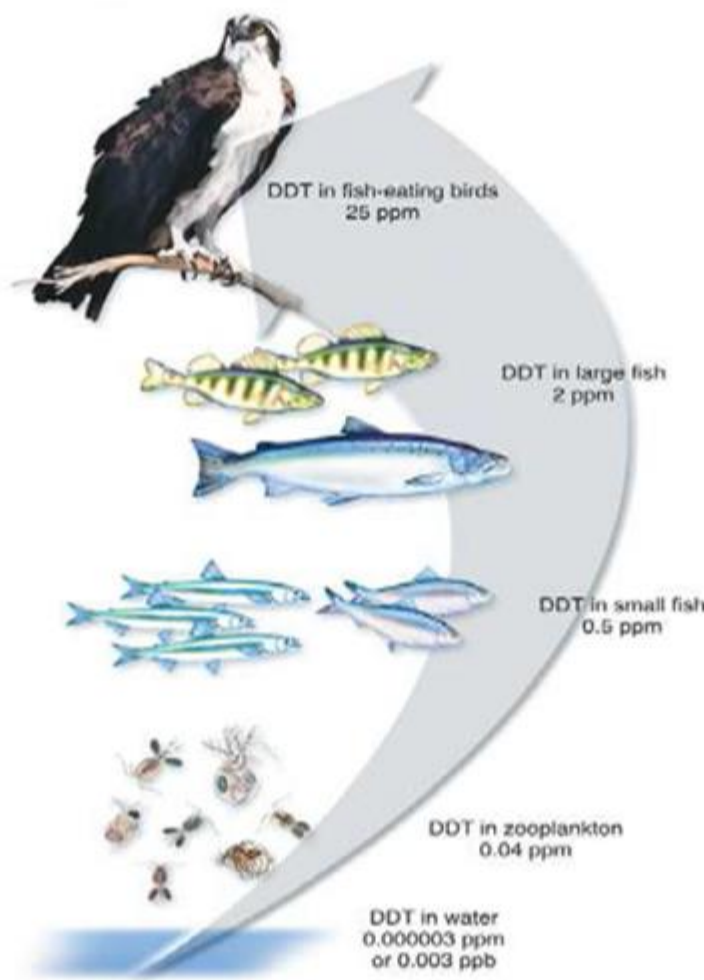


Biomagnification

- Increase in concentration of certain stable chemicals (heavy metals or fat-soluble pesticides) in successively higher trophic levels of a food chain or web.

- E.g. mercury, PCBs, pesticides, dioxins

Note: Not all contaminants biomagnify



Bioaccumulation = Bioconcentration + Biomagnification

Stockholm Convention

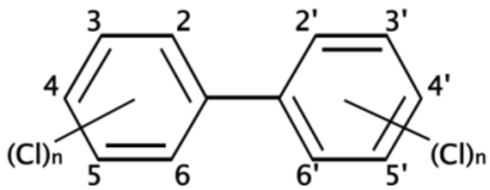
- The Stockholm Convention is an international treaty aimed at restricting and ultimately eliminating POPs, production, use, release and storage.

- Originally 12 organochlorinated compounds were included – “dirty dozen”: **Aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCB, mirex, toxaphene, PCBs, PCDDs, PCDFs**

- The chemicals are listed in 3 annexes (A, B, C)
  - *A – elimination of production and use of chemicals*
  - *B – restriction of the production and use of chemicals*
  - *C – reduction of unintentional release of chemicals*

Polychlorinated biphenyls (PCBs)

- Man-made chlorinated industrial chemicals (trade name Aroclor)
- 209 different PCB compounds (*congeners*)
- 1 to 10 chlorine atoms attached to biphenyl



- Tend to be chemically stable and non-flammable, with high boiling points and electrical insulating properties

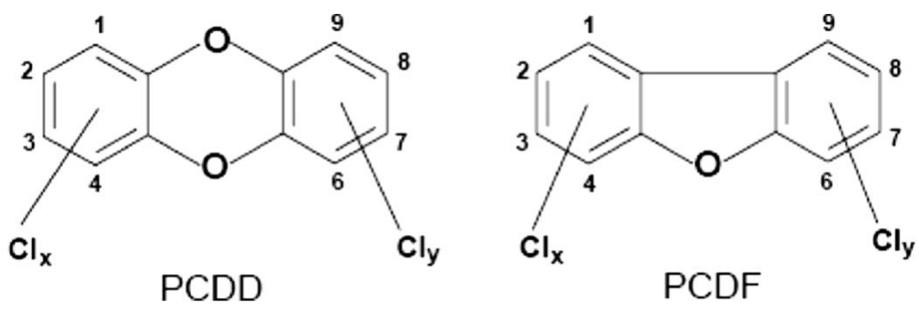
Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs)

- Commonly used as lubricants in hydraulic fluid, transmission oil, and in electrical transformers
- **Probable human carcinogens**, endocrine disruptors, harmful to the circulatory, nervous and digestive systems, liver damage

Dioxins (PCDDs/PCDFs)

- 75 different dioxins, or polychlorinated dibenzodioxins (PCDDs),
- 135 different furans, or polychlorinated dibenzofurans (PCDFs)

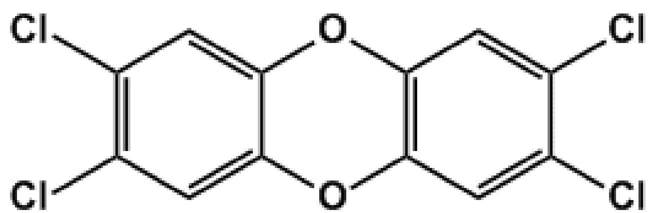


- Natural by-products from volcanoes and forest fires
- Burning household trash and/or fuels like coal, wood or oil also forms dioxins

Dioxins (PCDDs/PCDFs)

- Formed as by-products in several chemical manufacturing processes such as manufacturing, incineration, paper and pulp bleaching and exhaust emissions

- They may be contaminants in PCB mixtures or in other chemical mixtures. (*Herbicide 2,4,5-T was made from chlorophenol compounds and was contaminated with 2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin) - Agent Orange.*)



2,3,7,8-Tetrachlorodibenzo-p-dioxin
(TCDD)

Dioxins (PCDDs/PCDFs)

- Dioxins build up in living tissue (bioaccumulation) over time, so even small exposures may accumulate to dangerous levels
- **TCDD,** the most toxic of dioxins

  Toxic equivalency factors (TEFs) - The TEFs are used to weight the measured levels of the congeners present in a sample in relation to the most toxic dioxin congener, TCDD, which is defined as having a TEF of 1.

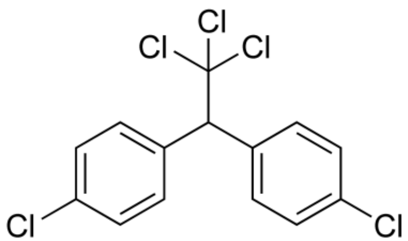
- Human carcinogens, endocrine disruptors, birth defects
- Exposure to high levels of dioxin in humans causes a severe form of persistent acne, known as chloracne

Dioxins (PCDDs/PCDFs)

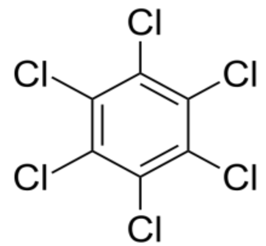
Ukrainian presidential candidate Viktor Yushchenko has been suffering from dioxin poisoning. He had ulcers in his stomach and intestines, problems with his liver and spleen, and disfiguring facial cysts that have left him looking far older than he is.

Organochlorine pesticides (OCPs)

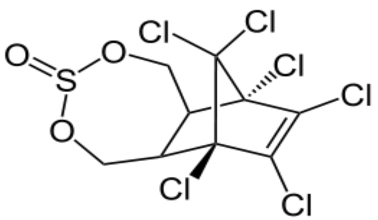
- Group of **chlorinated hydrocarbons**



DDT



HCB



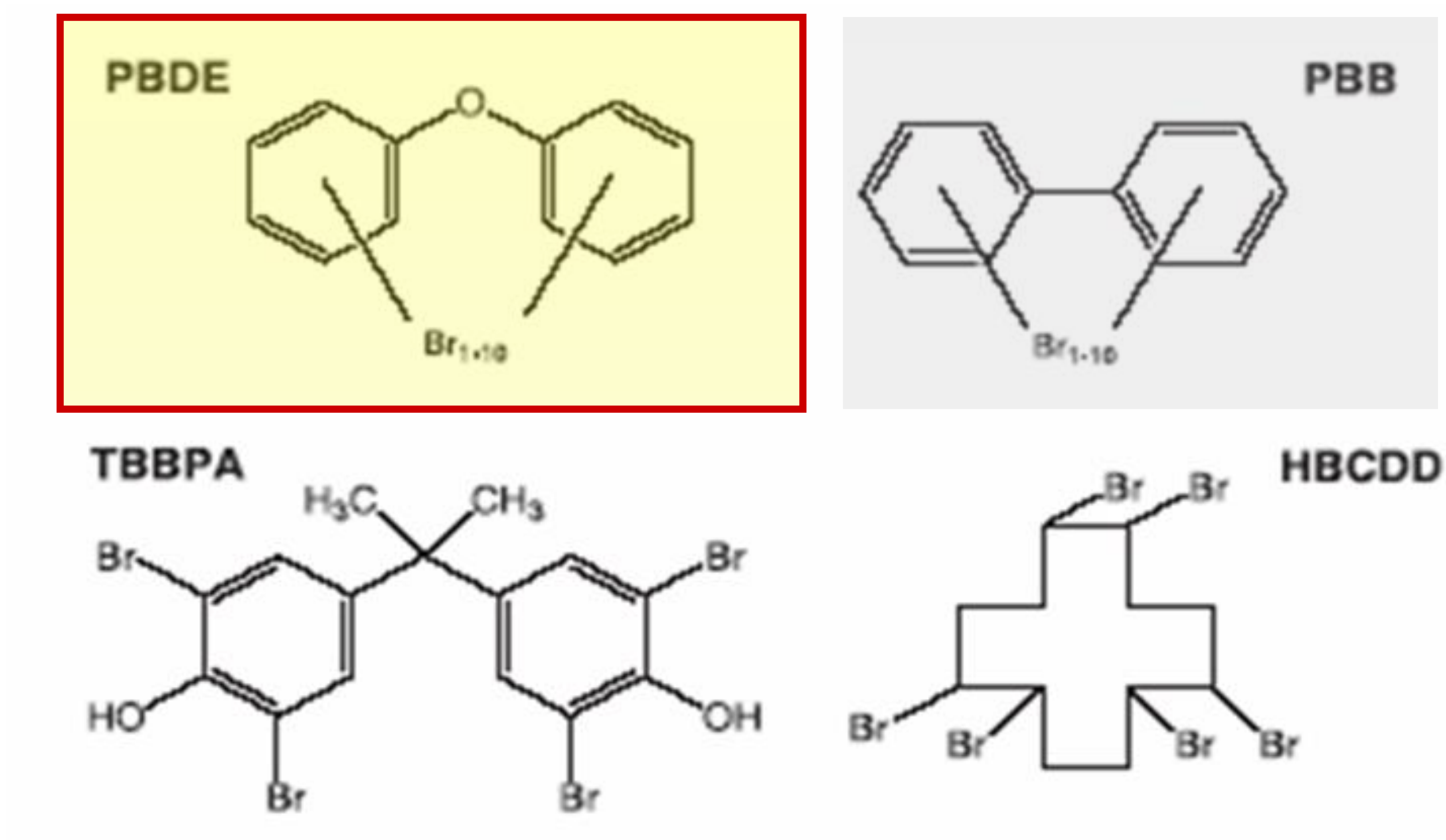
endosulfan

- Very common group of **insecticides** used in agriculture and vector-borne disease control
- Persistent and ubiquitous
- Bioaccumulate in the food chain

Organochlorine pesticides (OCPs)

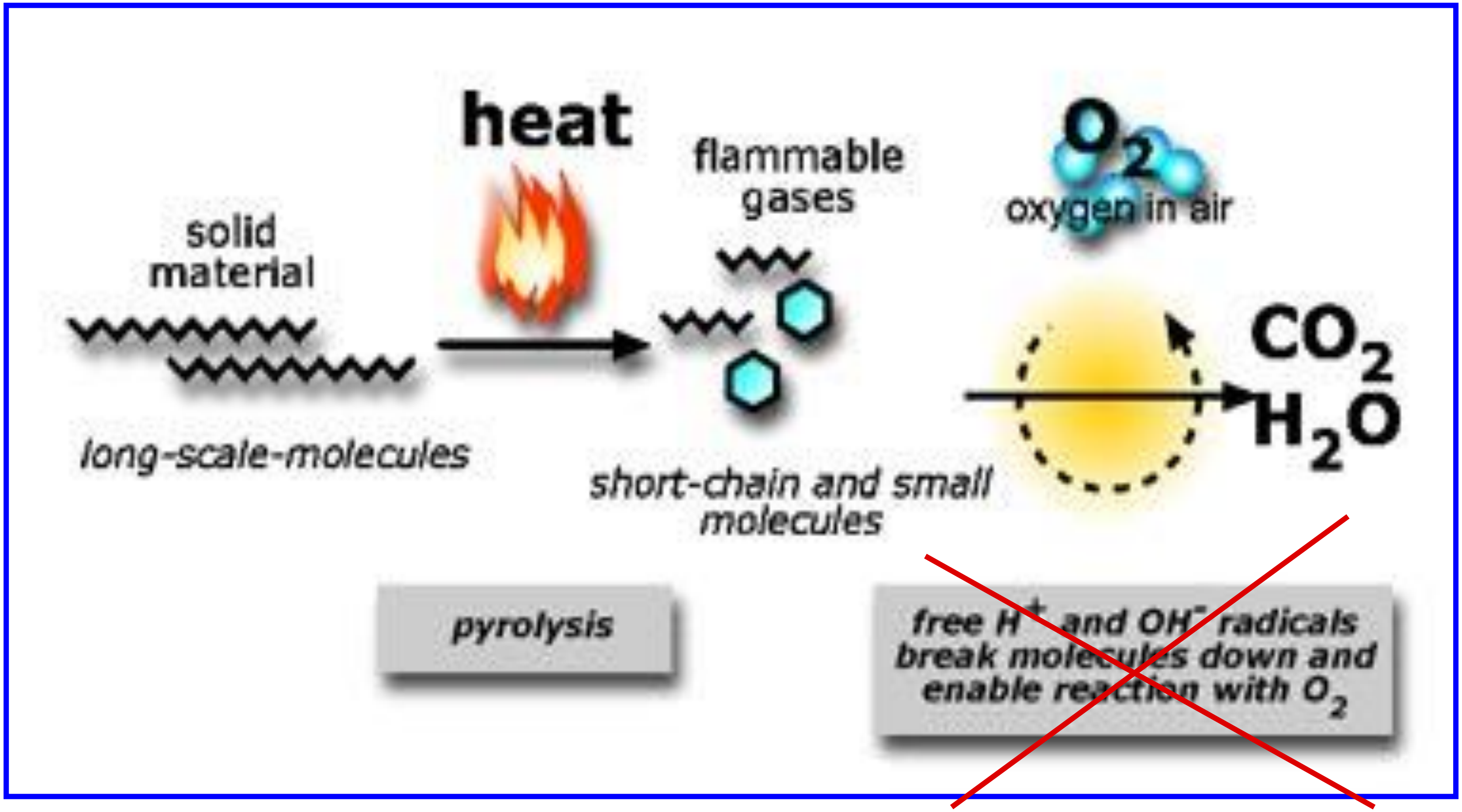
- DDT and many OCPs tend to accumulate in soils, rather than in air and water
- During the 1970s, many OCPs (DDT especially) were found to be harmful to wildlife populations and were banned in many developed nations

Brominated flame retardants (BFRs)



Altogether 75 different BFRs

Brominated flame retardants (BFRs)



Brominated flame retardants (BFRs)

- **Uses:**
  - Flame retardants in furniture foam (pentaBDE),
  - Plastics for personal computers and small appliances (octaBDE)
  - Plastics for TV cabinets, electronics, wire insulation, back coatings for draperies and upholstery (decaBDE)

without BFRs

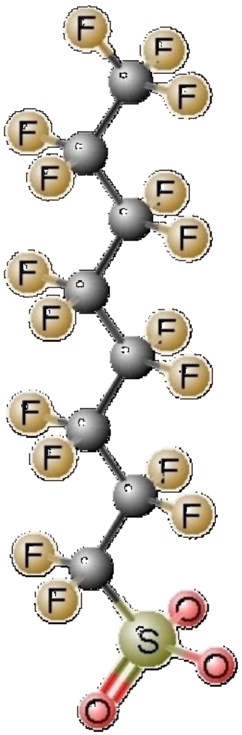
with BFRs

Brominated flame retardants (BFRs)

- **Pathways into the environment:**
  - Manufacturing processes (of plastics or textiles)
  - Ageing and wear of the end consumer products
  - Direct exposure during use (e.g. from furniture)
- **Potential health concerns:**
  - Toxicological tests indicate the potential for liver and thyroid toxicity, and neuro-developmental toxicity
  - Traces of several PBDEs are found in human breast milk, fish, aquatic birds, and elsewhere in the environment

Perfluorinated compounds (PFCs)

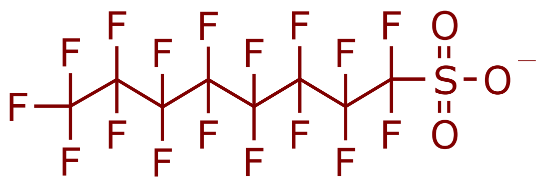
- A class of organofluorine compounds that have all hydrogens replaced with fluorine on the carbon chain – but also contain at least one different atom or functional group
- Usually 4 – 20 carbon atoms in the molecule
- The most abundant C8 compounds (derived from octane)
- **Main groups of PFCs** - Perfluorocarboxylic acids, Perfluorosulphonates, Perfluorosulfonamides, Telomeric alcohols



Perfluorinated compounds (PFCs)

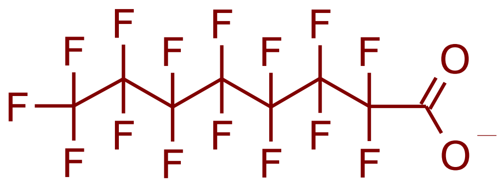
- **Most important PFCs**

PFOS = perfluorooctanesulfonic acid



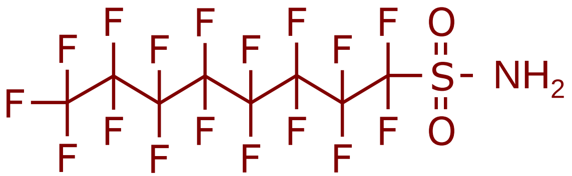
M_R 499 g/mol

PFOA = perfluorooctanoic acid



M_R 414 g/mol

FOSA = perfluorooctanesulfonamide



M_R 498 g/mol

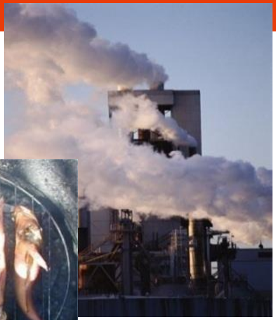
Perfluorinated compounds (PFCs)

- Hydrophobic and lipophobic so do **not accumulate in fatty tissue.**
- Resistant to degradation by natural processes such as metabolism, hydrolysis, photolysis, or biodegradation making it persist indefinitely in the environment
- Can release into the environment: directly from industrial sites, waste dump, fire-fighting foams, emissions from the carpet, paper and electronics industries, fire service practicing areas, waste water treatment plants

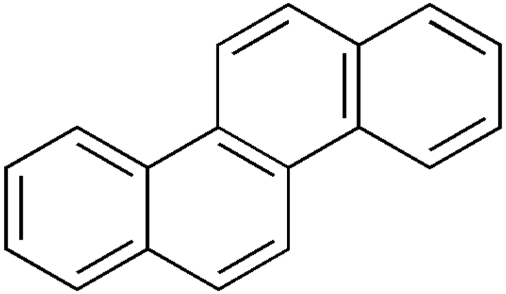
Perfluorinated compounds (PFCs)

- **Application:** cleaning agents, impregnation agents for textiles, carpets, paper, packaging, furniture, paint and varnish, fire-extinguishing liquids, wax, floor polishing agents
- **Fate in the environment: a**dsorption onto sediments, air or ocean stream long distance transfer of volatile PFCs
- Broad spectrum of health effects

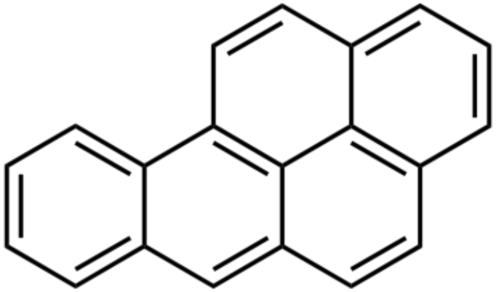
Polycyclic aromatic hydrocarbons



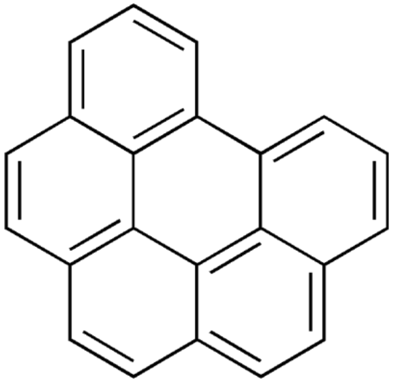
- More than 100 different compounds
- Composed of two or more aromatic rings



chrysene



benzo[*a*]pyrene

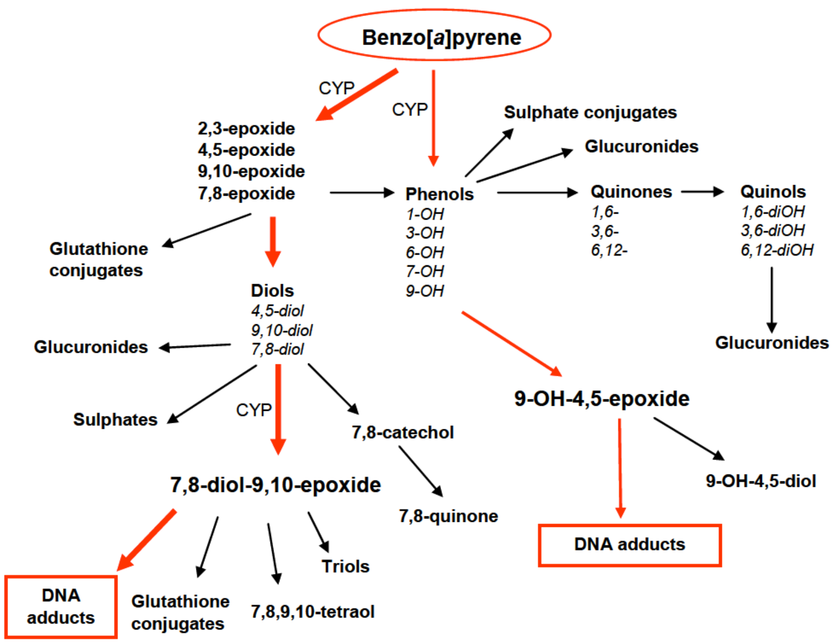


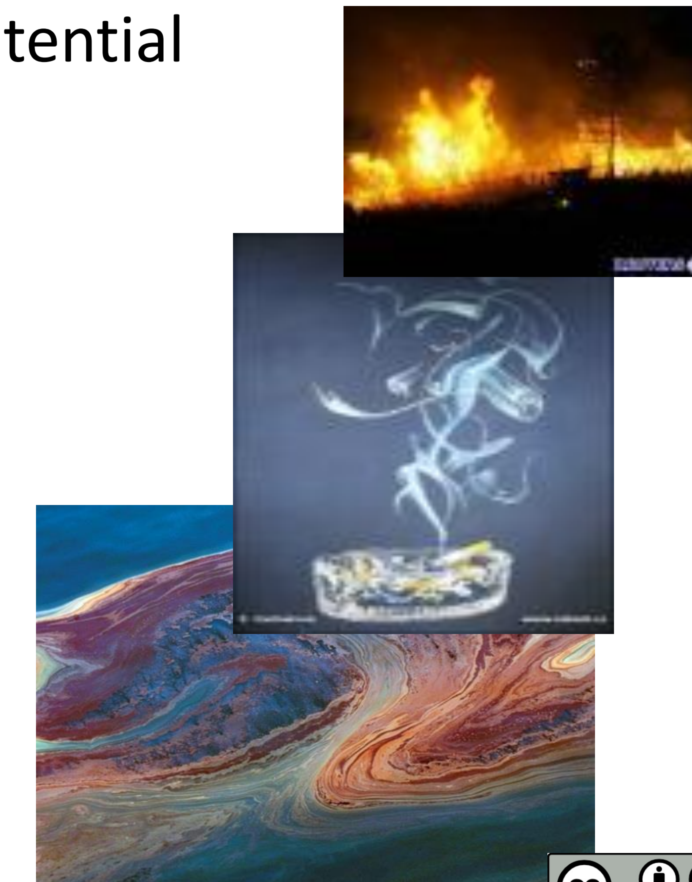
benzo[*ghi*]perylene

- Formed during incomplete combustion of organic matters
- **Sources:** forest fires, oil seeps, oil spills, vulcanic eruption, burning of fosil fuel, coal tar, garbage, municipal solid waste incineration, petroleum spills

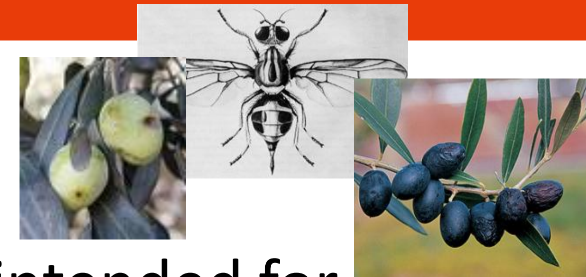
Polycyclic aromatic hydrocarbons

- Do not degrade easily under common condittions
- Persistence increases with increasing molecular weight
- **Toxicity:** mutagenic, carcinogenic potential





Pesticides



- Any substance or mixture of substances, intended for preventing, destroying, or mitigating any pest, or intended for use as a plant growth regulator, defoliant or desiccant

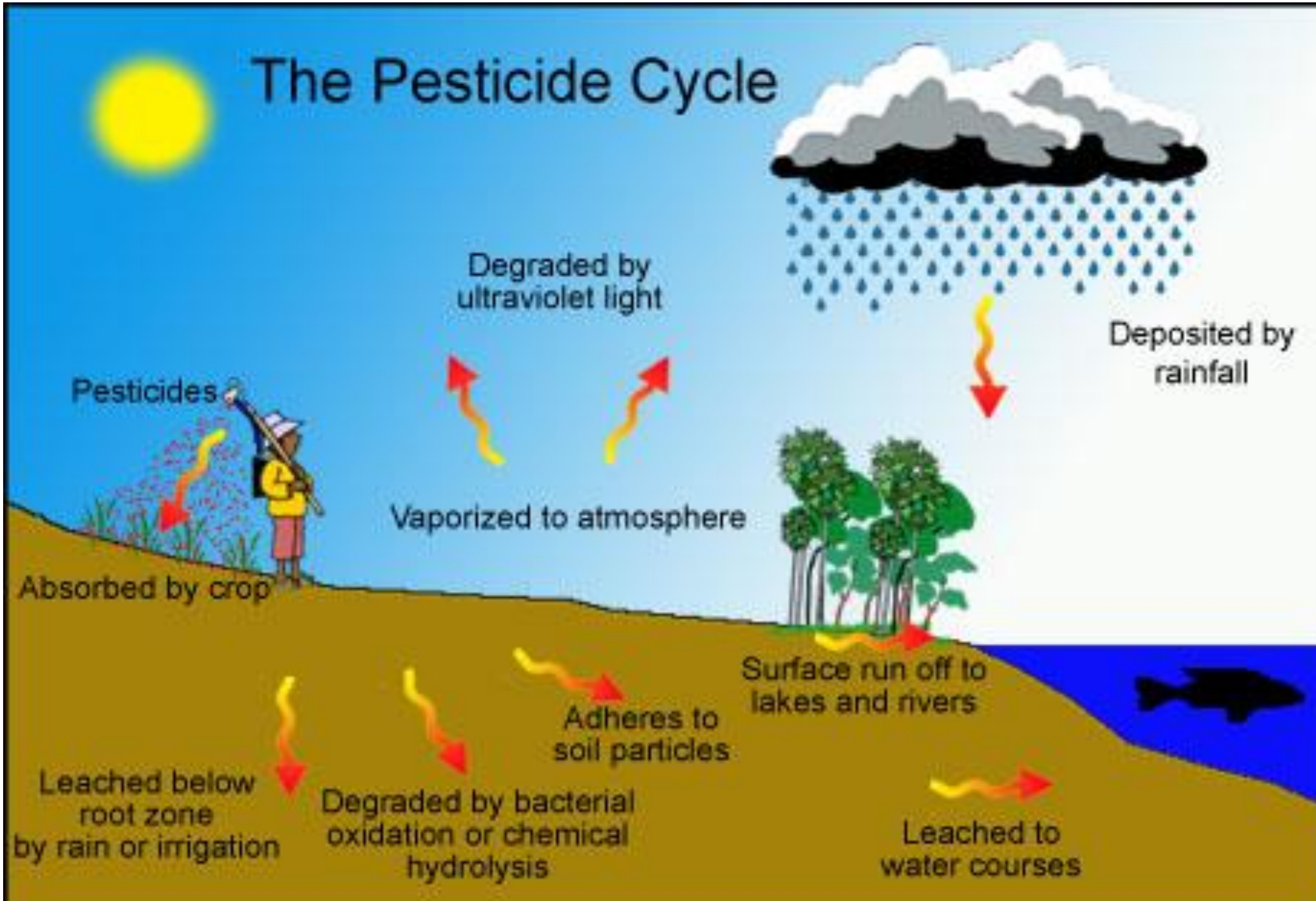
- Preparations applied during the pre-harvest period and/or storage

  - Crops protection against pests
  - Influence on life cycle / processes in plants
  - Prevention of sprouting or plant products preservation
    - Elimination of undesirable plants growth (or their parts); growth prevention

Pesticides

- Many pesticides are mobile in the environment (air, soil, water).
- This movement can be beneficial (moving pesticide to target area, such as roots) but can also reduce the effect on the target pest and injure nontarget plants and animals.
- Each type of pesticide acts on different functions in the body:
- ***Organophosphates:*** *neurotoxins, enzyme disruptors, damage DNA/RNA*
- ***Pyrethroids:*** *neurotoxins*
- ***Chlorphenoxy compounds:*** *neurotoxins, metabolic poissons, skin and mucous membrane irritants*

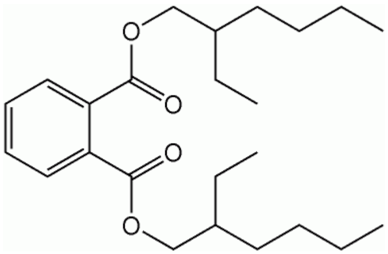
Pesticides



The Pesticide Cycle
Degraded by ultraviolet light
Deposited by rainfall
Pesticides
Vaporized to atmosphere
Absorbed by crop
Surface run off to lakes and rivers
Adheres to soil particles
Leached below root zone by rain or irrigation
Degraded by bacterial oxidation or chemical hydrolysis
Leached to water courses

Phthalates

- Phthalates (esters of phthalic acid) are a class of widely used industrial compounds used as plasticizers especially in PVC (polyvinyl chloride)
- Various types of phthalates:
  - range from one carbon to seventeen carbons
  - PVC plasticizers generally range from 4-13 carbons
- The most widely used phthalates are the di(2-ethylhexyl) phthalate (DEHP), the diisodecyl phthalate (DIDP), and the diisononyl phthalate (DINP)



DEHP

Phthalates

- **Uses:** Used primarily as plasticizers in polyvinyl chloride (PVC) products, child's toys, kitchen floor, building materials, blood bags, fixatives for perfume, slowing down evaporation and making the scent linger longer
- **Toxicity:** human carcinogens, endocrine disruptors



Legislation

Environment contaminantion

L 24/8 | EN | Official Journal of the European Union | 29.1.2008

DIRECTIVES

DIRECTIVE 2008/1/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 15 January 2008

concerning integrated pollution prevention and control

11.6.2008 | EN | Official Journal of the European Union | L 152/1

I

(Acts adopted under the EC Treaty/Euratom Treaty whose publication is obligatory)

DIRECTIVES

DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 21 May 2008

on ambient air quality and cleaner air for Europe

DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 24 November 2010

on industrial emissions (integrated pollution prevention and control)

Stockholm Convention on persistent organic pollutants (POPs)

Food contaminantion

20.12.2006 | EN | Official Journal of the European Union | L 364/5

COMMISSION REGULATION (EC) No 1881/2006

of 19 December 2006

setting maximum levels for certain contaminants in foodstuffs

The published materials are intended for students of the University of Chemistry and Technology, Prague as a study material. Some text and image data contained herein are taken from public sources. In the case of insufficient quotations, the author's intention was not to intentionally infringe the possible author(s) rights to the original work.

If you have any reservations, please contact the author(s) of the specific teaching material in order to remedy the situation.

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

9. Modern pesticides and veterinary drugs, organic products

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Pesticides

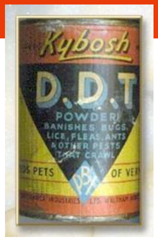


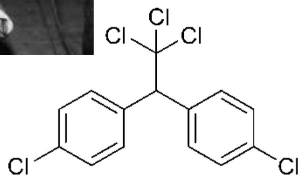

- **Any substance or mixture of substances, intended for preventing, destroying, or mitigating any pest, or intended for use as a plant growth regulator, defoliant or desiccant**





Pesticide uses





DDT

- **First Generation Pesticide Control:**
- Sumerians controlled insects with sulfur 5,000 years ago.
- Chinese used mercury and arsenic to control pests 2,500 years ago.
- People have used organic compounds and biological controls for a long time.
  - Biological controls – rotenone (made from roots of tropical plants)
  - Physical controls - Romans burned fields and rotated crops to reduce crop disease.
- **Second Generation Pesticide Control**
- **Modern era of pest control began in 1939 with DDT.**
  - Cheap, stable, soluble in oil, and easily spread over a large area.
    - **Highly toxic to insects, but *relatively* nontoxic to mammals.**
      - Paul Mueller received Nobel prize in 1948 for the discovery.

Pesticide application

- Preparations applied during the pre-harvest period and/or storage

- Crops protection against pests

- Influence on life cycle / processes in plants

- Prevention of sprouting or plant products preservation

- Elimination of undesirable plants growth (or their parts); growth prevention

Pesticide application

POSITIVE ASPECTS

- **Saves Lives** (*malaria-mosquitoes (DDT), Plague – rat fleas, Sleeping Sickness – Tsetse Fly*)
- **Increased Food Supply**
- **Lower Food Costs**
- **Work Faster** than alternatives – such as biological controls; physical controls

Pests destroy ~40% of food crops per year!! Costs 65 million dollars a year!

NEGATIVE ASPECTS

- **Residues** in agriculture products

RISK FOR PEOPLE: POTENTIAL TO ENTER THE FOOD CHAIN

- **Influence** on non-target organism
- **Resistance** of pest

Classification of pesticides

(i) According to target pest group

(ii) Modern, Historical (Traditional)

(iii) Inorganic, Organic

(iv) Mode of action (Translocated, Contact, Systemic)

(v) According the chemical structure: organochlorine, carbamates, pyrethroids, dithiocarbamates, phthalimides, phenoxy alkanoic acids, quaternary ammonium salts (quats), triazines

Classification of pesticides

(i) According to target pest group

Type of pesticide	Target pest group
Herbicides	Plants
Algicides or Algaecides	Algae
Avicides	Birds
Bactericides	Bacteria
Fungicides	Fungi and Oomycetes
Insecticides	Insects
Miticides or Acaricides	Mites
Molluscicides	Snails
Nematicides	Nematodes
Rodenticides	Rodents
Virucides	Viruses

Classification of pesticides

- **(iv) Mode of action - plants**
- ***Movement in the plant***
  - ***Contact –*** One which causes injury to only the plant tissue to which it is applied, or one which is not appreciably translocated within a plant
  - ***Translocated –*** One which is moved within a plant from the point of application to the point of action; may be either phloem-mobile or xylem-mobile

- ***Action in the plant***
  - Inhibit protein synthesis, photosynthesis, or growth

Classification of pesticides

- **(iv) Mode of action - animals**
  - ***Contact Insecticide -*** Pesticide which causes injury or death of insect through the touch rather than through inhalation or ingestion
  - ***Systemic Insecticide -*** Pesticide which is moved within a plant from the point of application to the point where the insect will contact or ingest it
  - ***Attractant -*** Pesticide which lures animals to a predetermined spot

    Pheromones are biochemicals either released by the animal or synthesized which are sex attractants

    Baits are chemicals which entice animals for reasons other than sex (smells like food)

Classification of pesticides

- **(iv) Mode of action - animals**
  - ***Repellant*** **-** Pesticide which discourages animals from coming to a specific area

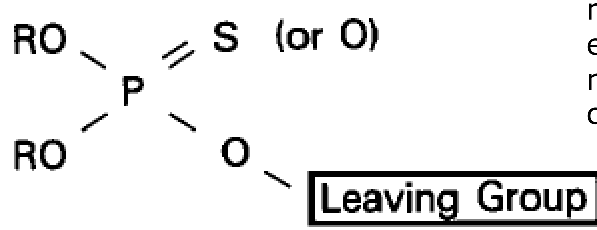
    Many chemicals unrelated to sexual activity (due to smell or other physical characteristic) are repellant to animals

    Pheromones in low concentration are attractive to animals but, often, in high concentration become repellant

Classification of pesticides

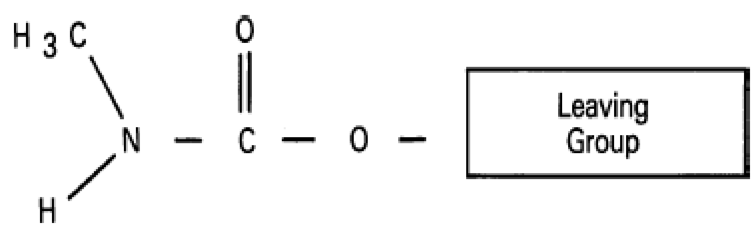
(v) According to chemical structure:

- **Organophosphate Pesticides** → They have become the most widely used insecticides available today, used in agriculture, in the home, in gardens, and in veterinary practice. Some are very poisonous. However, they usually are not persistent in the environment.



main mechanism is blocking the enzyme acetylcholinesterase causing nervous and respiratory damages – chlorpyrifos, azinphos, naled, parathion

- **Carbamate Pesticides** → N-Methyl carbamate insecticides are widely used in homes, gardens, and agriculture.

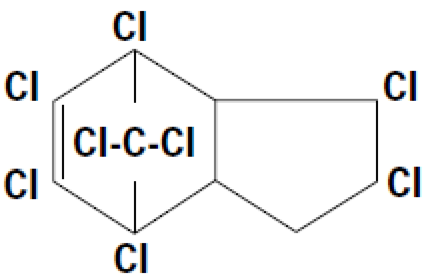


aldicarb, carbofuran, fenobucarb

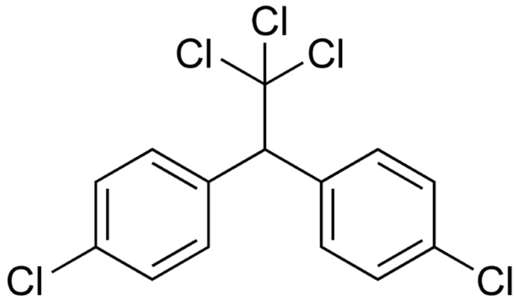
Classification of pesticides

(v) According to chemical structure:

- **Organochlorine Insecticides** → Commonly used in the past, but many have been removed from the market due to their health and environmental effects and their persistence (e.g. DDT and chlordane).



Chlordane

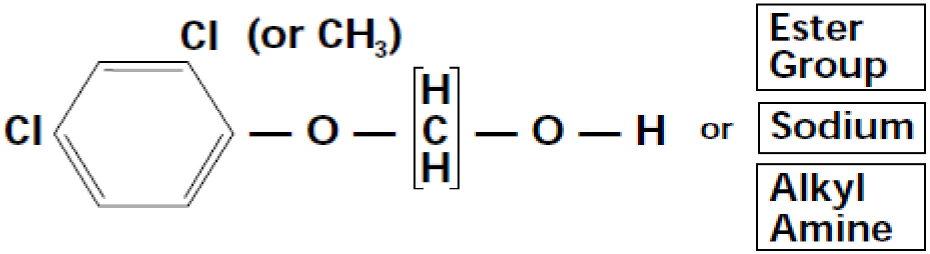


DDT

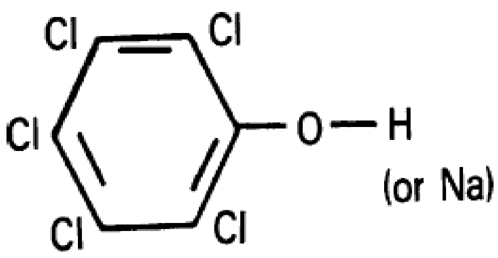
Classification of pesticides

(v) According to chemical structure:

- **Chlorophenoxy Herbicides** → They are sometimes mixed into commercial fertilizers to control growth of broadleaf weeds.



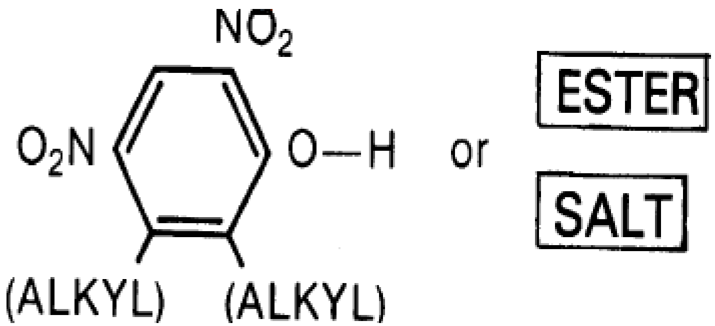
- **Pentachlorophenol (PCP)** → They act as herbicide, algacide, defoliant, wood preservative, germicide and fungicide.



Classification of pesticides

(v) According to chemical structure:

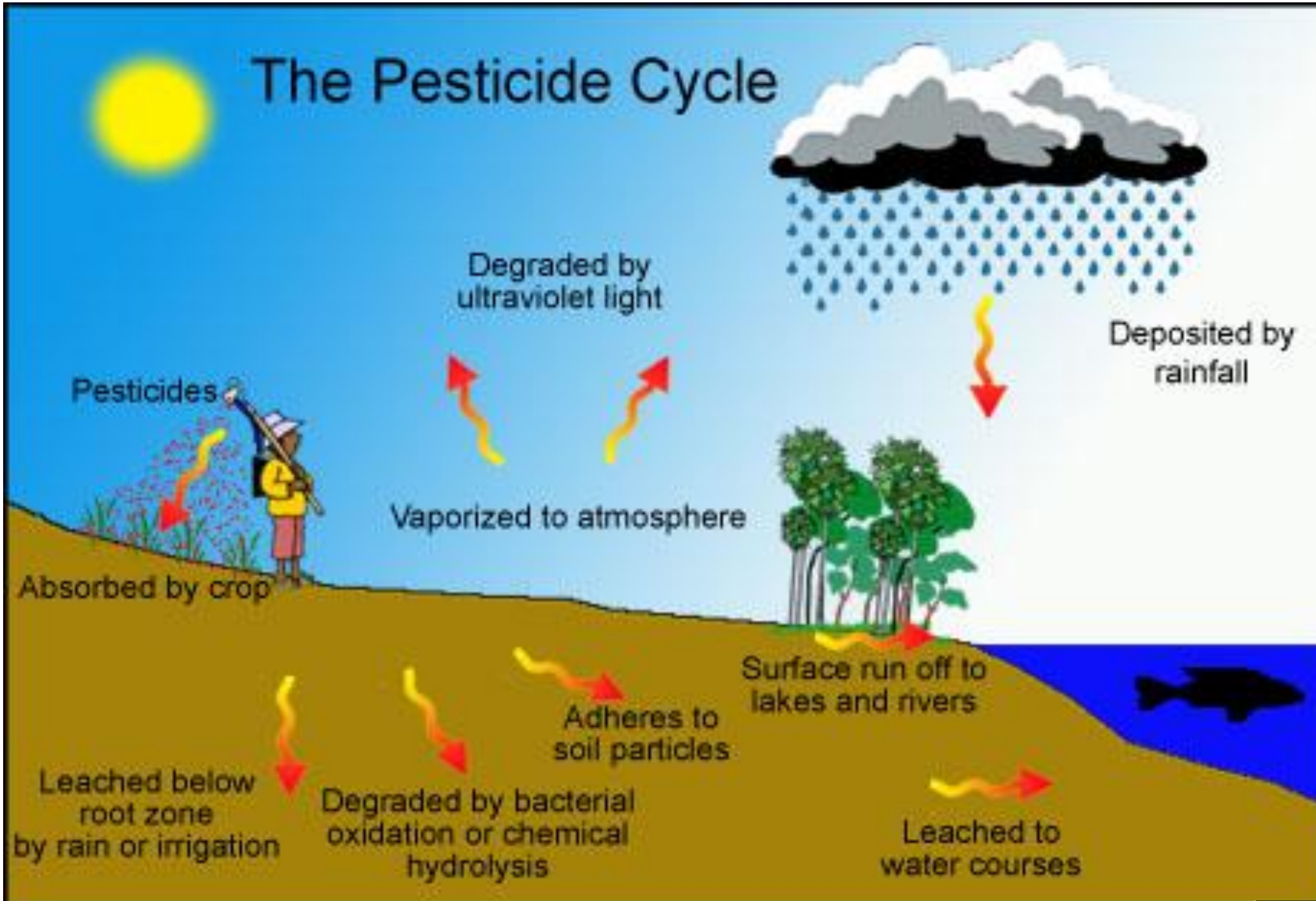
- **Nitrophenolic and Nitrocresolic Herbicides** → These highly toxic chemicals have many uses in agriculture worldwide, as herbicides (weed-killing and defoliation), and fungicides.



Pesticides

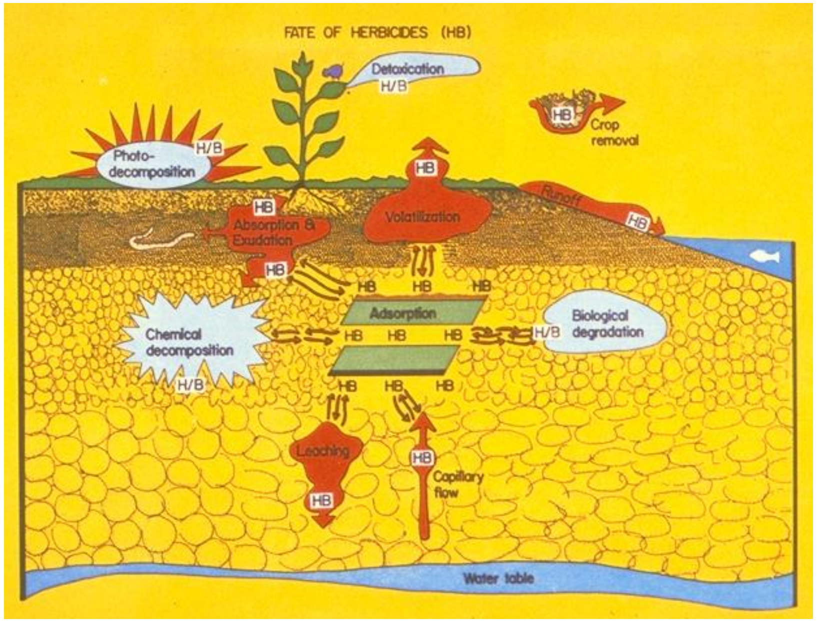
- Many pesticides are mobile in the environment (air, soil, water).
- This movement can be beneficial (moving pesticide to target area, such as roots) but can also reduce the effect on the target pest and injure nontarget plants and animals.
- Each type of pesticide acts on different functions in the body:
- ***Organophosphates:*** *neurotoxins, enzyme disruptors, damage DNA/RNA*
- ***Pyrethroids:*** *neurotoxins*
- ***Chlorphenoxy compounds:*** *neurotoxins, metabolic poissons, skin and mucous membrane irritants*

Pesticides


The Pesticide Cycle
Degraded by ultraviolet light
Deposited by rainfall
Pesticides
Vaporized to atmosphere
Absorbed by crop
Surface run off to lakes and rivers
Adheres to soil particles
Leached below root zone by rain or irrigation
Degraded by bacterial oxidation or chemical hydrolysis
Leached to water courses

Persistence/Degradation:

- **Process Drivers**
  - Temperature
  - Relative humidity / Rainfall
  - pH
  - Insolation
  - Soil or water biota
    - Macrophytes
    - Microbial populations
    - Worms and microfauna
  - **Degradation**
    - Microbial
    - Physical
      - Hydrolysis - breakdown of a pesticide by water
      - Photolysis - breakdown of a pesticide by sun or other light
      - Pyrolysis - breakdown of a pesticide by heat or fire



European Maximum Residue Levels (MRL)

MRL: the highest concentration of pesticides (or metabolites) which is acceptable in food (after the use of a plant protection product according to specified use conditions (Good Agricultural Practice, GAP)

2005R0396 — EN — 10.04.2008 — 002.001 — 2

REGULATION (EC) No 396/2005 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 23 February 2005

on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC

(Text with EEA relevance)

➔ **Process of harmonisation**

http://ec.europa.eu/sanco_pesticides/public/index.cfm

Pesticides pose different risks to children

- Infants and young children have been shown to be very sensitive to certain toxic effects as a result of their immature physiological development
- In accordance to their weight children consume more food per weight unit than adults (e.g. 6x more fruit, 2x vegetables, 3-5x more cereals)

→ The baby food Directives established **MRLs at 0.01 mg/kg or less** for all pesticides in **industrially processed baby food**

Consumption of other fresh fruit and vegetable: significantly higher limits

Example of different MRLs:

MLRs of **dodine a dithianon** in apples : **5 and 3 mg/kg** →

500x a 300x more than "baby food limit" !!!

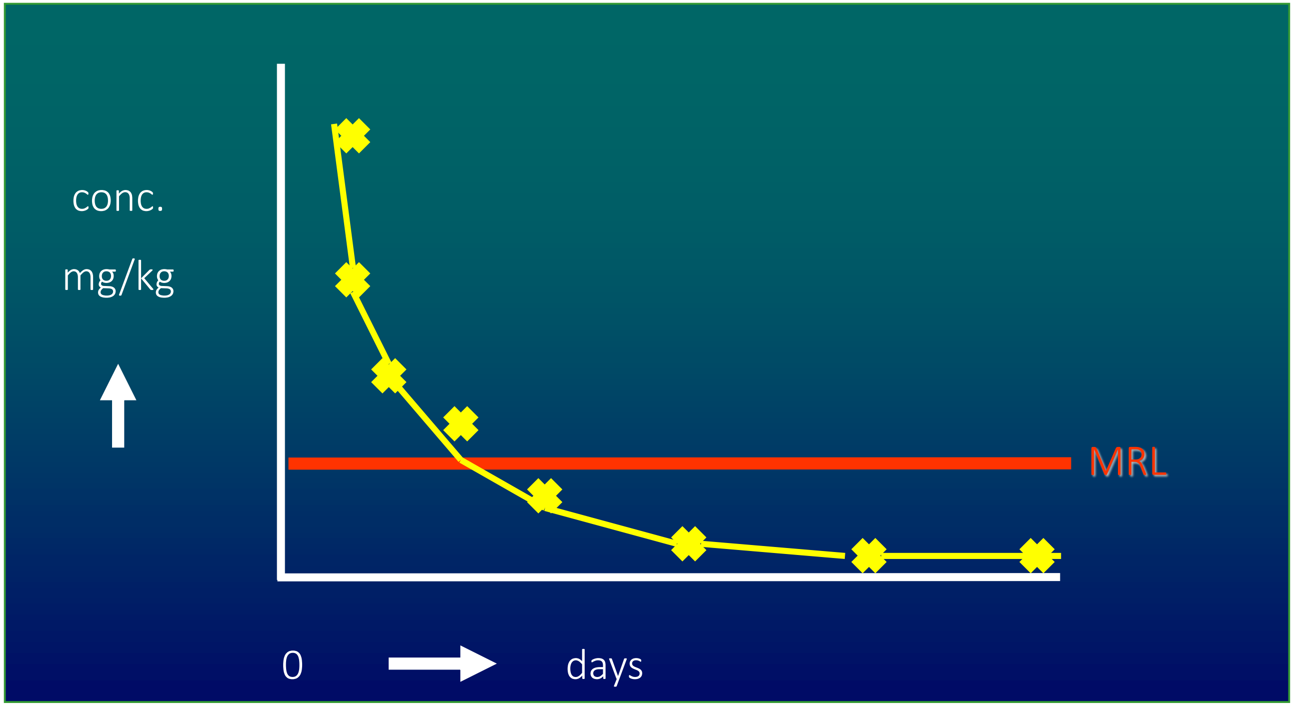
ICT PRAGUE

Protection period

= time from application to plant harvest / time since the last administration of the product for which the animal must not be slaughtered and for which its products (milk, eggs, honey) should not be used for human nutrition

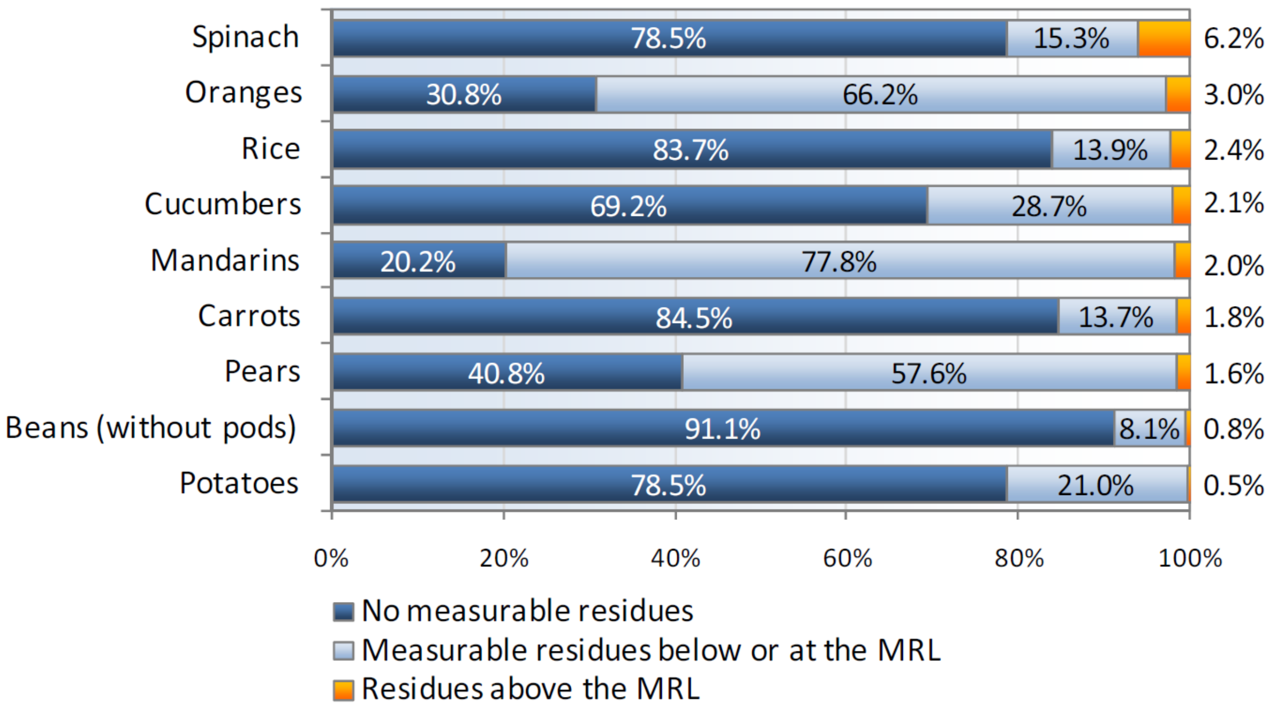
- nationally specific
- part of the registration of each product
- in the days / hours / so-called "Steppe" for aquatic animals

Dynamics of residues after application



Monitoring program EU – pesticides

- **Results based on food commodities**



Antibiotics

- The health of animals is very important to the farmers and ranchers who raise them, as well as the veterinarians who work with them. Despite this, animals may still become sick and require treatment, just like people.
- If farm animals become sick, or are at risk of becoming sick, there are antibiotics available to farmers and veterinarians to help control, prevent, and treat disease in farm animals.

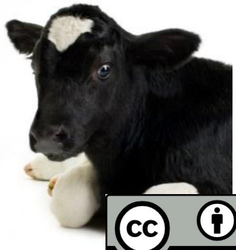
Veterinary drugs

- Pharmacologically and biologically active chemical compounds for the treatment, prevention and diagnosis of diseases of animals

Major Classes of Veterinary Drugs

- **Antibiotics – Antibacterials –** to assure a long-term care, health and welfare of food-producing animal species or to prevent infectious diseases in both domestic and food-producing animal species (*e.g., aminocyclitols, aminoglycosides, amphenicols, β-lactams, fluoroquinolones, lincosamides, macrolides, nitrofurans, sulfonamides, tetracyclines*)

- **Anthelmintics** - used to treat parasitic worms infection, including flatworms and roundworms, which usually infect human, livestock and crops, affecting food production (*e.g., benzimidazoles, nicotinic receptor agonists and macrocyclic lactones*)



Veterinary drugs

Major Classes of Veterinary Drugs

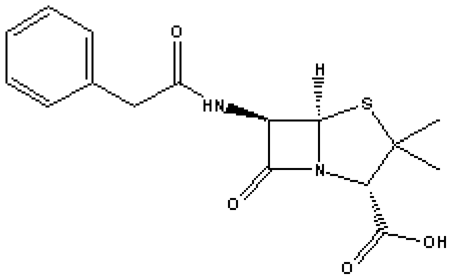
- **Coccidiostats** - Coccidiosis – important enteric disease of wild and domestic birds caused by highly host-specific intestinal protozoan intracellular parasites which belong to the genus Eimeria, characterized by high mortality. (*e.g., benzamides, carbanilides, nitroimidazoles, polyether ionophores, quinolone derivatives, triazines*)
- **Antimicrobial growth promoters** (Organic arsenicals, Peptide antibiotics, Quinoxaline-1,4-dioxides)
- **Hormonal-type growth promoters** (Endogenous sex steroids, Synthetic steroidal compounds, Synthetic nonsteroidal compounds, Polypeptide hormones)
- **Other drugs** (e.g., antifungal, thyreostatic, dye, diuretic, NSAIDs, corticosteroids, β-adrenergic agonists, sedatives and β-blockers)

Residues

- Residues are the metabolites of veterinary drugs, and their associated parent compounds, that remain in the animal or its produce (eggs, milk, honey) after treatment.
- **Their behaviour depends:**
    - nature of drug/metabolite
    - Pharmacokinetics of the drug
- Those that are slowly metabolised may also deplete rapidly if their excretion is not dependent on metabolism.
- Others may be subject to slow excretion, especially those that bind to macromolecules and are thus not available for metabolism and/or excretion.

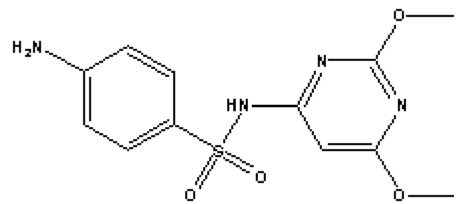
Classes of Antibiotics

β-Lactams



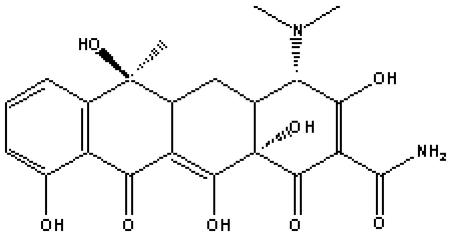
Penicillin G

Sulfonamides



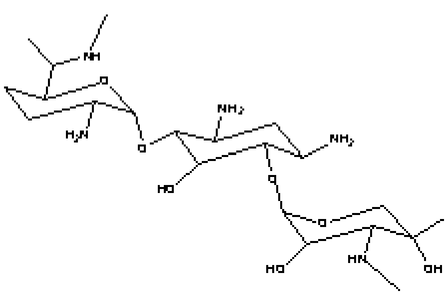
Sulfadimethoxine

Tetracyclines



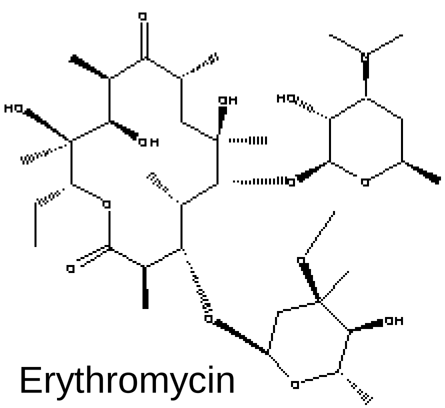
Tetracycline

Aminoglycosides



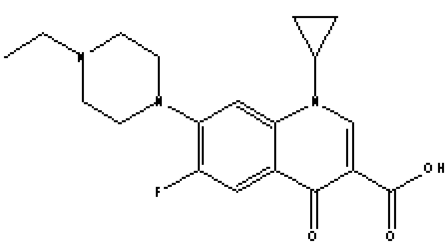
Gentamicin C_1

Macrolides



Erythromycin

Fluoroquinolones



Enrofloxacin

Antibiotic residues

- Antibiotics are used in both human medicine and veterinary practice.
- In the livestock industry and fish farming, antibiotics are employed for therapeutic (disease control), prophylactic (disease prevention), and subtherapeutic (growth promotion) purposes
- If the withdrawal time after treatment is not respected, or if antibiotics are not used correctly, it could lead to the presence of antibiotic residues in food of animal origin.
- It may provoke allergic reactions in some hypersensitive individuals, or cause the problem of drug-resistant pathogenic bacterial strains.

Antibiotic residues

- Some antibiotics such as chloramphenicol, and nitrofurans and their metabolites are associated with serious toxic effects in humans causing bone marrow depression and aplastic anemia, and/or mutagenic and carcinogenic effects. Therefore, they are not allowed to be present in food.
- To ensure the safety of food for consumers and to facilitate the interest of international trade, EU, FDA, Canada, FAO/WHO, and other international regulatory bodies have established the relevant regulations and maximum residue limits (MRLs) to monitor the level of approved antibiotics present in food.

- http://www.authorstream.com/Presentation/vetvet2008-1269093-residues/

WHAT IS ORGANIC FARMING?

Organic production is an overall system of farm management and food production that combines best environment practices, a high level of biodiversity, the preservation of natural resources and the application of high animal welfare standards

KEY PRINCIPLES

- The use of chemical pesticides and synthetic fertilisers is banned
- Antibiotics are severely restricted
- GMOs are not allowed
- Crops are rotated

The EU's organic logo guarantees EU rules on organic farming have been respected

europarl.eu

Sources:
EPRS, Eurostat, Eurobarometer

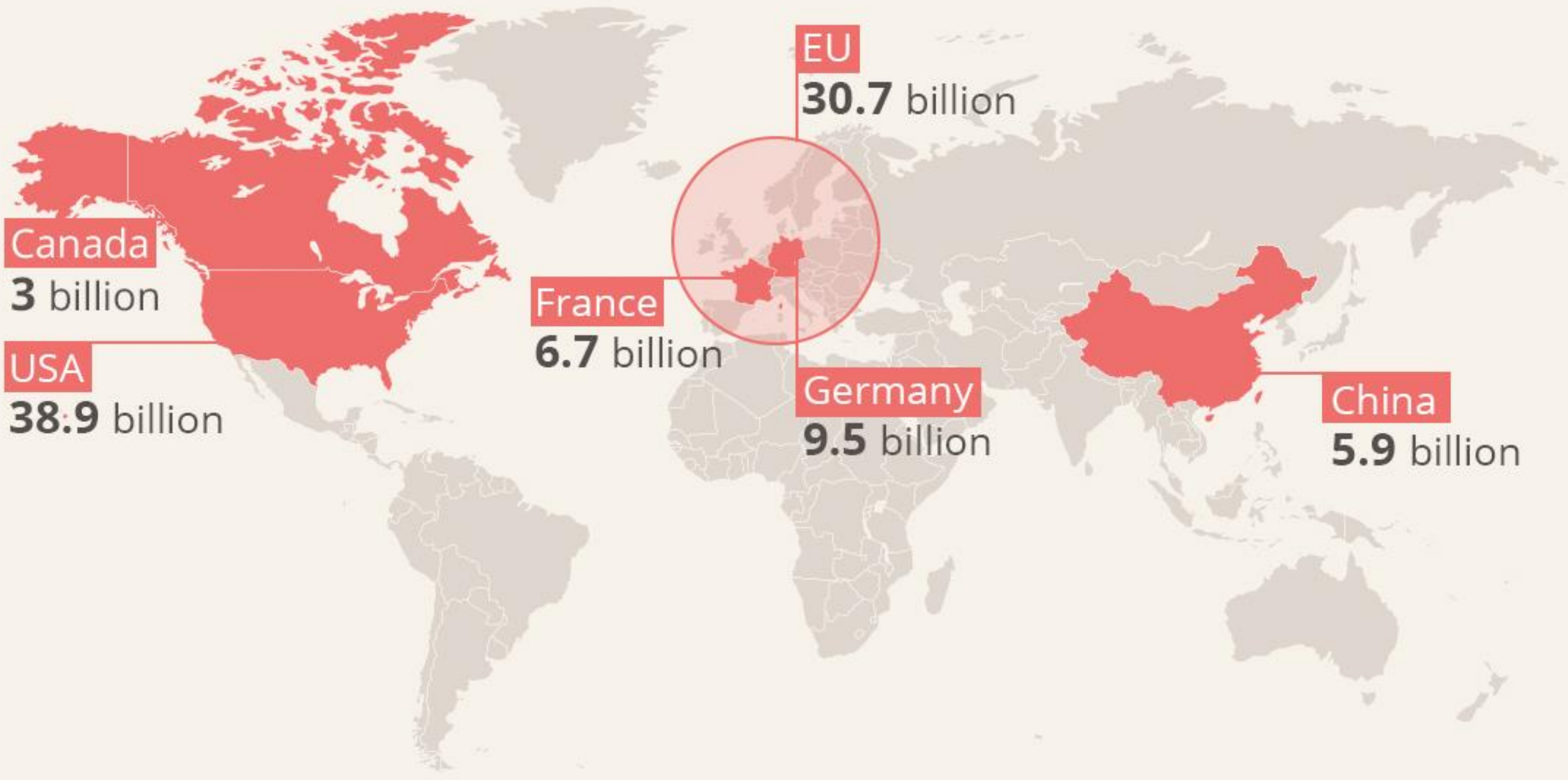
Organic farming practices in the EU include:

- Crop rotation for an efficient use of resources
- A ban of the use of chemical pesticides and synthetic fertilisers
- Very strict limits on livestock antibiotics
- Ban of genetically modified organisms (GMOs)
- Use of on-site resources for natural fertilisers and animal feed
- Raising livestock in a free-range, open-air environment and the use of organic fodder
- Tailored animal husbandry practices

THE ORGANIC FOOD MARKET

WHO CONSUMES THE MOST ORGANIC FOOD?

Retail sales (€) in 2016



UCT PRAGUE

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

10. Toxic metals, nitrates and radionuclides

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Types of pollutants

Inorganic

metals/metaloids, nutrients/salts, acids, greenhouse gases, radionuclides, nanoparticles

Organic

sewage/manure, VOC, hydrocarbons (aliphatic, cyclic, polycyclic, heterocyclic), POPs, organo-metals, pharmaceuticals, personale care products

pollutants

Biological

microorganisms (and their toxins)

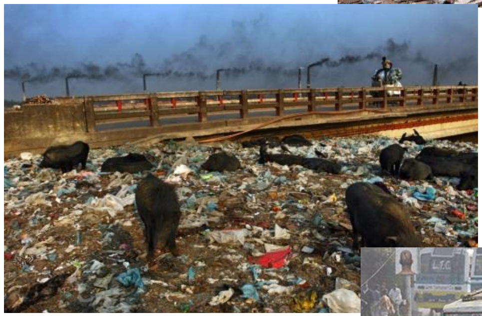
Other

sound, light, heat

Types of pollution

- **Air pollution**
- **Water pollution**
- **Soil pollution (Land pollution)**
- Noise pollution
- Radioactive pollution
- Thermal pollution
- Light Pollution
- Visual Pollution






Sources of pollutants

Air pollution

- Vehicle or manufacturing exhaust
- Forest fires, volcanic eruptions, dry soil erosion, and other natural sources
- Building construction or demolition

- **Major pollutants produced by human activity include:** sulphur oxides (SO_x), nitrogen oxides (NO_x) - especially nitrogen dioxide, carbon monoxide (CO), volatile organic compounds (VOCs), lead, mercury, chlorofluorocarbons (CFCs), radioactive pollutants

Sources of pollutants

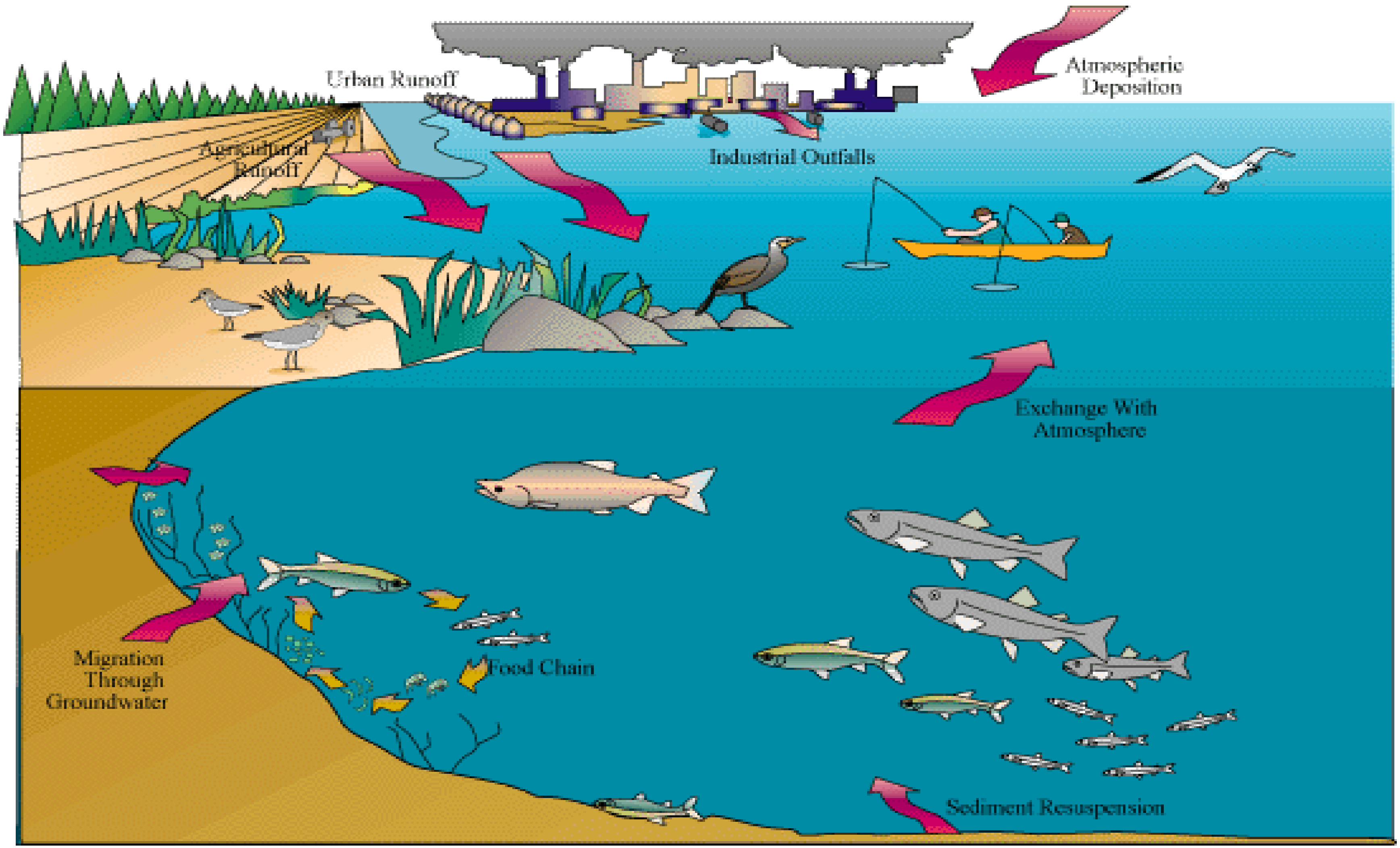
- **Water pollution**
  - Increased sediment from soil erosion
  - Improper waste disposal and littering
  - Leaching of soil pollution into water supplies
  - Organic material decay in water supplies

- **Water pollutants include:**

detergents, residues of pesticides, solvents, PCBs, heavy metals, fertilizers (nitrates and phosphates), compounds found in personal hygiene and cosmetic products

Sources of pollutants

- **Water pollution**



Sources of pollutants

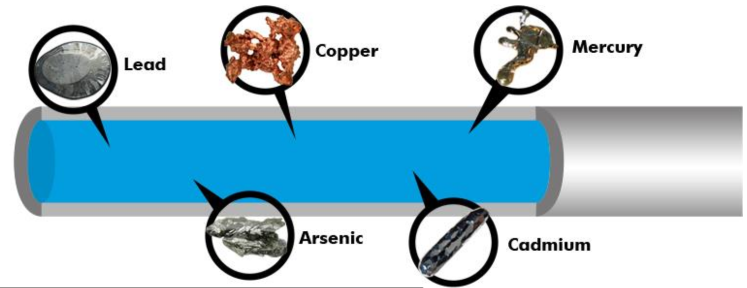
Soil pollution

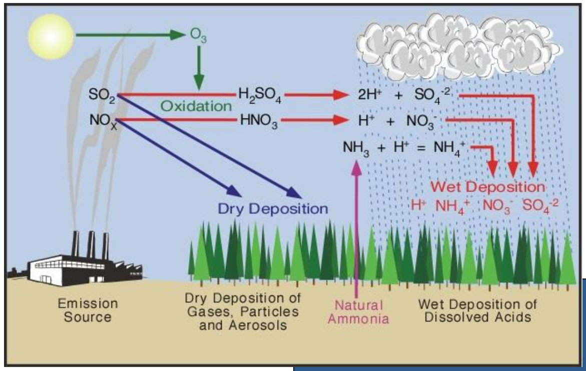
- Hazardous waste and sewage spills
- Non-sustainable farming practices, such as the heavy use of pesticides
- Strip mining, deforestation, and other destructive practices
- Household dumping and littering

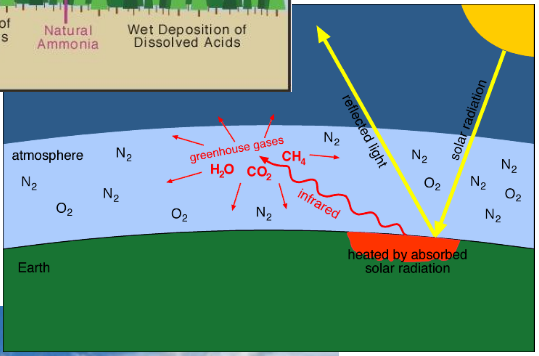
- **The most common chemicals:**
  petroleum hydrocarbons, solvents, pesticides, PAHs, lead, and other heavy metals

Inorganic pollutants

- **Heavy metals**
  - Hg, Pb, Cd, As, Cu
- **Acids**
  - Acid rain
- **Greenhouse gasses**
  - Carbon dioxide (CO_2)
  - Nitrous oxide (N_2O)
- **Radionuclides**
  - ^{90}Sr, ^{134}Cs, ^{137}Cs , ^{241}Am
- **Nanoparticles**







Inorganic pollutants

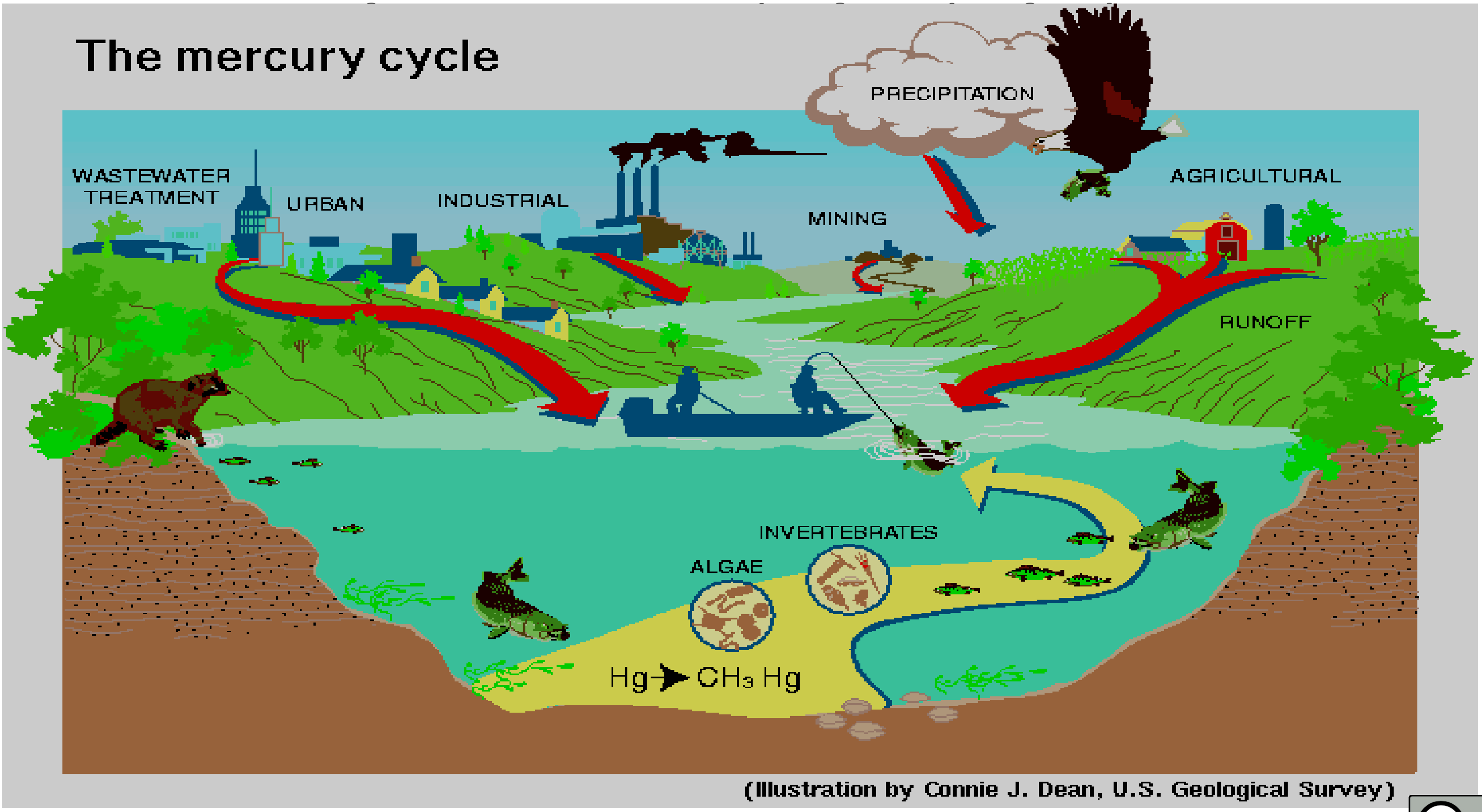
- **Heavy metals**
- **Mercury (Hg)**

- Most volatile of all metals
- Found in three forms: elemental, inorganic, and organic
- Highly toxic in vapor form
- Used to make electrical products, dental supplies, caustic soda, chlorine, instruments and paints
- Health effects: neurotoxic, brain and kidney damage

Inorganic pollutants

- **Heavy metals**

- **Methylmercury (CH_3Hg^+)**



Inorganic pollutants

- **Heavy metals**
- **Lead (Pb)**
  - Used in automotive batteries, electronics, plastics and glass
  - Ubiquitous in the environment after use in gas and paint
  - **Toxic effects:** brain damage, kidney disease, and hypertension

Inorganic pollutants

- **Heavy metals**
- **Cadmium (Cd)**

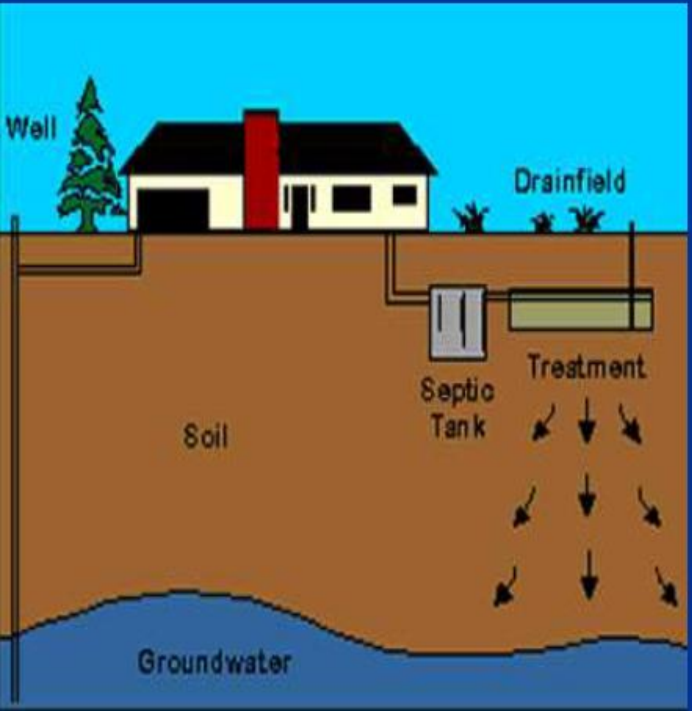
- Sources: natural rock weathering, copper, lead and zinc smelting auto exhaust, cigarette smoke (a cigarette contains 1-2 μg Cd)
- Used in plastics, household batteries, electronics, paint pigments (blue) and fungicides
- Readily absorbed and accumulated in plants
- Highly toxic, range of health effects from hypertension to cancer

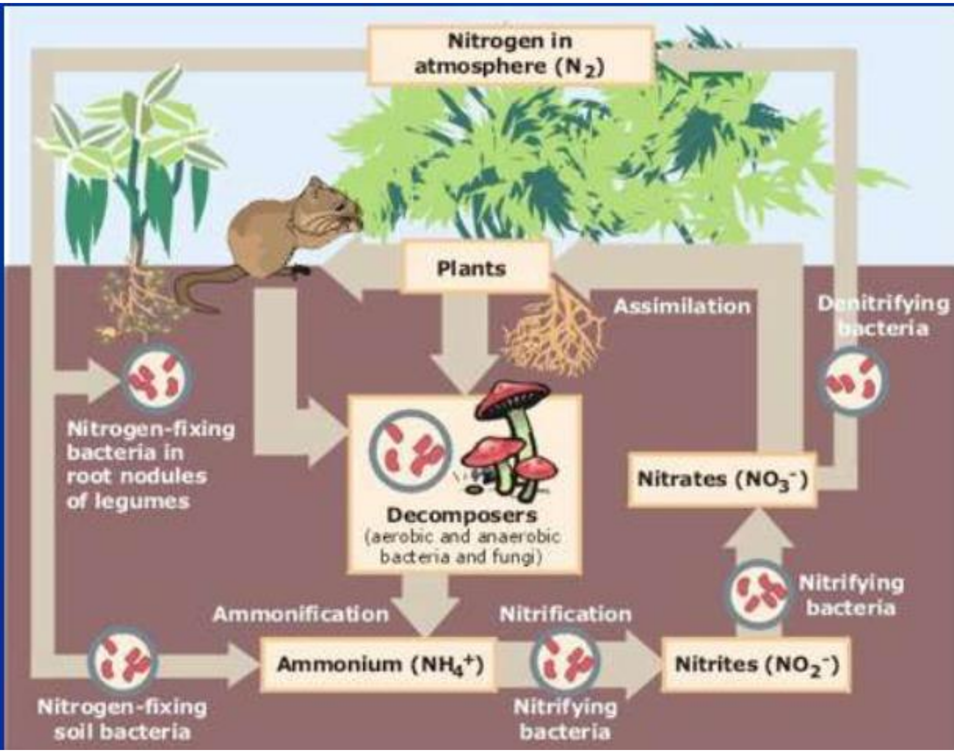
Inorganic pollutants

- **Heavy metals**
- **Arsenic (As)**
  - Natural sources: volcanic ash, weathering of arsenic-containing minerals and ores
  - Antropogenic: production of pesticides, treated wood products, used in optical glass
  - Drinking water
  - Poison, human carcinogen

What are nitrates and nitrites?

- Nitrate (NO_3) and nitrite (NO_2)
  - Originate from human/animal wastes (septic systems), fertilizers and crop residues





Nitrate and nitrite

- Inorganic chemicals that are highly soluble in water. Microbes break down animal’s and human’s organic wastes (in soil and water) into ammonia, which then oxidizes into nitrite and nitrate.
- Nitrates also occur naturally : in the environment, in mineral deposits, soil, seawater, freshwater systems, and the atmosphere.
- The body also makes approximately 62 mg / day of nitrate in addition to what is ingested. Infection and illness can cause the body to produce even greater levels of nitrate.

Uses of nitrate and nitrite

- **Artificial manures and fertilisers** (sodium , potassium and ammonium nitrate)
- **As a preservative** (some meats and meat products contain sodium nitrate and / or sodium nitrite as preservatives**).**
- **Medications** (nitroglycerine , amyl nitrite , nitroprusside ..)
- **As color enhancement of processed meats** (although the amount added to these products have been substantially reduced from the levels once used).
- **In dynamites** (contain ammonium nitrate)
- **Industry (**purified potassuim nitrate for glass making).

Source of exposure

- **Major sources of nitrate toxicity in drinking water** include fertilizers, sewage and animal manure**.**

  *****_Nitrite can also be formed chemically in distribution pipes by Nitrosomonas bacteria during stagnation of (nitratecontaining and oxygen-poor) drinking-water in galvanized steel pipes._

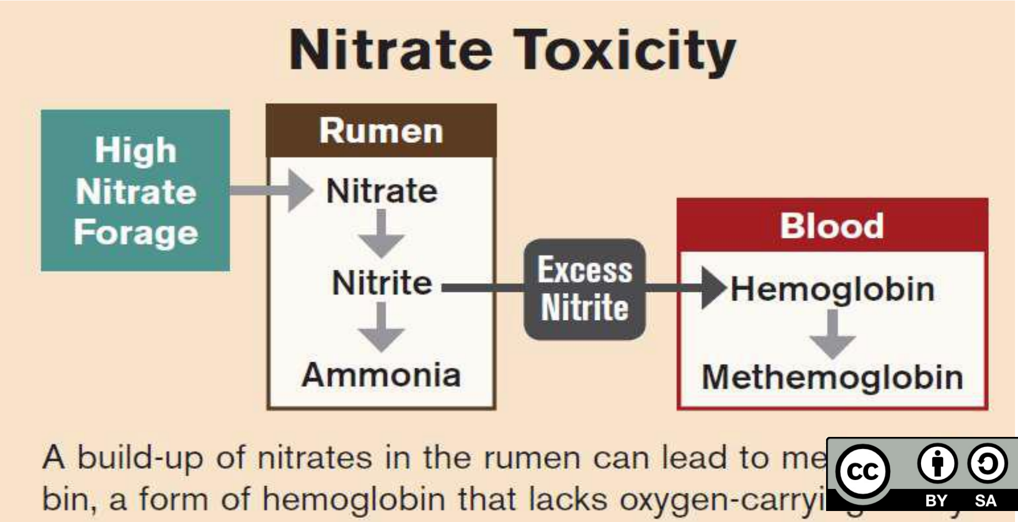
- **Food is usually the major source of nitrate exposure**. Ingestion of up to 250 mg / day of nitrate has been reported for people whose diets consist mainly of food from vegetable sources.

Nitrate content of selected vegetables

Vegetable	Nitrate content, mg/100g fresh weight
Celery, lettuce, red beetroot, spinach	Very High (> 2500)
Parsley, leek, endive, Chinese cabbage, fennel	High (100-250)
Cabbage, dill, turnip	Medium (50-100)
Broccoli, carrot, cauliflower, cucumber, pumpkin	Low (20-50)
Artichoke, asparagus, eggplant, garlic, onion, green bean, mushroom, pea, pepper, potato, summer squash, sweet potato, tomato, watermelon	Very Low (<20)

Why we care about nitrates and Nitrites

- **High Levels Can Lead to the Death of Infants**
  - High nitrate/nitrite levels may cause a potentially fatal blood disorder in infants under six months of age called methemoglobinemia or "blue-baby" syndrome.
  - With this disorder there is a reduction in the oxygen carrying capacity of blood, which can cause shortness of breath and blueness of the skin of infants or even lead to the infant's death.



Maximum Contaminant Levels (MCL)

- The Environmental Protection Agency (EPA) has set the Maximum Contaminant Level (MCL) for nitrate and nitrite to the following for the safety of drinking water:

Nitrates MCL = 10.0 mg/L

Nitrites MCL = 1.0 mg/L

Acute and Chronic effect of Nitrates

- **1.Short term effect (acute):**

Development of methemoglobinemia (excess of methemoglobin in the blood) that cannot carry oxygen. High conc. can result in a temporary blood disorder in infants called **methemoglobinemia**, commonly called "**blue baby syndrome**". In severe, untreated cases, brain damage and eventually death can result from suffocation due to lack of oxygen.

- **Predisposing factors :**

Age (infants 6 months of age are considered to be the most sensitive population)

Pregnant women (due to a natural increase in methemoglobin levels during the later stage of pregnancy beginning around the 30th week).

Acute and chronic effects of nitrates

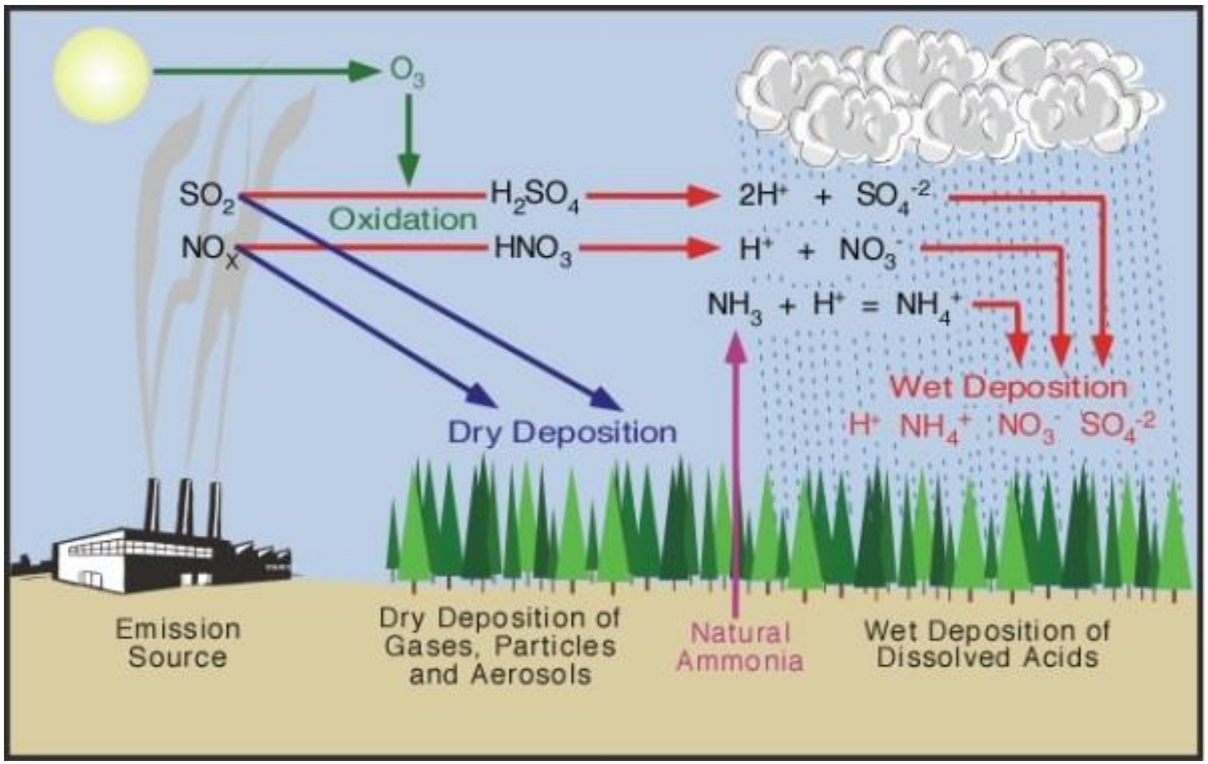
- **Individuals with digestive difficulties (**due to reduced stomach acidity are also at higher risk).
- **Chronic effect (carcinogenic effect):**
- It is believed that after nitrate is converted to nitrite in the body, it can react with certain amine- containing substances found in food to form nitrosamines, which are known to be potent cancer causing chemicals. Nitrosamine formation is inhibited by antioxidants that may be present in food such as Vitamin C and Vitamin E.
- **Reproductive / Developmental Effects:**
- A study in which an association between nitrate levels and an increase in neural tube defects was observed.

Clinical symptoms

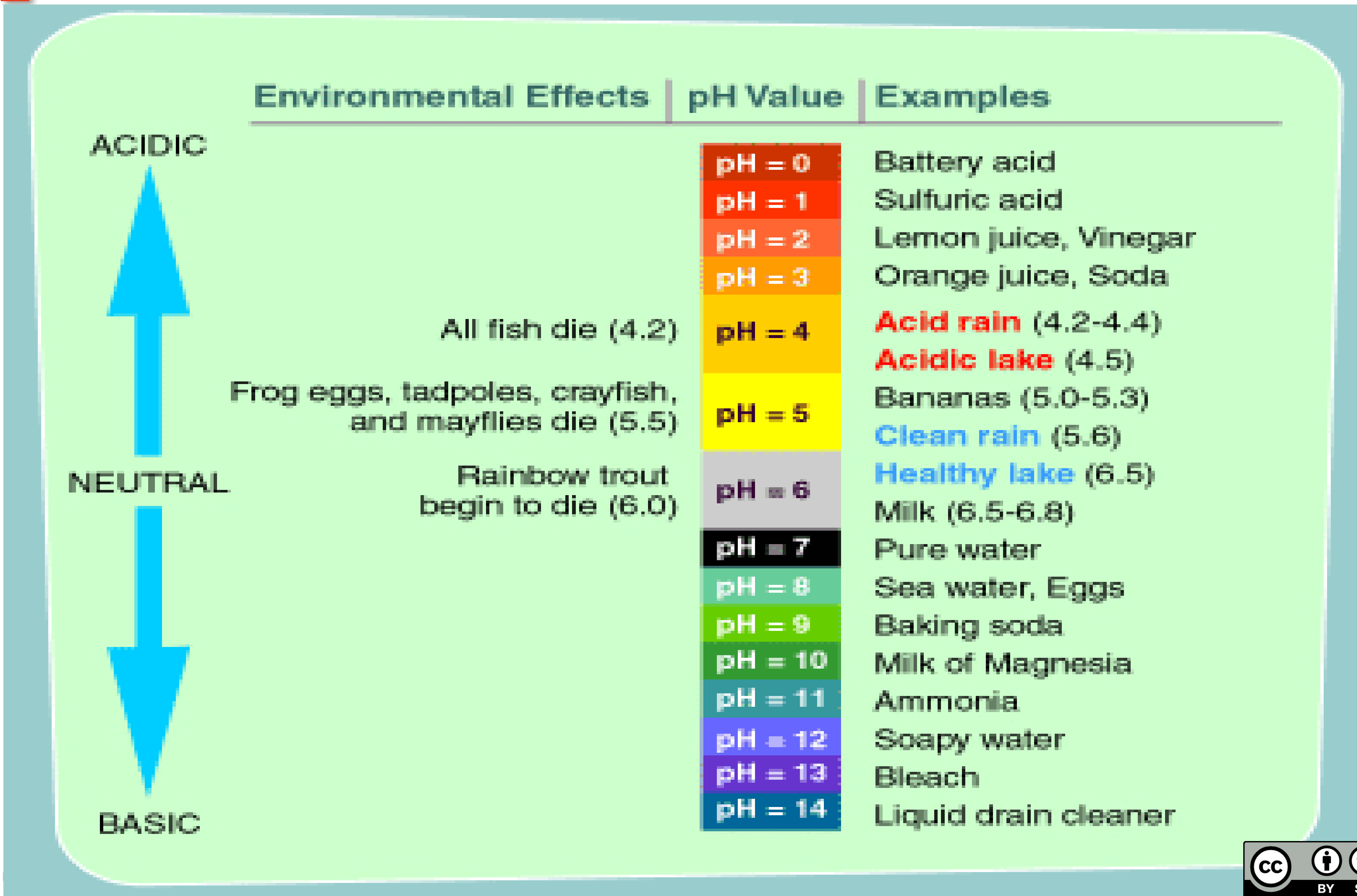
- Irritability, lack of energy, headache, dizziness, vomiting, diarrhea.
- Labored breathing.
- Blue – gray or pale purple coloration to areas around the eyes, mouth, lips, hands and feet.
- Cyanosis (blue skin) of limbs / trunk, weakness, and rapid heart rate, due to methaemoglobinemia.
- CNS depression.
- Brief loss of consciousness, shock, convulsions, coma.
- Irregular heart beats.
- Death occur when methaemoglobin levels exceed 50%.

Acids (H_2SO_4, HNO_3)

- The main precursors of acid rain – emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_x)
- **Sources:** fuel combustion in power plants (SO_2), automobile exhaust (NO_x), volcanic eruption, forest fires, etc.



Environmental effects

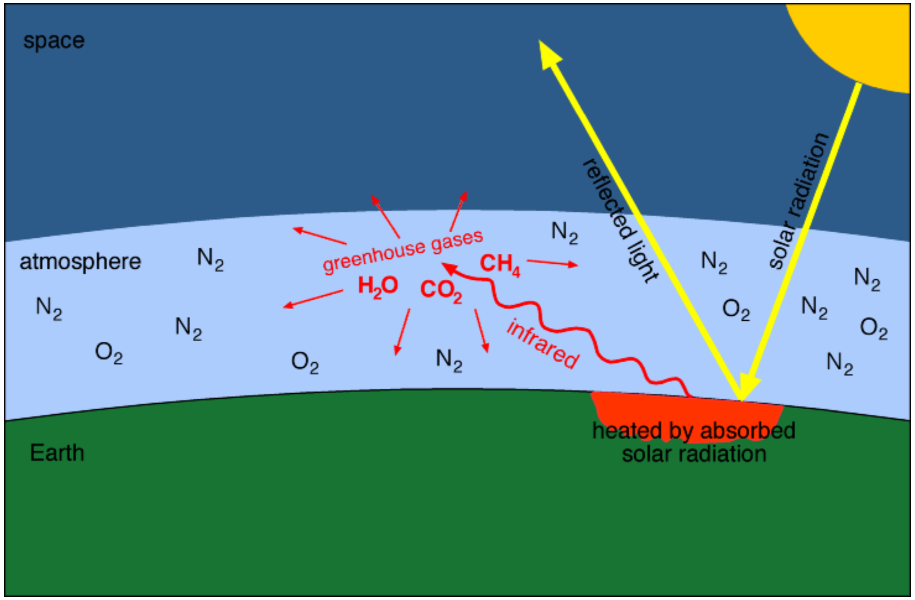


Acid Rain Effects:

Forests	Animals	Humans	Manmade Objects
•Acid rain can make trees lose their leaves or needles •Trees can also suffer from stunted growth •Trees have damaged bark and leaves, which makes them difficult to survive some weather, disease, and insects	•Fish die off, and that removes the main source of food for birds. •Birds can die from eating "toxic" fish and insects. •Fish can die from eating animals that are toxic. •Acid rain can even kill fish before they are born.	•One of the major problems that acid rain can cause in a human being is respiratory problems. •Many can find it difficult to breath. •When humans eat plants or animals which absorbed acid rain, the toxins inside of their meals can affect them.	•Architecture and artwork can be destroyed by acid rain. • Acid particles can land on buildings, causing corrosion. •When sulfur pollutants fall of the surfaces of buildings, they react with the minerals in the stone to form a powdery substance that can be washed away by rain.

Greenhouse gases

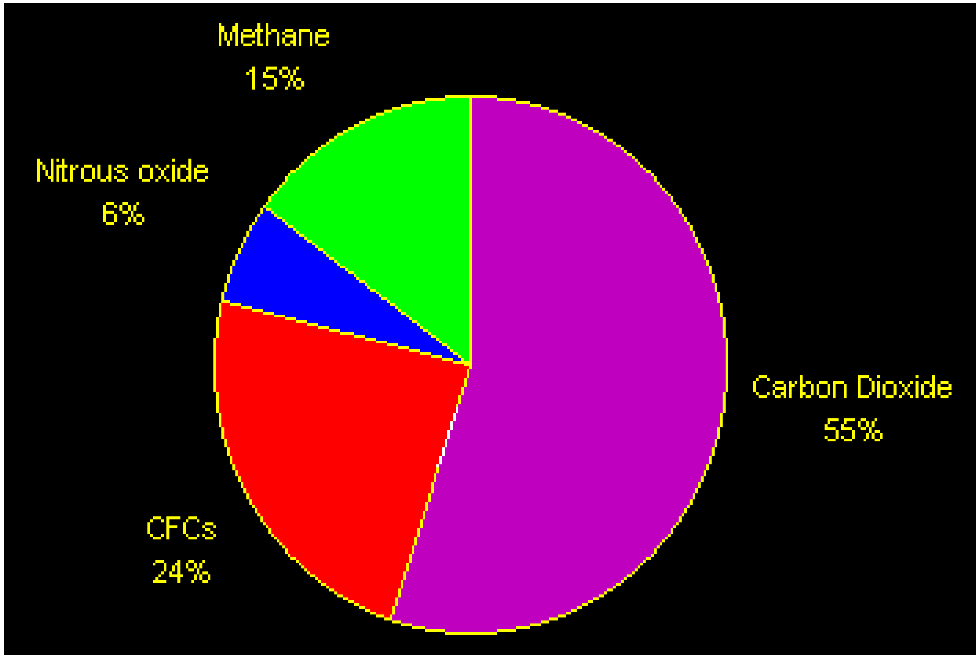
- Gases present in the atmosphere which reduce the loss of heat into space, and therefore contribute to global temperatures.
- The term greenhouse gas is applied to: **carbon dioxide, methane, nitrous oxide, ozone and CFCs**
- Produced by many natural and industrial processes



Greenhouse gases

- By their percentage contribution to the greenhouse effect on Earth, the four major gases are:
- water vapor, 36–70%
- carbon dioxide, 9–26%
- methane, 4–9%
- ozone, 3–7%

role in the greenhouse effect



Selected greenhouse gases

- **Carbon Dioxide (CO_2)**

  Source: Fossil fuel burning, deforestation

  Anthropogenic increase: 30%

  Average atmospheric residence time: 500 years ?

- **Methane (CH_4)**

  Source: Rice cultivation, cattle & sheep ranching, decay from landfills, mining

  Anthropogenic increase: 145%

  Average atmospheric residence time: 7-10 years

- **Nitrous oxide (N_2O)**

  Source: Industry and agriculture (fertilizers)

  Anthropogenic increase: 15%

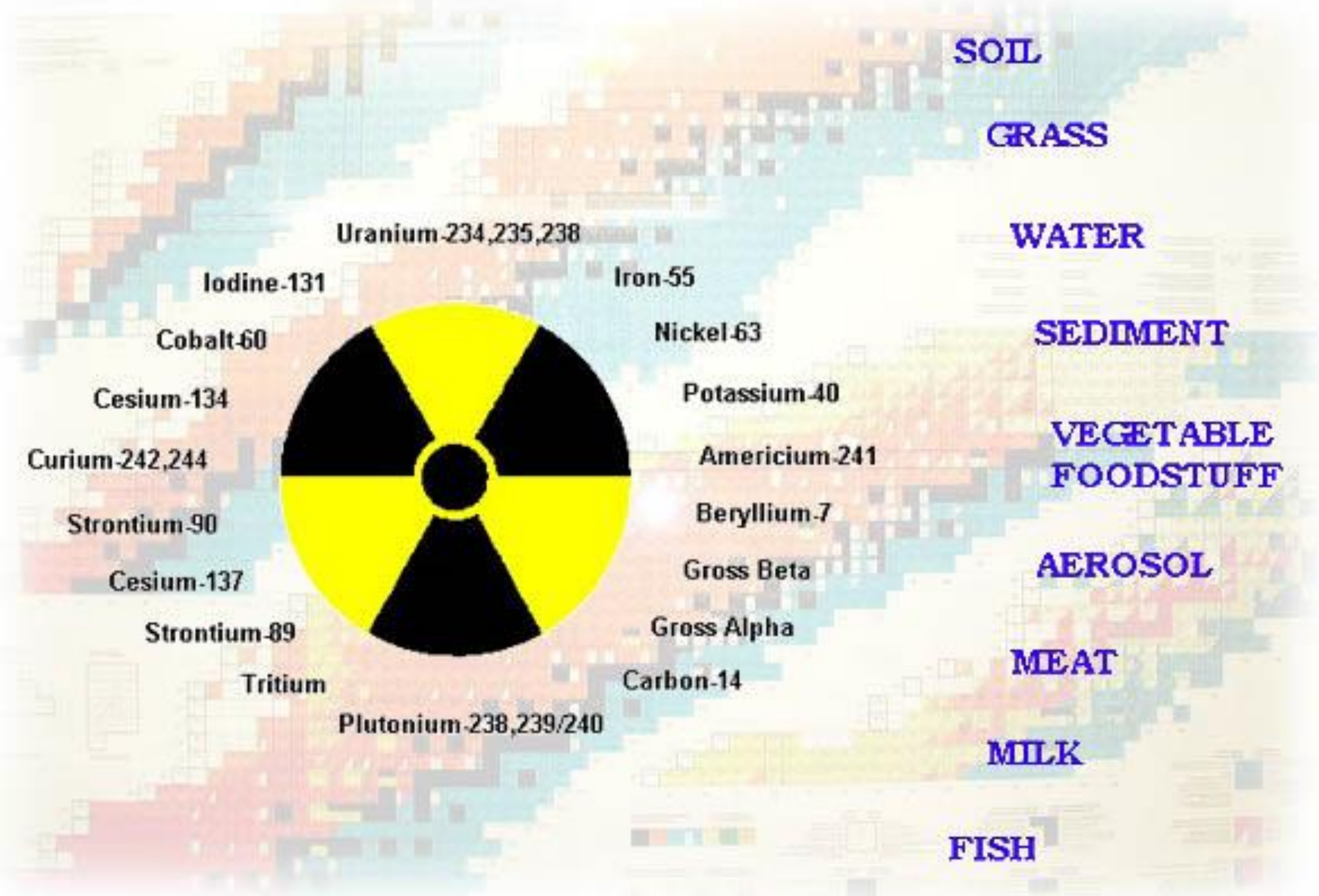
  Average atmospheric residence time: 140-190 years

Radionuclides

- **Sources:** nuclear power plant accidents or leakage, improper nuclear waste disposal, uranium mining operations
- Mobility in the environment depends on chemical properties of the element:

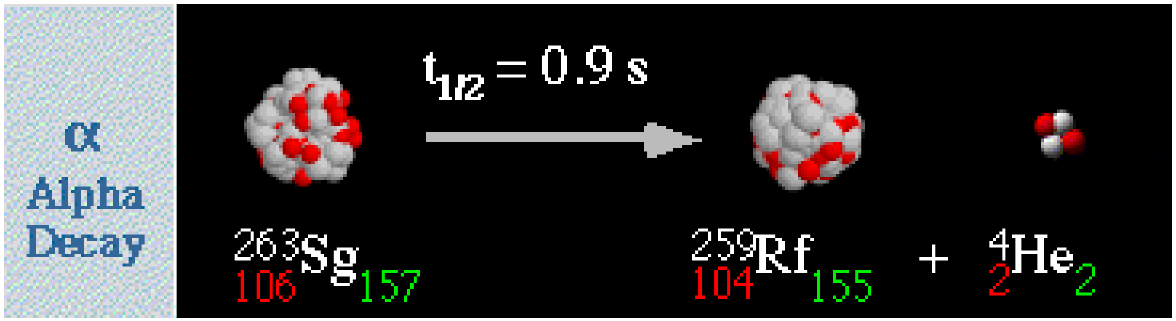
  high mobility: halogens (^{129}I, ^{36}Cl), alkali metals (^{40}K, ^{134}Cs, ^{137}Cs), alkaline-earth metals (^{89}Se, ^{90}Sr)
- cause birth defects, cancer, sterility and other health problems

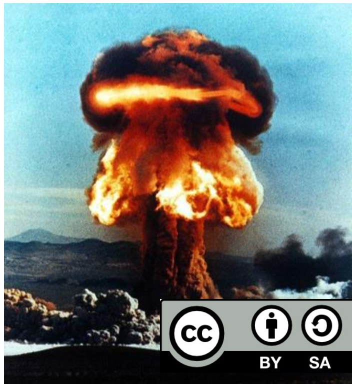
Radionuclide Pollution



Introduction of Radionuclides into Soils and Natural Waters

- Extensive above ground testing in US and USSR 1946-1962
- Above ground testing by other countries
- Waste generated from weapons grade uranium and plutonium production
- spent nuclear fuel --- processing to enrich U and Pu generates large amount of other radionuclide "waste“ which has to be "discarded" -- buried? stored?



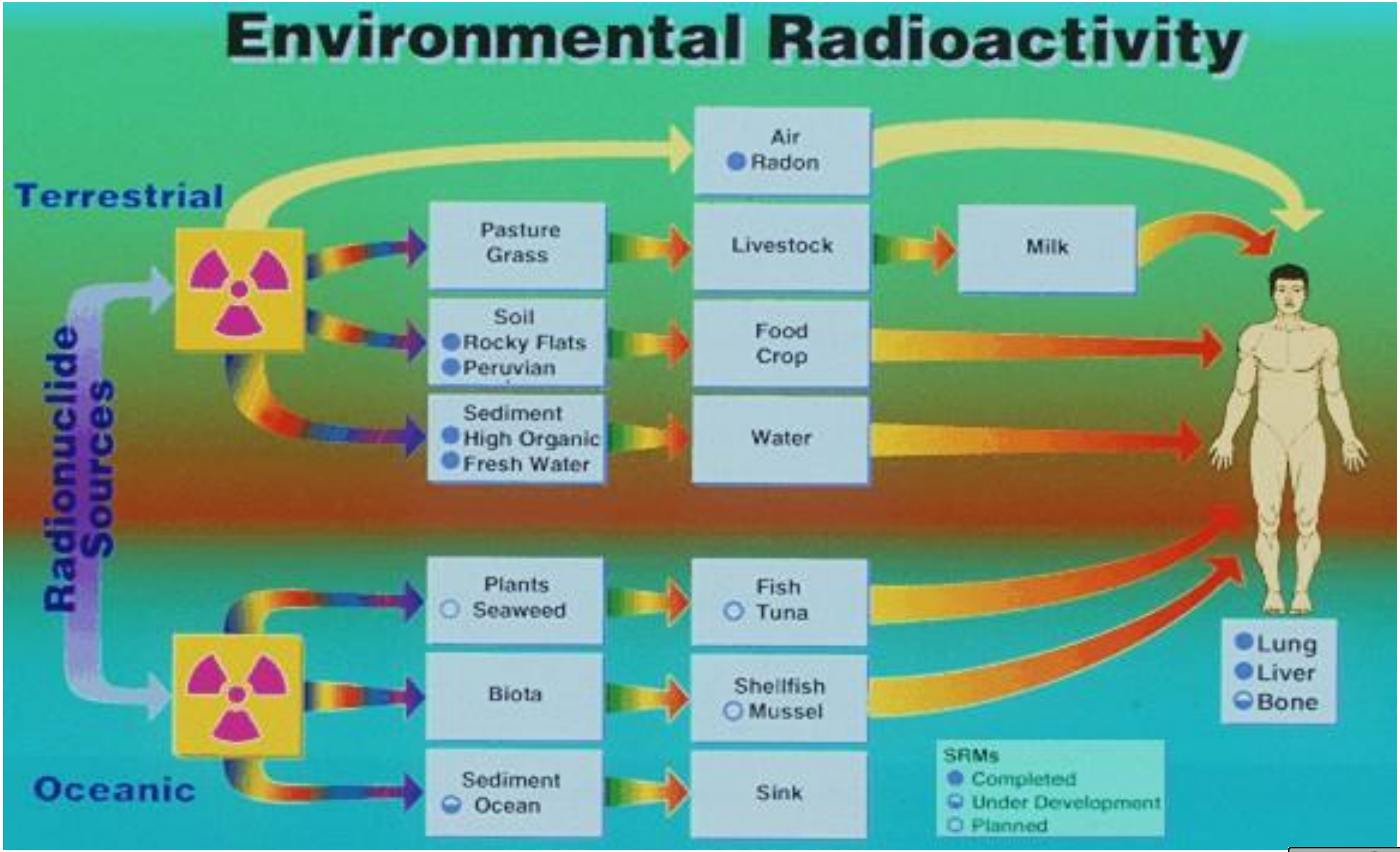


Anthropogenic occurring radionuclides – biomedical waste

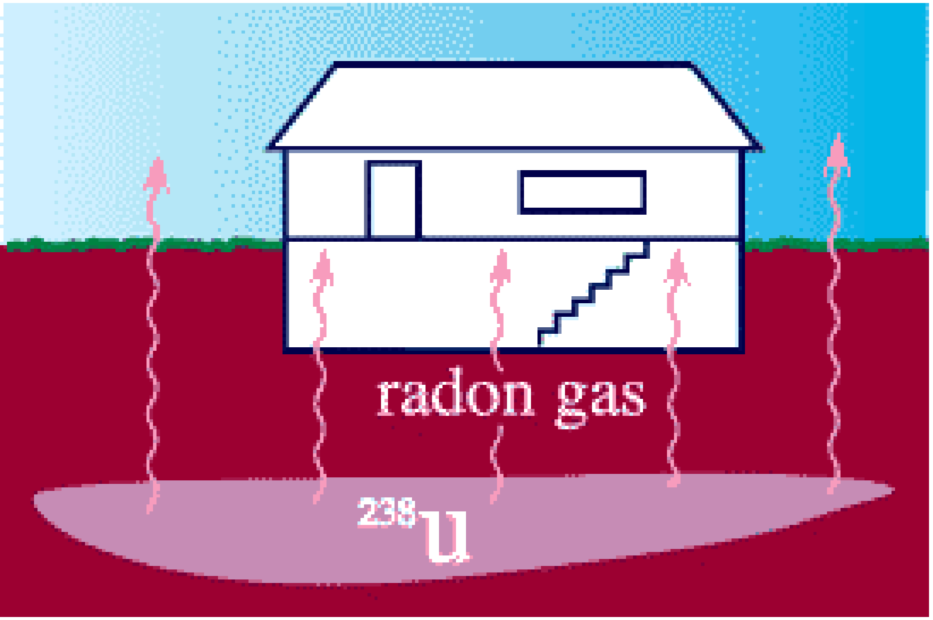
Table 1–4. Common isotopes used in the life sciences.

Isotope	Use	Half life
^{3}H	Tracer	12.3 yr
^{11}C	PET scan	20 min.
^{14}C	Tracer	5730 yr
^{18}F	Diagnostics	1.8 h
^{32}P	Bone cancer therapy, tracer	14.3 d
^{35}S	DNA labeling	87.2 d
^{51}Cr	Blood cell survival	27.8 d
^{54}Mn	Liver diagnosis	313 d
^{57}Co	Instrument calibration	271 d
^{60}Co	Radiation therapy source	5.3 yr
^{65}Zn	Biochemistry	244 d
^{67}Ga	Biochemistry	3.3 d
^{68}Ge	Tumor imaging	3.26 d
^{75}Se	Antibody labeling	120 d
^{85}Sr	Biochemistrty	64.7 d
^{90}Y	Colon cancer therapy	29 yr
^{99}Mo	Radioimmunotherapy	2.7 d, to ^{99}Tc, 2.1×10^{5} yr
^{103}Pd	Diagnostics	17 d
^{111}In	Diagnostics and therapeutics	2.8 d
^{113}Sn	Diagnostics	115 d
^{123}I	Colon cancer therapy	13.1 h
^{125}I	SPECT brain imaging	59.7 d
^{131}I	Therapeutics	8.1 d
^{133}Xe	Diagnostics, thyroid disorders	3.3 d
^{153}Sm	Diagnostics and therapeutics	1.9 d
^{153}Gd	Bone cancer therapy	242 d
^{169}Yb	Osteoporosis	31 d
^{201}Tl	Radiography	3.0 d

Exposure Pathways



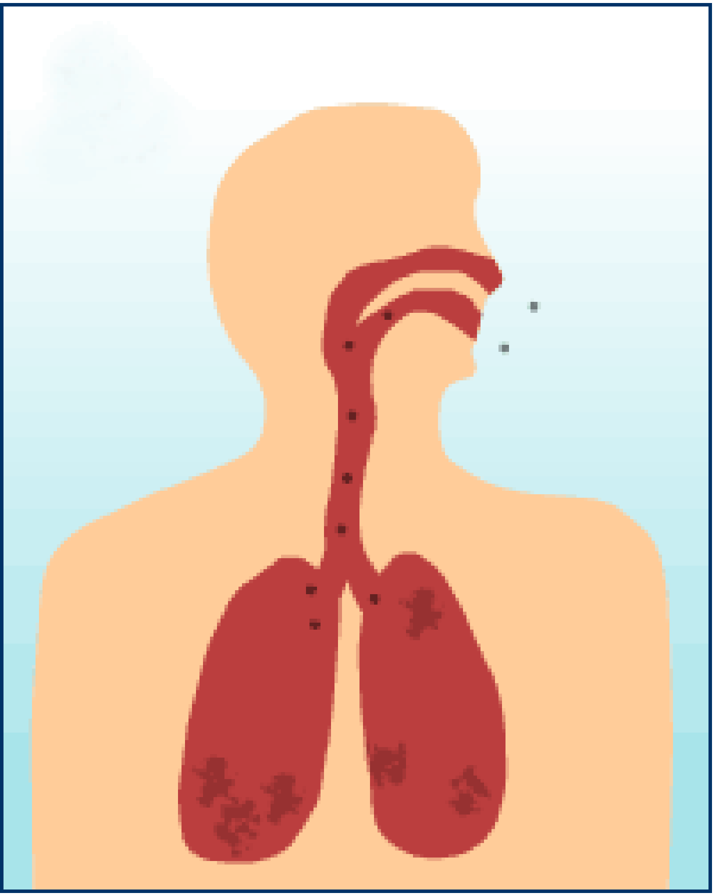
Natural occurring gaseous radioisotope radon



$^{238}U \rightarrow {}^{226}Ra \rightarrow {}^{222}\mathbf{Rn} \rightarrow {}^{218}Po \rightarrow\rightarrow {}^{208}Pb$ (stable)

GAS

Health effects of radon



$^{222}Rn \rightarrow \; ^{218}Po + {}^{4}_{2}He$

Alpha particle
α radiation

Concern: Lung cancer from alpha radiation

USEPA limit: >4 pCi/Liter of air
in house air
remediation required

National avg: 1.3 pCi/L for house air

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

11. Food additives – most important groups- E number

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Food additives

- Food additives are substances added intentionally to foodstuffs to perform certain technological functions, for example to colour, to sweeten or to help preserve foods

- In the European Union (EU) all food additives are identified by an E number

- Food additives are always included in the ingredient lists of foods in which they are used.

Food additives

- Product labels must identify both the function of the additive in the finished food (e.g. colour, preservative) and the specific substance used either by referring to the appropriate E number or its name (e.g. E 415 or Xantham gum).

- The most common additives to appear on food labels are **antioxidants** (to prevent deterioration caused by oxidation), colours, emulsifiers, stabilisers, gelling agents and thickeners, **preservatives** and sweeteners.

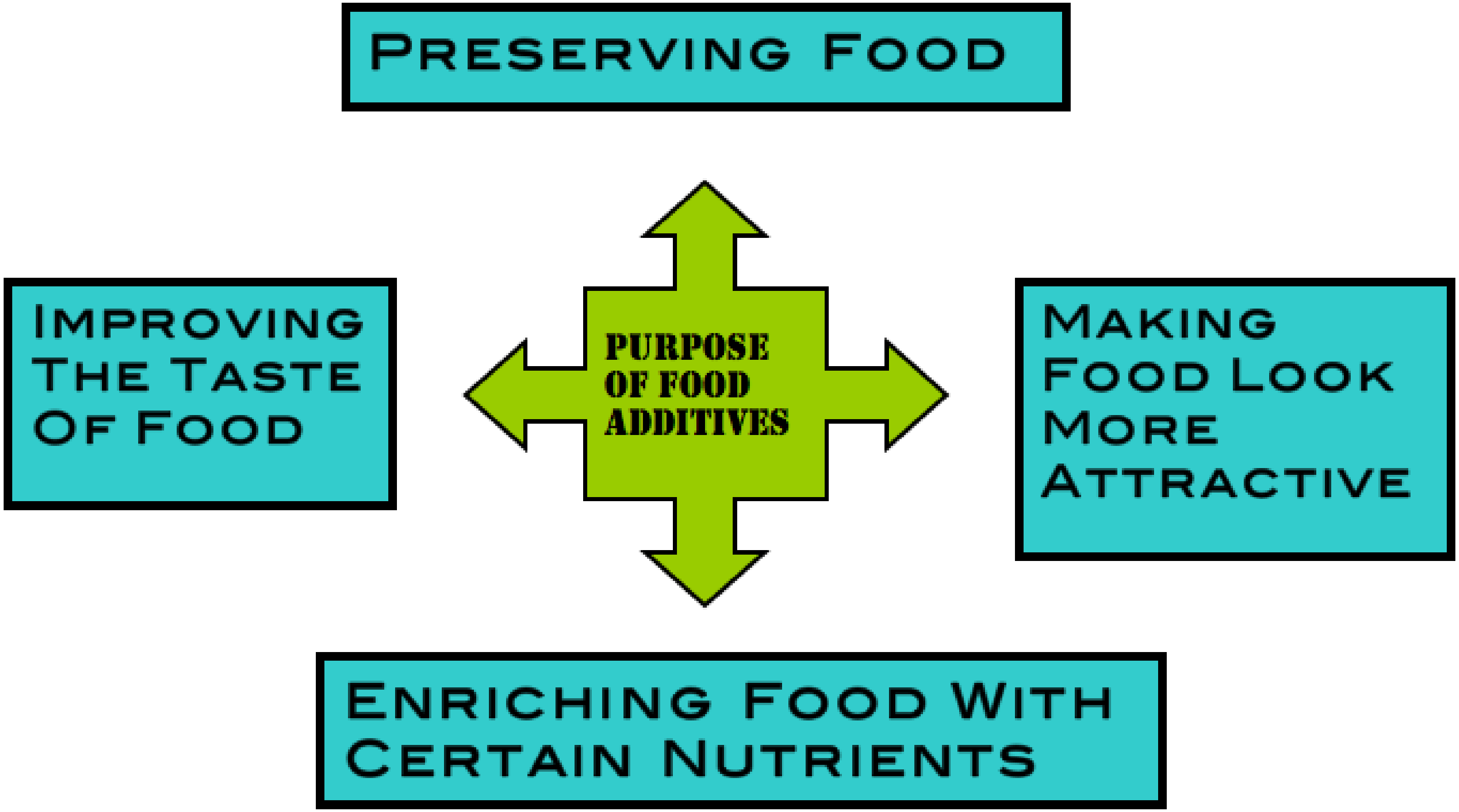
Food additives legislation

- Under EU legislation, food additives must be authorized before they can be used in foods.
- As part of its safety evaluations of food additives, EFSA establishes, when possible (i.e. when sufficient information is available), an Acceptable Daily Intake (ADI) for each substance.
- The ADI can apply to a specific additive or a group of additives with similar properties.
  - The ADI is the amount of a substance that people can consume on a daily basis during their whole life without any appreciable risk to health. ADIs are usually expressed in mg per kg of body weight per day (mg/kg bw/day).

EU rules on food additives, enzymes and flavourings

- The common EU authorization procedure for all food additives and food enzymes, called the "Food Improvement Agent Package" includes:
    - **Regulation EC 1331/2008** - EU authorization for food additives, food enzymes and food flavourings.
    - **Regulation EC 1332/2008** - food enzymes
    - **Regulation EC 1333/2008** - food additives
    - **Regulation EC 1334/2008** - flavourings and certain food ingredients with flavouring properties

Why add food additives, enzymes and flavourings to food?



Requirements for food additives

- Additive is safe in food at intended level
- Performs intended function
- Not used to deceive customer
- NOT used to cover faulty manufacturing practices
- Does not cause substantial reduction in food nutritional value
- Not used where GMP can achieve the same
- Method of analysis exists to police its use

Functional classes of food additives (26)

1. **sweeteners** – aspartam, acesulfam K, steviosil glycoside,
2. **colours** – *vary color of foods* – caramel coloring (E150), tartrazine, green S
3. **preservatives** – *prevent microbial spoilage* – benzoic acid, parabens, sulfites
4. **antioxidants** – *used to stabilize foods against oxidative deterioration* – Vit C, BHT
5. **carriers** – carbon dioxide, ethanol, glycerol
6. **acids** – *control the acidity for safety and stability of flavour* – citric acid, sorbic acid, ammonium lactate,
7. **acidity regulators** – *control the acidity or alkalinity of food, for safety and stability of flavour* – sodium salts of sorbic, acetic and benzoic acid
8. **anti-caking agents** – *ensure free movement or flow of particles, e.g. in dried milk or table salt* – E500 sodium bicarbonate, E460(ii) powdered cellulose
9. **anti-foaming agents** – *Anti-foaming agents prevent or disperse frothing, e.g. in the production of fruit juices* – insoluble oils, certain alcohols and stearates

Functional classes of food additives (26)

10. **bulking agents** – *increase the bulk of a food without affecting its taste* – potassium bitartarate, sodium hydrogen carbonate
11. **emulsifiers** – *help mix ingredients together that would normally separate* – lecithin, monoglyceride, calcium stearate, brominated vegetable oil
12. **emulsifying salts** – sodium stearoyl lactylate, sodium Stearate
13. **firming agents** – *precipitate residual pectin, thus strengthening the structure of the food and preventing its collapse during processing* – calcium citrates (E333), magnesium sulfate (E518)
14. **flavour enhancers** – *bring out the flavour in foods without imparting a flavour of their own* – monosodium glutamate
15. **foaming agents** - acetylated distarch phosphate, ammonium alginate
16. **gelling agents** – *are used to change the consistency of a food* – agar, carrageenan, guar gum
17. **glazing agents, lubricants** – *provide a protective coating or sheen on the surface of foods, e.g. confectionary (for appearance and shelf-life)* – beeswax, acetylated monoglycerides, candelilla wax

Functional classes of food additives (26)

18. **humectants** – *additives that bind water and control a_w* -propylene glycol, honey, lithium chloride
19. **modified starches** – dextrin
20. **packaging gases** – used to pack sensitive materials such as food into a modified atmosphere environment – carbon dioxide (E290), nitrogen (E941), argon (E938)
21. **propellants** – help expel the food from its container – carbon dioxide (E290), nitrous oxide (E942)
22. **raising agents** – something that makes bread and otherfoods rise – sodium hydrogen carbonate (E500ii), glucono delta–lactone (E575)
23. **sequestrants** – Are stabilizers. React with metals hence synergists to antioxidants - calcium chloride (E509), potassium gluconate (E577)
24. **stabilisers** – prevent ingredients from separating again – agar or pectin, brominated vegetable oil
25. **thickeners** – Used to give body and texture – acetylated starch, agar
26. **flour treatment agents** – ascorbic acid, azodicarbonamide (E927), phosphates

Classification of additives – E number

Colourings:	E100-199
Preservatives:	E200-299
Antioxidants:	E300-399
Physical conditioning agents:	E400-E499
Flavourings:	No E number
Flavour Enhancers:	E600-699
Sweeteners:	E900-999
Nutritive additives:	No E number

Advantages of additives

- Increase shelf life – preservatives
- Reduce risk of food poisoning – preservatives
- Prevent waste – preservatives
- Make food more appetising – colouring
- Improve taste – flavouring
- Improve texture – physical conditioning agents
- Increase nutritive value
- Provide wider variety of foods
- Ensure consistency of quality

Disadvantages of additives

- Allergies: migraine, hyperactivity, rashes e.g.tartrazine
- Little known about cumulative or combined effect of additives.
- Bulking agents can deceive consumers
- Some additives destroy nutrients, e.g. sulphur dioxide destroys vitamin B
- Sweeteners can leave bitter aftertaste e.g. saccharine

Acceptable Daily Intake

- **ADI:**

  an estimate … of the amount of a food additive, expressed on a bodyweight basis, that can be ingested daily over a lifetime without appreciable health risk (JECFA)

  The concentration or amount of a chemical that can be consumed **daily for a lifetime in the practical certainty, on the basis of all known facts, that no harm will result (JMPR)**

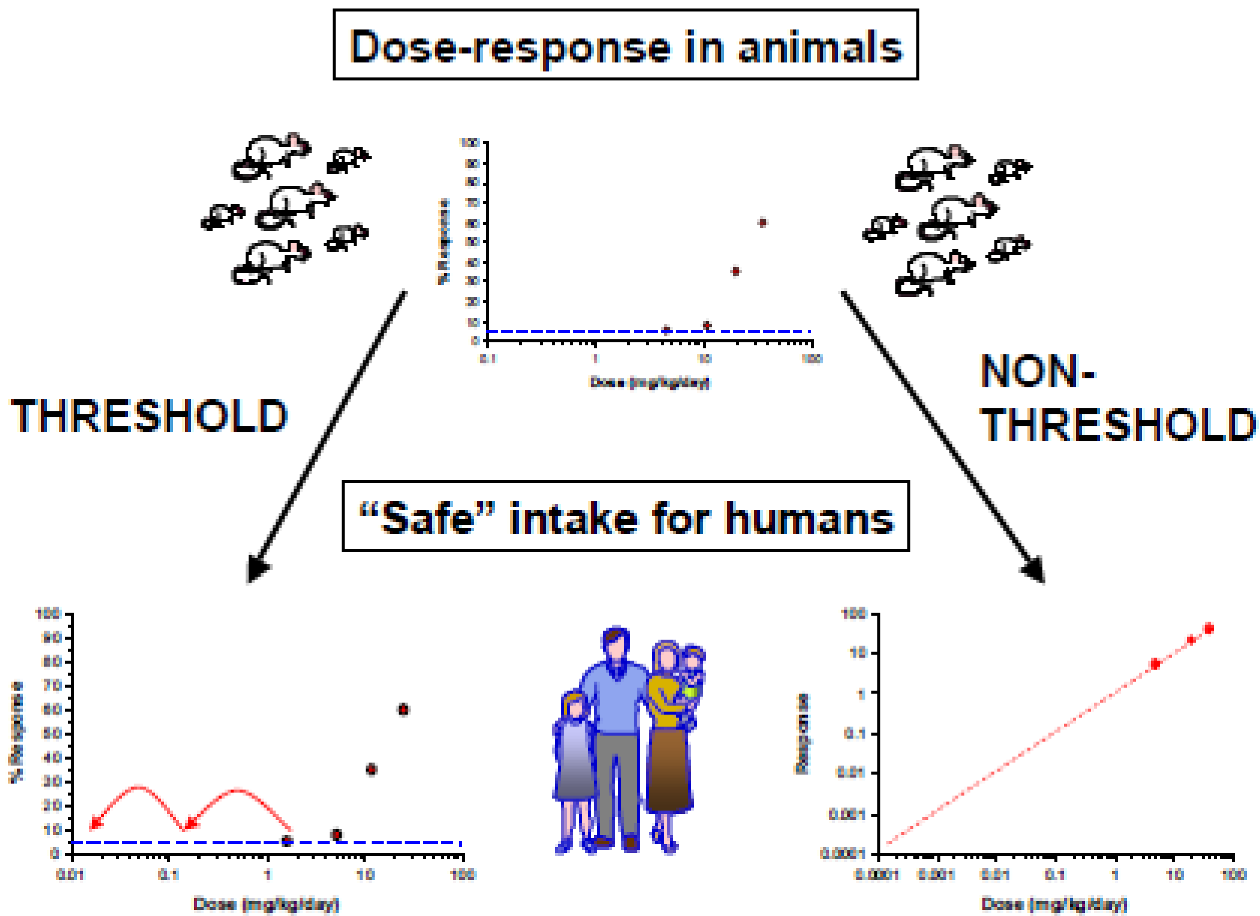
- **ARfD:**

  the amount of a chemical that can be consumed at one meal/in one day in the practical certainty…….

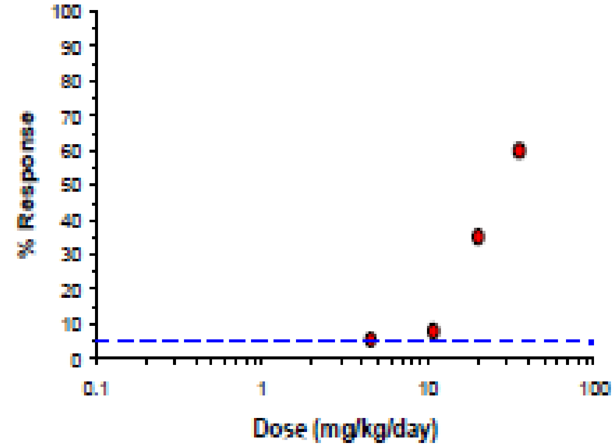
Tolerable intakes: definitions

- Tolerable Daily Intake (TDI) - similar to ADI, but not the same.
  - **ADI** refers to chemicals that have been deliberately added to a product or ingredient, or which are found in food because of, for example, crop treatment with pesticides or antifungal preparations.
  - **TDI** is an estimate of the amount of chemical contaminant that we are exposed to from environmental contamination and which, when in food, can be consumed daily during life without posing a significant health risk.
  - Exposure to these contaminants is undesirable but cannot be ruled out because some of these substances are found in food because of environmental pollution (e.g. lead, dioxins)

Safety evaluation / risk assessment paradigms

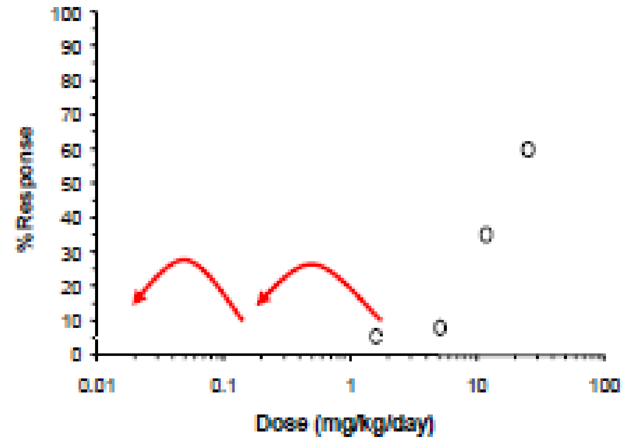


Dose-response in animals

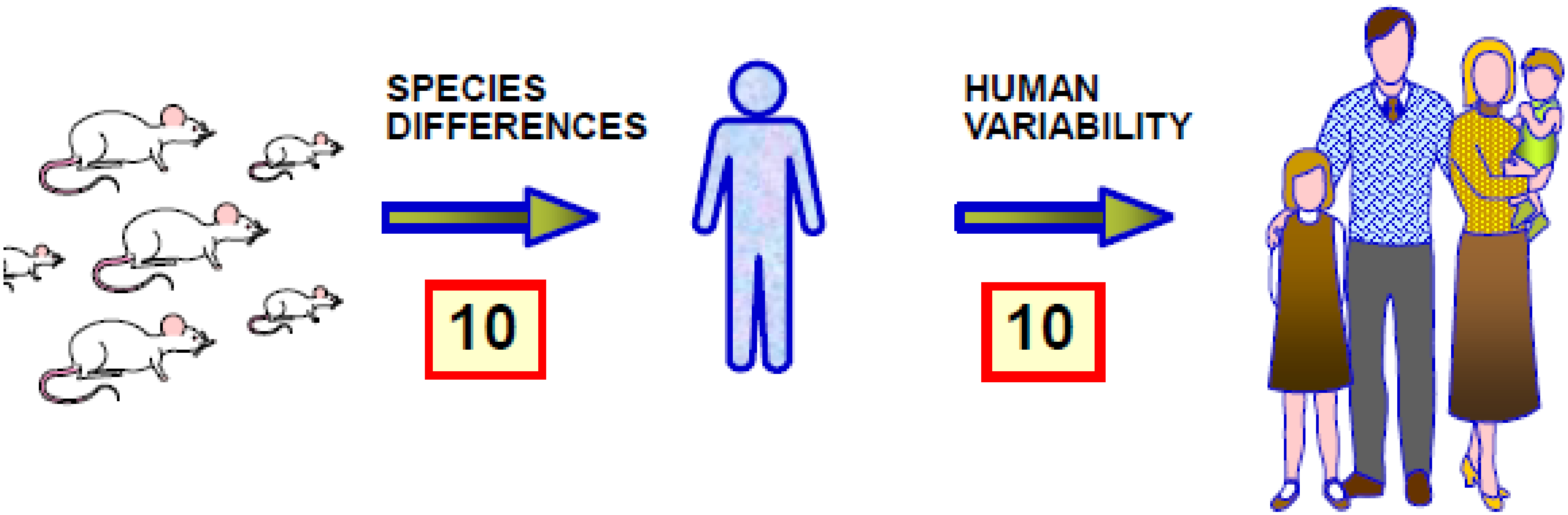


Divide NOAEL by safety or uncertainty factors

Safe intake for humans



The use of uncertainty or safety factors



Uncertainty or safety factors are used to extrapolate from a group of test animals to an average human and from average humans to potentially sensitive sub-populations

$$\text{ADI (or TDI)} = \frac{\text{NOEL}}{\text{SAFETY FACTOR}}$$

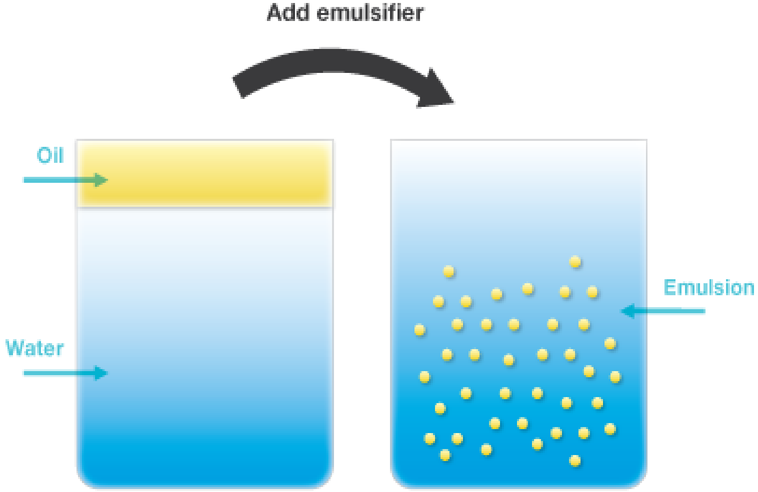
NOEL = No Observed (Adverse) Effect Level – which is derived from safety studies, usually in animals, which identify the hazard and the most sensitive species

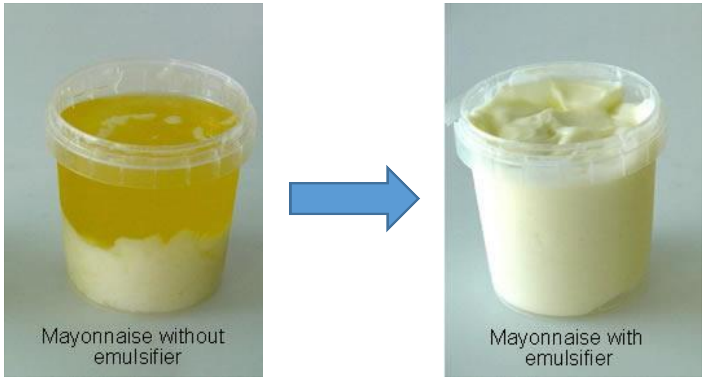
SAFETY FACTOR = factor applied to allow for differences between animals and humans, and between different humans

Substances modifying texture

- Main additive substances used

- **Most important groups:**
  - Thickeners, stabilizers and gelling agents
  - Emulsifiers

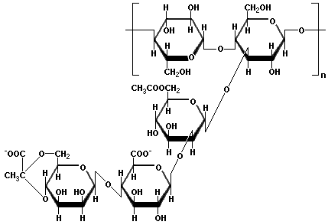


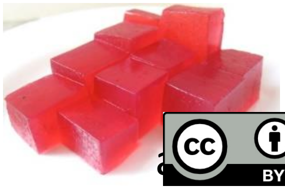


Thickeners, stabilizers and gelling agents

arabic gum

- classified separately but overlap in functionality
- When dissolved or added to foods, they create stiffness, stabilize emulsions or form gels
  - **Natural plant polysaccharides** (starch, cellulose, pectins)
  - **Seaweed polysaccharides** (arabic gum, agar, carragenan)
  - **Extracellular bacterial polysaccharides** (gellan, xanthan gum)
  - **Modified polysacchrides** (modified starches and celluloses)





Thickeners

- Range from flavorless powders to gums and are chosen for their ability to work in a variety of chemical and physical conditions.
- Variables affecting choice of thickener include pH, frozen state, clarity and taste.
- **Starches, pectin and gums** are the most common
- Used in soups, sauces and puddings.

Stabilizers

- Substances that increase stability and thickness by helping foods remain in an emulsion and retain physical characteristics.
- Ingredients that normally do not mix, such as oil and water, need stabilizers. Many low-fat foods are dependent on stabilizers.
- **Lecithin, agar-agar, carrageenan and pectin** are common
- **Where:** ice cream, margarine, dairy products, salad dressings and mayonnaise.

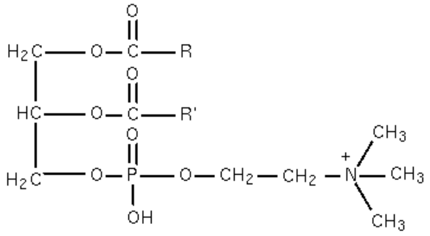
Gelling agents

- function as stabilizers and thickeners to provide thickening without stiffness through the formation of gel in jellies, jams, desserts, yogurts and candies.
- **Gums, starches, pectin, agar-agar and gelatin** are common gelling agents.

Emulsifiers

- Surfactants enabling the formation of emulsion (especially dispersion of fat in various products)
- **Clasification:**
  - **According structure:** esters of glycol, sucrose esters, lecithin and its derivatives etc…
  - **According to the properties:** hydrophilic, lipophilic
  - **According to their ability to form ions:** ionogenic, non-ionogenic
- With the exception of lecithin, all emulsifiers used in foods are synthetic
- All the synthetic emulsifiers are derivatives of fatty acids
- Most common food emulsifiers are non-ionogenic

Emulsifiers



- Lecithin is the commercial name of a mixture of phospholipids obtained as a byproduct of the refining of soybean oil
- Crude soybean lecithin is dark in colour and can be bleached with hydrogen peroxide or benzoyl peroxide
- The emulsifying properties, especially Hydrophilic Lipophilic Balance value (HLB) , are determined by the chain length and unsaturation of the fatty acid chain
- Hydroxycarboxylic and fatty acid esters are produced by esterfying organic acids to monoglycerides
- This increases their hydrophilic properties

Emulsifiers

- Organic acids used are
  - **Acetic, citric, fumaric, lactic or tartaric acid**
- Acetic acid esters can be produced from mono- and diglycerides by reaction with acetic anhydride or by transesterification
- They are used to improve aeration in food high in fat content and to control fat crystallization
- Sucrose fatty acid esters can be produced by esterification of fatty acids with sucrose, usually in a solvent system

Emulsifiers

- When the level of esterification increases to over five molecules of fatty acid, the emulsifying property is lost
- At high levels of esterification the material can be used as a fat replacer because it is not absorbed or digested and therefore yields no calories

Classes	Examples	Use	Origin	Function
Emusifiers	Lecithin Alginates E401-404	Mayonnaise Hollandaise Ice cream	Eggs, soya beans Sea weed	To make permanent emulsions
Stabilisers	Carageen Guar gum E412	Ice cream Confectionary	Sea weed Guar plant	To stabilise emulsions by thickening them
Poly-phosphates	Magnesium carbonate	Salt- as anti-caking agent, Cake mixes	Lab	To prevent lumping
Pectin E440		Jams / jellies	fruit cell walls	To set mixtures
Humectants	Sweeteners sorbital and mannitol	Confectionary and sweets Cakes/ buns	Lichen	They absorb water vapour from air and keep foods moist

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

12. Nanotechnologies and their use as additives in food production

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Products and Applications of Nanotechnology

- Cosmetics and personal care products
- Paints & coatings
- Catalysts & lubricants
- Security printing
- Textiles & sports
- Medical & healthcare
- Food and nutritional supplements
- Food packaging
- Agrochemicals
- Veterinary medicines
- Water decontamination
- Construction materials
- Electrical & electronics
- Fuel cells & batteries
- Paper manufacturing
- Weapons & explosives

Nanomaterials in the Food Sector

Nanomaterials in the Food Sector

- Nanotechnology applications are expected to bring changes to the food sector:
  - improved production and processing techniques
  - improved food contact materials
  - modification of taste, texture and sensation
  - monitoring food quality and freshness
  - reduced fat and salt content
  - enhanced nutrient absorption
  - improved traceability and security of food

Nanotechnology Applications for (health)Foods

- **Here & Now**

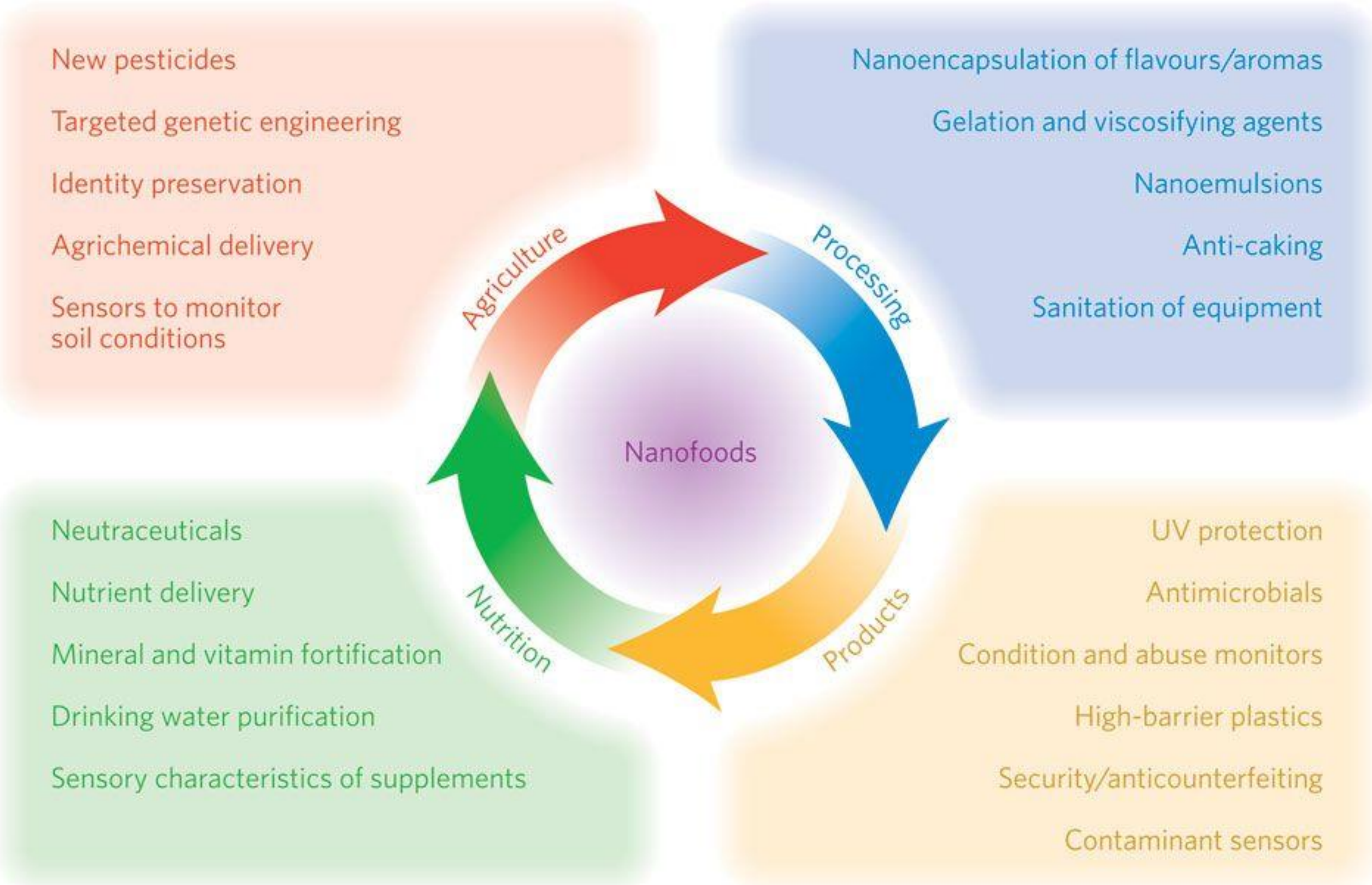
  (health)food supplements, nutraceuticals, flavours, stabilisers, antibacterials, nano-membranes, nano-filters, novel food packaging, sensing and warning devices

- **Under R&D**

  Novel & functional foods, pathogen and contaminant sensors, environmental monitors

- **Unlikely**

  Unlimited synthetic food through assembling atoms and molecules



New pesticides
Targeted genetic engineering
Identity preservation
Agrichemical delivery
Sensors to monitor soil conditions
Nanoencapsulation of flavours/aromas
Gelation and viscosifying agents
Nanoemulsions
Anti-caking
Sanitation of equipment
Agriculture
Processing
Nanofoods
Nutrition
Products
Neutraceuticals
Nutrient delivery
Mineral and vitamin fortification
Drinking water purification
Sensory characteristics of supplements
UV protection
Antimicrobials
Condition and abuse monitors
High-barrier plastics
Security/anticounterfeiting
Contaminant sensors

Creation of Nanomaterials

- use of mechanical or thermal energy
  - plant material, mineral materials
- creation of nanoparticles from singles molecules
  - by chemical reactions (e.g. enzymatic cross-linking of proteins)
  - molecular self association / self aggregation (e.g. micelles)

Food Processing

Food Processing →

raw material

↓

naturally occurring nanostructures

proteins, starches, fats undergo structural changes at the nm and μm scales

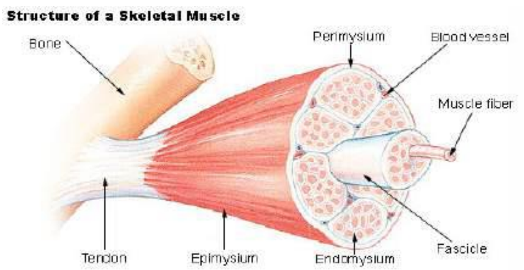
huge variety of food products

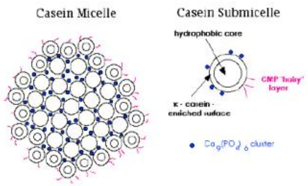
↓

naturally occurring nanostructures
+
nanostructures introduced through processing

Naturally Occurring Nanostructures

- many food proteins are globular structures between 1 and 10 nm in size (true nanoparticles)
- structure of meat (myofibrils)
- the majority of polysaccharides and lipids are linear
- polymers less than one nm in thickness (1 dimensional nanostructures)
- planar assemblies of cellulose fibrils in plant cell walls (2 dimensional nanostructure)





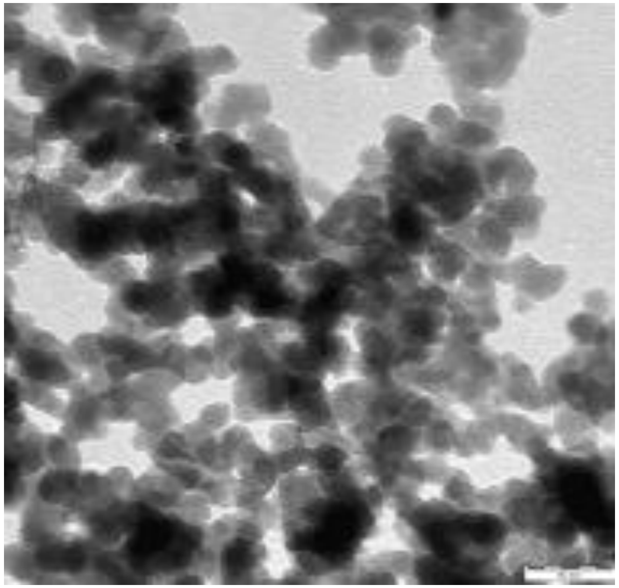
P. Walstra and R. Jenness In: P. Walstra and R. Jenness, Editors, *Dairy chemistry and physics*, Wiley, New York (1984)
http://www.foodscience.uoguelph.ca/deicon/casein.html

Nanostructures Introduced Through Processing

- many food processing operations such as coagulation, emulsifying or homogenising produce new nanostructures
- **milk**
  - fat globules of about 100 nm in size are produced through homogenisation
- **foams**
  - their creation and stabilisation requires the production of two dimensional nanostructures (e.g. the head on a glass of beer, ice cream, whipped cream, sauces, butter, margarine)
- **custard / yogurt**
  - involves creation of three dimensional networks

Food Structures

- **Properties**
  - texture
  - consistency
  - mouth feeling
  - sensation
  - energy density
  - ....



Fat-reduced ice cream

Nano-sized Ingredients/ Additives

Technology

- Processing of food ingredients to develop nano-structures
- Use of nano-sized ingredients & additives

Benefits

- Improved texture, flavour, taste
- Reduction in the amount of salt, fat, sugar, and other additives
- Enhanced bioavailability/ health benefits

Examples

- Nano additives (colours, flavouring agents, preservatives, antioxidants)
- Nano-salt, WOW Mayonnaise


Concerns

- Need to show that they are solubilised/ digested in the gut and that insoluble free nanoparticles do not enter the blood

Delivery Systems for Supplements/ Nutraceuticals

Technology

- Nanoencapsulation of ingredients, additives and supplements
- Based on micelles & liposomes

Benefits

- Taste masking, protection from degradation during processing
- Enhanced bioavailability of nutrients/ supplements
- Antimicrobial and other health benefits

Examples

- Food additives (benzoic acid, citric acid, ascorbic acid), Supplements (vitamins A and E, isoflavones, ß-carotene, lutein, omega-3 fatty acids, coenzyme-Q10)

Concerns

- Need to ensure that greater bioavailability does not lead to increased health risks
- Tissue distribution is not different from that of conventional forms

Engineered Nanoparticulate (ENP) Additives

Technology

- Manufactured nanoparticle forms of additives and supplements

Benefits

- Enhanced bioavailability of nutrients/ supplements
- Antimicrobial and other health benefits

Examples

- Mineral supplements (calcium, magnesium, iron, zinc, silica, diatomaceous earth, silver, gold)
- Nano-tea; “slim-shake chocolate”

Concerns

- Possible exposure to insoluble free ENPs, inside and outside the gut
- Toxicological properties of most ENPs are not known yet

Food Additives and Supplements

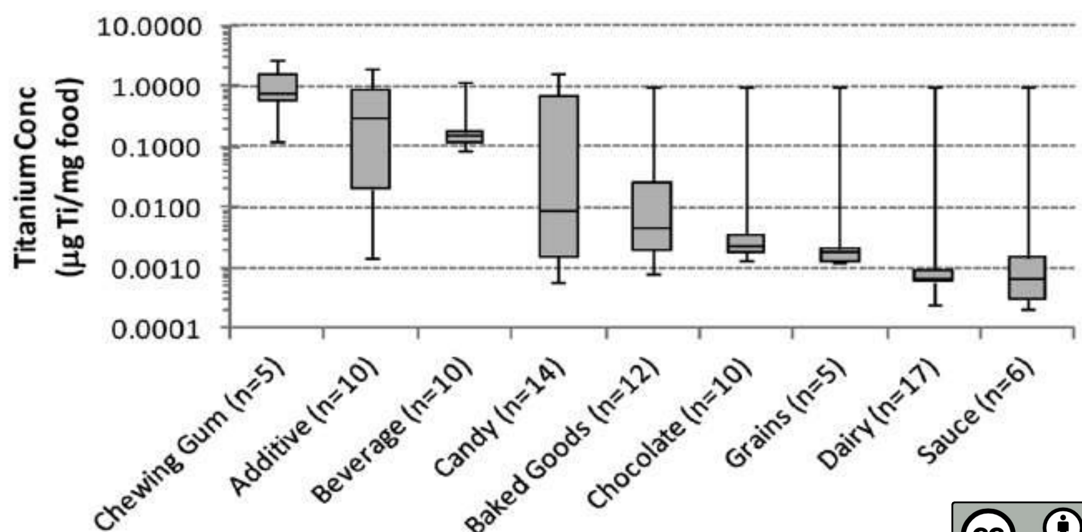
Silicon dioxide (E 551)

- dietary supplement (source of silicon)
- to improve technical properties
  - nano-scale amorphous SiO_2 → agglomerated particles
  - anti-caking agent for powdery ingredients (e.g. whole egg powder, dried spices, tomato powder, coffee creamer)
  - addition in the single-digit percentage range
  - widely used since the 60ties

Food Additives and Supplements

Titanium dioxide (E 171)

- white pigment, icing material,
- flavour enhancer
  - candies, confectionaries
  - dried vegetables, nuts, seeds, soups, mustard, beer, wine
  - chewing gum
  - food icing



Weir *et al.*, Environ. Sci. Technol. 46, 2242–2250 (2012)

Food Additives and Supplements

Nano-lycopene (Lycovit®, since 2009 approved as a novel food)

- BASF produces a synthetic form of the tomato carotenoid lycopene
- mean particle diameter in the range of 300 nm
- nanoparticles in powders or in oil
- additive for beverages and other foods
- addition not only for health purposes, but also for colouring

BASF 2006

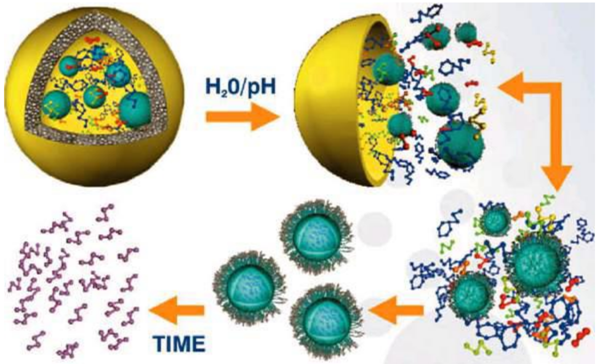
Food Additives and Supplements

Food Supplements

- bioavailability (nano-Se, nano-Pt, nano-Mg, nano-Zn, nano-Ca, nano-Fe)

Nano-encapsulation

- bioavailability (e.g. fat-soluble vitamins)
- protection / stabilisation (e.g. acid-labile compounds)
- masking (e.g. omega-3 fatty acids)
- controlled release

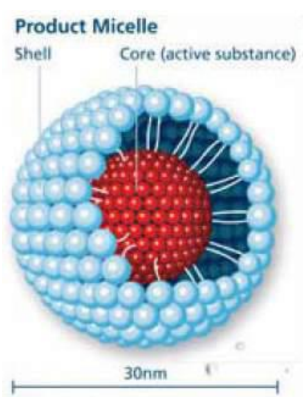


Organic Carrier Systems

- coenzyme Q10 / α-lipoic acid
- benzoic acid
- citric acid
- ascorbic acid (vitamin C)
- vitamin A, D, E, K
- soybean isoflavones
- ß-Carotene
- lycopene
- lutein
- omega-3 fatty acids
- phytosterols

Examples:

- NovaSOL® solubilisates (Aquanova AG, Germany)
- Nutralease™ (NutraLease Ltd., Israel)
- VESIsorb®
- (Vesifact AG, Switzerland)



Organic Carrier Systems

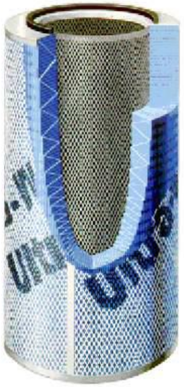
Easy Iron, Sunactive Fe™
Taiyo International, Inc. (Japan)
- iron supplemented milk (Maeil, Korea)

Slim Shake Vanilla
RBC Life Sciences® Inc. (USA)
- silicon dioxide particles (4-6 nm) coated with flavour molecules

Shemen Industries (Israel)
- active canola oil contains phytosterols

Food Processing

commercial air filter cartridge
using nanofibre filter media



Nano-filtration

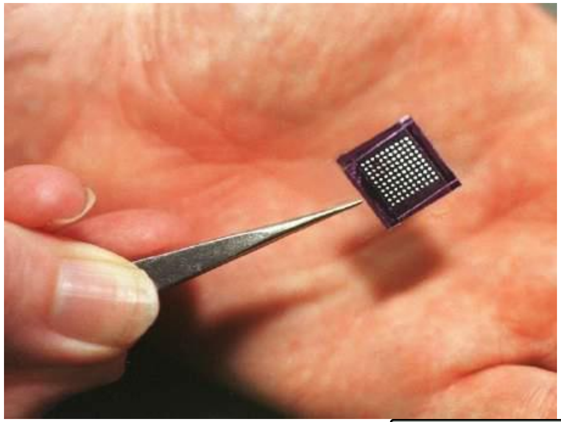
- nano-ceramics for restaurant deep-frying machines
- treatment of effluents from the food industry
- food industry
  - global market for nanofiltration membranes should reach USD 310.5 million by 2012
  - the water treatment sector was projected to account for 72.7% of total revenues in 2007
  - the main applications of nanofiltration in food production are in the dairy and sugar industry
  - around 300,000 m2 of nanofiltration membranes are assumed to be currently applied in the food

Food Analysis: Process- and Product Control

- ~**2 million** people die annually from diarrhoeal diseases, largely attributed to contaminated food and water
- Nanosensors could detect the presence of microbial contamination.
  - less cumbersome, more portable instrumentation with increased sensitivity and reduced detection time, and require less technical training of personnel necessary to conduct pathogen detection.

Nano-sensors / Nano-indicators

- Potential Applications:
  - Pathogen detection (bacteria, viruses)
  - Toxin and pesticide detection
  - Spoilage detection
  - Authenticity and traceability
  - Quality control



Electronic tongue

Food Packaging Applications

Improved nano-composites	• Polymers incorporating nanomaterials to improve flexibility, durability, temperature/ moisture stability, barrier properties
'Active' nano-composites	• Plastic polymers incorporating nanomaterials with antimicrobial properties
'Intelligent'& 'Smart' packaging	• Packaging incorporating nanosensors to monitor condition of the food

Examples





Concerns

• Potential risk due to migration of ENPs into food and drinks

Food Contact Materials

- anti-microbial coatings (e.g. **nano-Ag**, nano-MgO, nano-ZnO, release-systems)
- improved mechanical and technical properties (e.g. nano-clay, nano-titanium nitride)
- improved barrier properties for gas and moisture (e.g. nano-clay)

FresherLonger Miracle Food Storage,
The Sharper Image (USA)

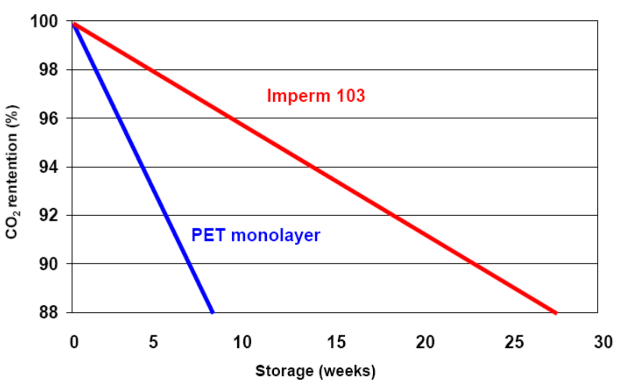
Nano Silver Spray,
Nanogist Co. Ltd. (South Korea)

Anti-bacterial Kitchen Utensils,
Nano Care Technology Ltd. (Hong Kong)

Baby Milk Bottles with Nano-Silver-Soother,
Baby Dream Co. Ltd. (South Korea)

Food Packaging

- **composite of polyamide (nylon) + nano-clay**
  - used for: bottles (multi-layer), wraps, films, containers
  - trade names: Imperm® (Nanocor® Inc., USA)), AegisTM NC (Honeywell Specialty Polymers, USA)
  - reduced entrance of oxygen (80%) and minimized loss of carbon dioxide
  - lighter and stronger
  - used in plastic beer bottles, films and multilayer bottles, could replace EVOH layer in ketchup bottles



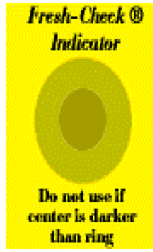
Nanotechnology Applications for ‘Smart’ Packaging

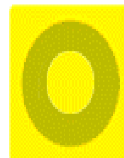
Nanotechnology derived intelligent packaging

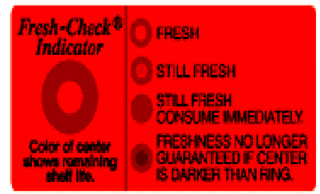
- nanoparticle based intelligent inks
- reactive nanolayers
- analyte recognition at nanoscale

Safety requirements

- non-toxic & compatible with legislation
- reliability of products
- waste issues







Temperature

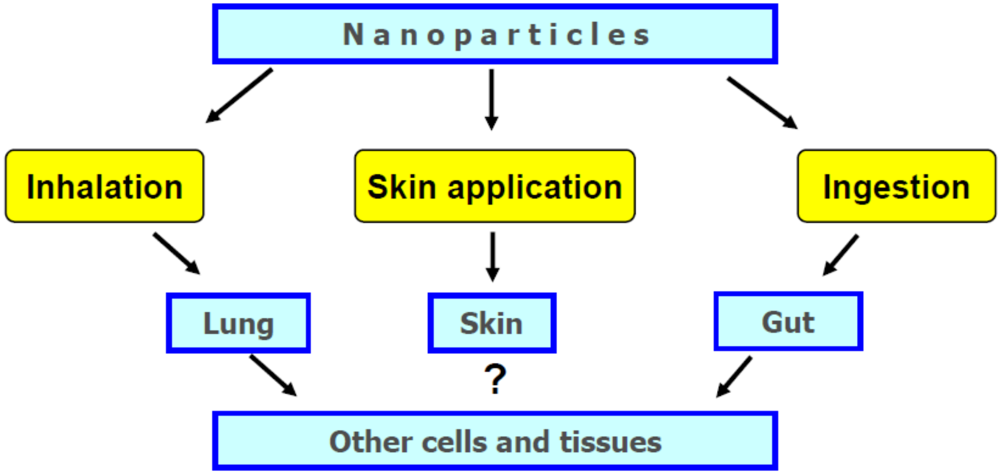
Pathogens

Freshness

Integrity

Humidity

Consumer Health Concerns



- Properties of nanoparticles may differ widely from conventional forms
- Growing scientific evidence indicates that:

  free nanoparticles can cross cellular barriers, and may reach those targets in the body where larger equivalents could have not reached

  exposure to some ENPs can increase production of oxyradicals that may lead to oxidative damage and inflammatory reactions

The published materials are intended for students of the University of Chemistry and Technology, Prague as a study material. Some text and image data contained herein are taken from public sources. In the case of insufficient quotations, the author's intention was not to intentionally infringe the possible author(s) rights to the original work.

If you have any reservations, please contact the author(s) of the specific teaching material in order to remedy the situation.

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

13. Substances regulating sensory quality – properties and use

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Substances regulating odour and taste

- Substances used for food flavouring are the most comprehensive group of additives.

- Main groups:
  - Flavourings
  - Sweeteners
  - Acidulants and acidity regulators
  - Bitter substances and stimulants
  - Flavour enhancers

Flavourings - No E number

- Substances that affect olfactory and gustatory receptors and induce human perception of smell and taste
- They are used to give food taste and/or odour that would otherwise be absent or is not present in a characteristic intensity
- Flavor has a profound influence on the consumption of food
- More than **1500 substances** are used as *food flavorings*. The majority are of natural origin or are nature-identical
- They are not substances which exclusively have sweet, sour, bitter or salty tastes.

Flavourings - legislation

- EU legislation defines different types of flavourings:
  - **Natural flavourings** – derived from natural materials using physical, biotechnological and other proceedures
  - **Natural identical** – obtained by synthesis, but they are identical to substances present in natural materials
  - **Artificial flavouring substances** – obtained by synthesis but are not identical to natural flavouring substances
- Only a few synthetic substances have been approved as food flavoring.
- Examples are ethylvanillin, ethylmaltol, and anisylacetone

Classes	Examples	Use	Origin	Functions
Natural	Sugar Salt Spices Herbs	Jam, tinned beans, cereals. Cheese, butter, convenience foods Meat products, sauces, stock cubes	Cane, beet, fruit Sodium chloride Rock or sea Root, seeds and leaves of plants	• To add flavour to food • To replace flavour lost in processing. • To enhance food flavour
Artificial	Ethyl acetate Amyl acetate Benzaldehyde Maltol	Rum flavour Pear flavour Cherry flavour Fresh baked smell	Chemical rxn. heating acetic acid and ethyl alcohol Tree Bark	
Flavour Enhancers E600-699	Monosodium Glutamate E621	Chinese food, soup, sauces, stock cubes	Glutamic acid an amino acid	

Sweeteners E 900 – E 999

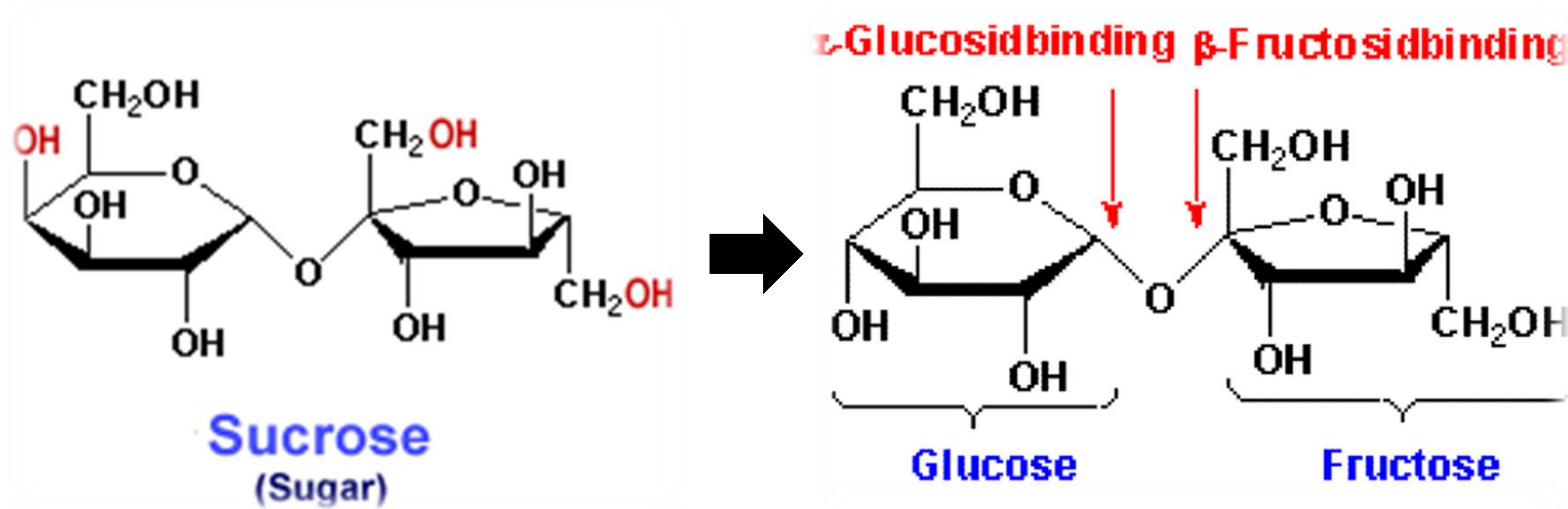
- Most important flavouring substance
- Source of energy
- Possibilty health problems
- Sugar free sweets and drinks all contain sweeteners

Sweeteners - classification

- **According to their origin**:
  - **Natural** (e.g. thaumatin)
  - **Natural-identical** – include synthetic substances identical to natural (sugar alkohols) or modified natural substances (neohesperidin)
  - **Synthetic** (saccharin)
- **Nutritional point of view**:
  - **Nutritional** (sugar alcohol)
  - **Non-nutritional** (virtually all other natural, modified natural and synthetic substances)

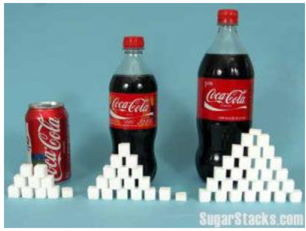
Nutritional sweeteners

- Nutritive sweeteners metabolize to produce calories
  - Examples are **sugar (sucrose), brown sugar, maple syrup, molasses, and honey.**
  - Sorbitol (taste ½ as sweet as sucrose, diabetics use this sugar)
  - Sorbitol absorbs more slowly from the intestinal tract than sucrose does, so the blood sugar level may not rise as high

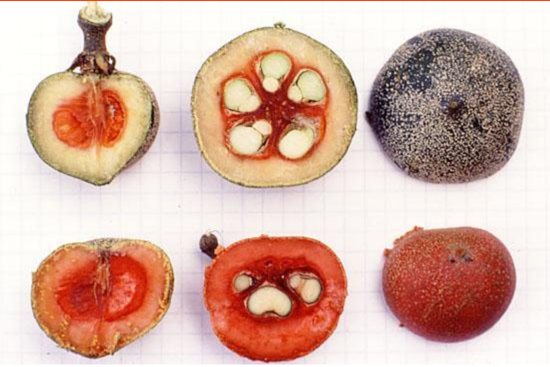


Natural sweeteners

- Naturally occurring sweet substances are almost all:
  - **monosacharides** – mainly glucose and fructose
  - **disaccharides** – sucrose and lactose
  - **sugar alcohols (glycitols)** – D-glucitol, D-mannitol
  - **other compounds**
- With the exception of sugar alcohols, mono- and disaccharides show cariogenic properties and dietary intake is also associated with obesity and many other diseases



Natural sweeteners



▪ Nutritional sweetners

Natural nutritional sweeteners are proteins, if they are used, they are not significant sources of energy

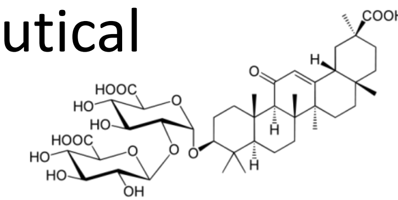
- **Brazzein** – composed of 54 amino acids, occurs in sweet fruits of the plant Pentadiplandra brazzeana
- **Monelin** – extracted from the fruit Dioscoreophyllum volkensii – no importance as a food additive
- **Thaumatin (thalin)** - extracted from the fruit of the plant Thaumatococcus danielli. Used in food and drinks in combination with other sweeteners.

UCT PRAGUE

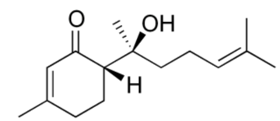
Natural sweeteners

▪ Non-nutritional sweeteners

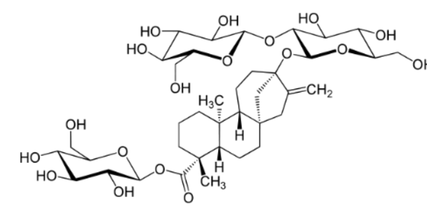
- **Glycyrrhizin** – extract from rhizome of liquorice, used to sweeten and flavour some candies, pharmaceutical preparations and tobacco products



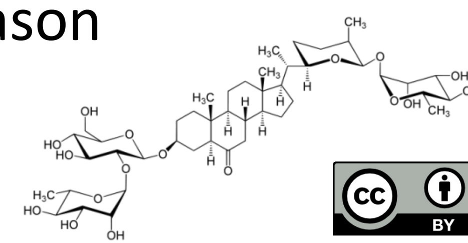
- **Hernandulcin** – limited use due to slightly bitter taste and minty after – taste



- **Stevioside (E960)** – from leaves of stevia, use in many types of food and beverages



- **Osladin** – no application – toxicological reason



Relative Sweetness of Simple Sugars

Sweetner	Degree of Sweetness
Sucrose	1
Lactose	0.4
Maltose	0.5
Galactose	0.6
D-Glucose	0.7
D-Fructose	1.1
D-Xylose	0.7
L- Tagatose	1.0
Sorbitol	0.5

Leavorotatory Hexose

Natural sweeteners

Sweetner	Degree of Sweetness
Sucrose	1X
Corn sweeteners made by glucoamylase and glucoisomerase action on corn starch (high fructose 55-80 %)	1.2X
Plant glycosides	
Phyllodulcin (Japan)	20X
Glycyrrhizin (Licorice roots)	50X
Stevia (Stevia Leaves)	200X
Lo-Han fruit	400X
Serendipity berries (Monellin)	2500X
Large Polypeptide “Talin”	2500X

Artificial non-nutritional sweeteners

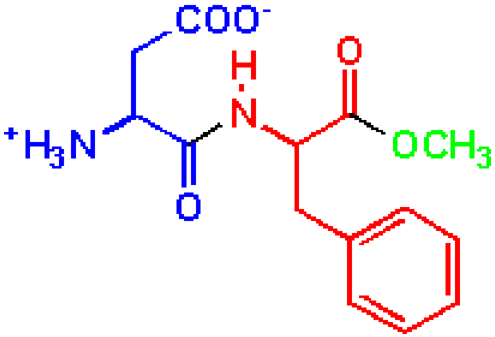
- Non-native sugars are also called artificial sweeteners. They have no calories but still taste sweet.
  - **Acesulfame K**– 200 times sweeter than sugar. Use in candies, baked goods, frozen desserts, and beverages
  - **Aspartame** – 200 times sweeter than sugar, supplies no calories and leaves no aftertaste. Cannot be used in baked goods or cooked products, it losses it's sweeteners , which is why many diet sodas have a use-by date
  - **Neotame** – wide range of products – beverages, desserts, candy, ice creams, bakery goods and many others
  - **Sucralose** – made from sugar but is 600 times sweeter. (produces no calories)
  - **Saccharin** – made from petroleum products, saccharin is 300 times as sweet as sucrose. If used in great amount, it leaves a bitter taste.
  - Other – Alitame, cyclamates, dihydrochalcones, dulcin,

Relative Sweetness of Synthetic Sweeteners

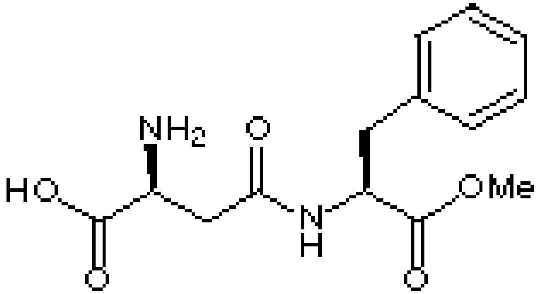
Sweetner	Degree of Sweetness
Sucrose	1
Aspartylphenyalanine methyl ester *(Aspartame, Neotame, Equal)*	100 – 200
Sodium Saccharin *(Sweet and Low)*	200 – 700
Sodium cyclohexylsulfamate *(Cyclamate)*	30 – 80
Sucralose *(Splenda)*	700-1000
Acesulfame K or Ace-K *(Sunett or Sweet One)*	200-300
Naringin dihydrochalcon	300

Popular sweeteners

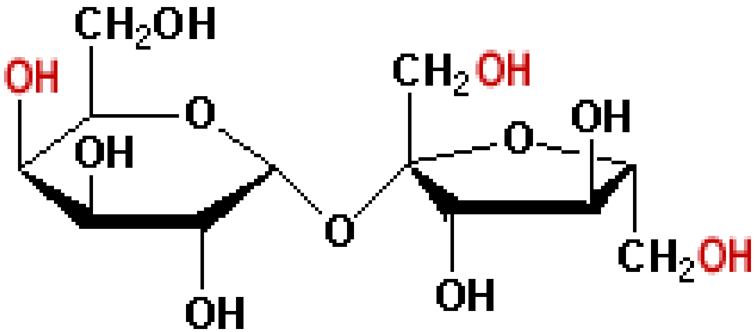
L-aspartyl-L-phenylalanine methyl ester



Aspartyl-phenylalanine methyl ester

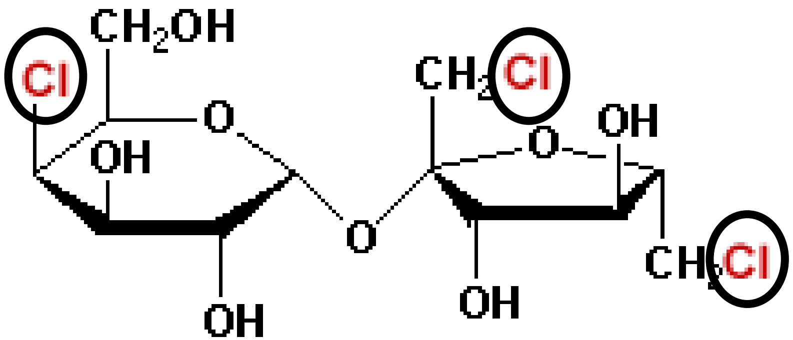


Aspartame



Sucrose

(Sugar)



Sucralose

(Splenda)

Concerns about synthetic sweeteners

Saccharin	Renal tumor in animals
Aspartame and Neotame ***(Equal)***	Neurotoxicity of phenylalanine with high intake. People with phenylketoneurea (PKU) at high risk.
Acesulfame K ***(Sunett or Sweet One)***	Increases insulin (hypoglycemic effects); not exhibit mutagenic or other toxic effects. ADI – 15 mg/kg bw
Stevia ***(Stevia Plant Extract)***	Bitter after taste; used in combination with other sweeteners, no toxic effects. ADI – 4 mg/kg
Sucralose ***(Splenda)***	Some breakdown seen in digestive track. No known toxic effects. ADI – 10 mg/kg

Conclusion: Use in moderation

Class	Examples	Use	Origin	Functions
Natural	Fructose Sucrose Glucose syrup	Tinned peas Biscuits, sweets, tinned fruit Tinned fruit, jelly	Fruit Sugar beet & sugar cane Fruit & honey	To sweeten food
Artificial	Aspartame E951 "*Nutrasweet, Canderel*" Saccharine E954 '*Hermesetes*'	Diet drinks Sweetener Diet drinks Sweetener	Dipeptide *(aspartic acid+ phenyalanine)* Coal tar	Used in low calorie / diabetic food & drinks
Bulk Sweetners	Sorbitol Mannitol E965	Diabetic food, sugar free food Sugar free gum, ice cream	Lichens Lichens	Sorbitol used in diabetic food as it does not need insulin

Acidulants and acidity regulators

- Inorganic and organic acids generally identical to those that occure naturally in foods
- Some acids:
  - **Exhibit antimicrobial effects** (simultaneously used as preservatives – acetic acid (E260), propionic acid (E 280)….
  - **Have significant organoleptic properties** (taste and smell) – acetic acid, succinic acid, fumaric acid, adipic acid, lactic acid, citric acid, malic acid
  - **Act as colour stabiliser** – ascorbic acid (meat products), citric acid (fruit products)
  - **Act as sequestrant and synergists of antioxidants** – citric acid, tartaric acid, malic acid, ascorbic acid, phosphoric acid

Acidulants and acidity regulators

- **Are substances that modify the texture** – citric acid allows the formation of some pectin gels, and Inhibits the formation of crystals in confectionery
- **Suppress the formation of hazes**, such as lactic acid in brine of fermented olives
- **Agents that hydrolyse proteins** – hydrochloric acid - production of acidic protein hydrolysates
- **Acidifying agents** – produce acids by hydrolysis or during heating – sodium, potassium, ammonium carbonates – sparkling beverages
- **Acidity regulators or pH regulators** – maintain the acidity and alkalinity of foods – di – ,tri-, polyphosphates, sodium carbonate, sodium hydroxide

Acidulants and acidity regulators

- Legislation:
  - May be used in food production only in the amount necessary to achieve the desired effect
    - Phosphoric acid – soft drinks – 700 mg/l
    - Phosphates – soft fresh cheese – 2000 mg/kg
    - Lactide metatartaric acid – wines – 100 mg/l
- Health assessment:
  - Natural food constituents
  - Adipic acid – affect growth of animals (ADI – 5 mg/kg bw)
  - Fumaric acid, malic acid, tartaric acid – acidosis in infants, vomiting, dehydration – not recommended to use in infant food

Bitter substances and stimulants

- Large number of organic and inorganic compounds have bitter taste
- Derived from plants – hops, wormwood, herbs
- None of these compounds have E number
- Caffeine, quinine, octaacetylsaccharose, …..
- Caffeine and quinine – used directly or as component of flavourings
- Beverages that contain caffeine concentration higher than 150 mg/l – labelled “**High caffeine content**“

Flavour enhancers

- *Flavor enhancers* intensify or modify the flavor of food.
- The most widely used flavor enhancer is salt (sodium chloride, NaCl).
- It is also a preservative and a nutrient.
- Generally, it is primarily regarded as a food additive.
- A well-known toxic effect of NaCl is high blood pressure.

Flavour enhancers

- They have no taste of their own.
- such as monosodium glutamate (MSG) and various nucleotides (purine 5’-nucleotides).
- These substances are present in Japanese seaweed (*Laminaria japonica,* traditionally used for seasoning), mushrooms, tomatoes, peas, meat, and cheese.
- They are often used in soups, sauces and oriental food.
- Umami – savory taste, which is one of the five basic tastes (salty, sour, sweet and bitter)

Flavour enhancers

- **No known adverse effects of flavor enhancers have been reported**, except for the case of **MSG** (monosodium glutamate).
- It is a synthetic product.
- MSG is an excitatory neurotransmitter.
- Humans have been found to be sensitive to food to which MSG has been added as a flavor enhancer.
- The symptoms, known as **"Chinese restaurant syndrome,"** include loss of feeling, general weakness, and heart palpitations.

Colours

(a)

(b)

Would you like this soft drink if no artificial flavouring and colouring had been added to it?

(a) The ‘normal’ look of the soft drink.

(b) What the soft drink would look like if no artificial colouring had been added.

Colours

Why are food colourings used?

Food colourings are dyes. They are added to food for the following purposes:

- To give food an attractive colour, so as to make it more appetizing and more saleable.
- To restore the original colour which may be changed or lost during food processing or storage.
- To ensure colour consistency.

History of color additives

- Food once was colored only with natural dyes
- Beets, peppers, grape skins, saffron, and even the brilliantly scarlet cochineal insects
- By the 19th century, colors derived from minerals came into use with sometimes serious health problem
- Lead chromate and copper sulfate began to be used to tint candy and pickles
- Arsenic and other poisonous impurities were added when mixing new color additives
- Dyes and pigments made from coal tar and petroleum derivatives

Colour types

- **There are two types of colour additives**
  - **Natural pigments**
  - **Synthetic dyes**

Natural food colours

- Natural colour can be obtained from natural sources such as leafy vegetables, grasses, fruit skins, roots and seeds from plants

- They can also be made from animals. Cochineal, or carminic acid, is a red colour that is obtained from the bodies of certain scale insects. These feed on cactus leaves and their bodies are commercially harvested in Africa, Spain and central America. Their bodies are dried and crushed to extract the red coloring.

Natural food colours

- **Anthocyanins**
  Anthocyanins are water soluble pigments responsible for the attractive red, purple and blue colours of many flowers, fruits and vegetables
  Used in drinks, jams and sugar confectionery.

- **Beetroot**
  The colour of beetroot is water soluble and has limited stability when exposed to light, heat and oxygen. It is particularly suited to frozen, dried and short shelf-life products, such as ice creams and yoghurt.

- **Cochineal**
  The water soluble pigment carminic acid (carmine) is derived from the female cochineal insect. Uses include alcoholic beverages and processed meat products.

- **Chlorophyll**
  Chlorophyll is the most widely distributed natural plant pigment, present in all green leafy vegetables. It is a green, oil soluble colour. Chlorophyllins are water soluble and relatively stable when exposed to heat and light. Uses include sugar confectionery and dairy products.

Natural food colours

- **Carotenoids**
  Over 400 different carotenoids have been identified in red/orange/yellow fruits, vegetables and plants. Nature produces carotenoids at the rate of 1000 million tons per year. Most are oil soluble, heat stable and are not affected by pH change. The uses of carotenoids include margarine, dairy products and soft drinks.

- **Curcumin**
  Turmeric is a well known spice, used widely in cookery. Its pigment, curcumin, is oil soluble and tends to fade in light, but has good heat stability. It gives a lemon yellow shade in food systems. Its applications include curry, soups and confectionery.

- **Riboflavin**
  Riboflavin, Vitamin B2, is used for fortification and colouring. It is water soluble, heat stable and is used in dairy products, cereals and dessert mixes

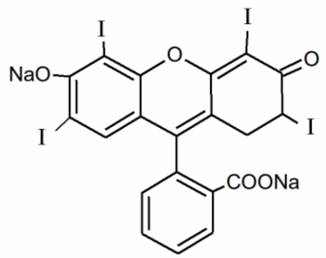
- **Carbon and metals**
  Vegetable carbon black is a heat and light stabile pigment, used primarily in sugar confectionery. Metals, such as gold, silver and aluminium are used for surface colouring, mainly in confectionary.

Synthetic food colour

- Synthetic colours are colours that are made in a factory and don’t occur in nature. They have been carefully tested to make sure that they are safe
- They have more intense colour than natural dyes, are more stable and do not introduce any characteristic odours and tastes into coloured food
- The good thing about Synthetic colors, is that they are usually water soluble and can be used in foods without any further processing
- Classes: azo dyes, pyrazolone dyes, nitro dyes, xanthene dyes, anthraquinone dyes, quinoline dyes and indigo dyes….

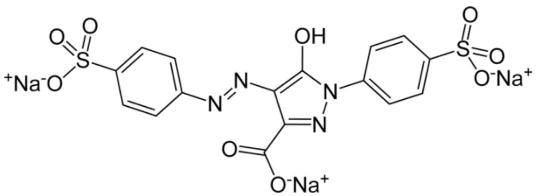
Classification of synthetic food colour

- **Physico-chemical properties:**



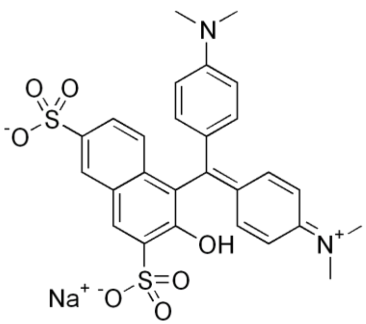
Erythrosine

- Sour dyes
- Alkaline dyes
- Neutral dyes



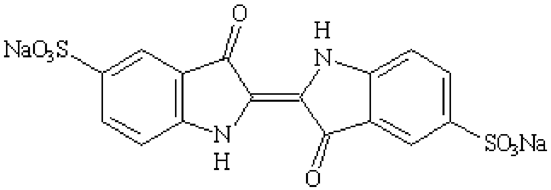
Tartrazine

- **According to their solubility:**



Green S

- Lyophylic dyes
- Lipophylic dyes



Indigotine

Synthetic food colours

- These colours are also known as food colors,colourings, food dyes, food additives, food lakes & food blends worldwide

Product/Colour Shade	C.I.No.	F.D. & C No	E.No.
QUINOLINE YELLOW	47005	-	E 104
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
TARTRAZINE	19140	Yellow 5	E 102
(Tri sodium salt of 5-hydroxy (1-p-sulphophenyl 4- (p-sulphophenylazo) pyrazol -3- carboxylicacid			
SUNSET YELLOW FCF	15985	Yellow 6	E 110
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
ERYTHROSINE	45430	Red 3	E 127
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
PONCEAU 4R	16255	-	E 124
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
ALLURA RED	16035	Red 40	E 129
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
CARMOISINEH	14720	-	E 122
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
AMARANT	16185	Red 2	E 123
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
CHOCOLATE BROWN HT	20285	-	E 155
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
BRILLIANT BLUE FCF	42090	Blue 1	E 133
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
PATENT BLUE V	42015	-	E 131
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
INDIGO CARMINE	73015	Blue 2	E 132
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
BLACK PN	28440	-	E 151
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
FAST RED E	16045	-	-
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
GREEN S	44090	-	E 142
(Di sodium salt of disulfonates of 2-(2quinolyl) - 1, 3 indandione.)			
RED 2G	18050	-	E 128
(Di sodium salt of 8-acetamido-1-hydroxy-2- phenylazonaphthalene-3,6 disulfonate)			

Colours

A growing number of natural food dyes are being commercially produced, partly due to consumer concerns surrounding synthetic dyes. Some examples include:

- **Caramel coloring** (E150), made from caramelized sugar
- **Annatto** (E160b), a reddish-orange dye made from the seed of the achiote.
- **Chlorophyllin** (E140), a green dye made from chlorella algae
- **Cochineal** (E120), a red dye derived from the cochineal insect, *Dactylopius coccus*
- **Betanin** (E162) extracted from beets
- **Turmeric** (curcuminoids, E100)
- **Saffron extract** (carotenoids, E160a)
- **Paprika extract** (E160c)
- **Lycopene** (E160d)
- **Elderberry juice**
- **Pandan** (*Pandanus amaryllifolius*), a green food coloring
- **Butterfly pea** (*Clitoria ternatea*), a blue food dye

Colours – health assessment

- They should not represent any health risk if used up to the maximum amount allowed
- Some dyes can cause health problems
  - Azo dyes – tartrazine, sunset yellow, azorubine, erythrosine
    - hyperactivity in children
    - sensitivity to sunlight
    - possible mutagenicity

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

14. Substances used for preservation - properties and use

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

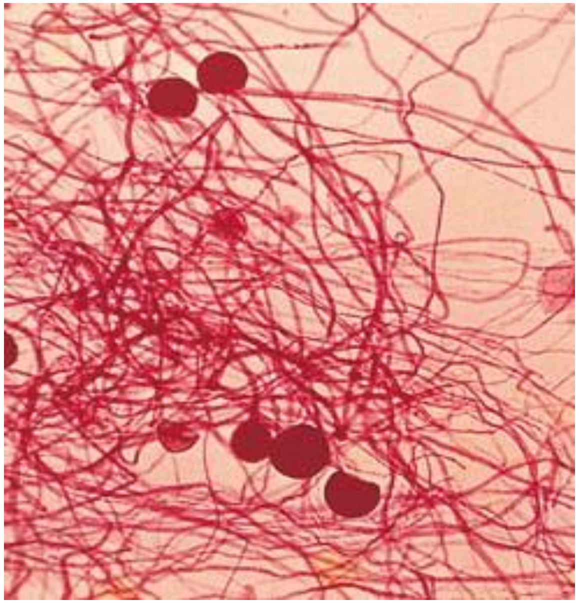
MINISTRY OF EDUCATION, YOUTH AND SPORTS

Preservatives E 200 – E 299

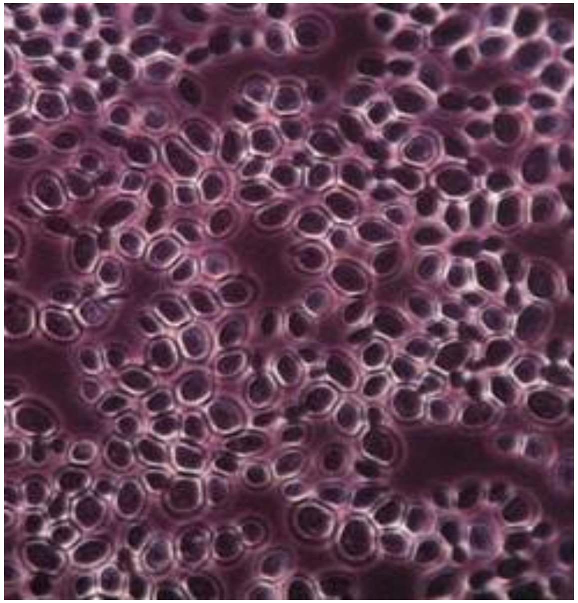
Preservatives are additives that inhibit the growth of bacteria, yeasts, and molds in foods

Three main types of micro-organisms

Bacteria



Mould



Yeast

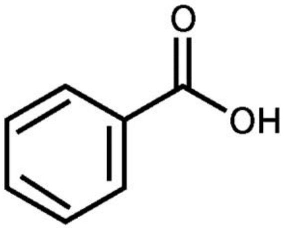
Preservatives

- Preservatives or antimicrobial agents play an important role in today's supply of safe and stable foods
- Increasing demand for convenience foods and reasonably long shelf life of processed foods make the use of chemical food preservatives imperative
- Some of the **commonly used preservatives** – such as **sulfites, nitrate, and salt** – have been used for centuries in **processed meats and wine**
- Common antimicrobial food additives are benzoic acid and benzoates, sorbic acid and sorbates, short-chain organic acids (acetic acid, lactic acid, propionic acid, citric acid), parabens (alkyl esters of *p*-hydroxybenzoic acid), sulfite, and nitrite.

Preservatives

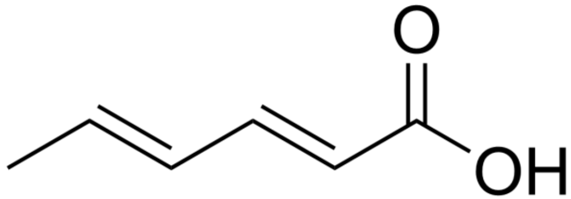
- The choice of antimicrobial agent has to be based on the knowledge of the
  - **antimicrobial spectrum** of the preservative
  - **chemical and physical properties** of both food and preservative
  - **conditions of storage and handling**,
  - assurance of a high initial quality of the food to be preserved
- They are **easily excreted and metabolized** by both animal and man.
- An exception should be made for one of them, namely **nitrite**. The intake of nitrite can lead to the **formation of nitrosamines**, which are **well-known carcinogens**

Benzoic Acid



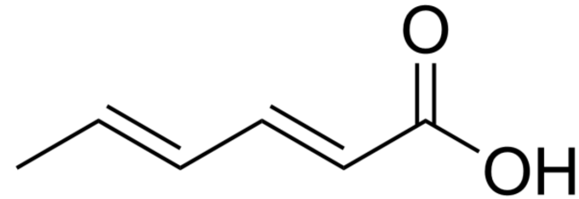
- Occurs **naturally** in many types of **berries, plums, prunes, and some spices**
- As an additive, it is used as benzoic acid or as benzoate
- The latter is used more often because benzoic acid is sparsely soluble in water, and sodium benzoate is more soluble
- The undissociated form on benzoic acid is the most effective antimicrobial agent
  - pK_a of 4.2; optimum pH range is from 2.5 to 4.0
- This makes it an effective antimicrobial in **high-acid foods, fruit drinks, cider, carbonated beverages, and pickles**
- It is also used in **margarines, salad dressings, soy sauce, and jams**

Sorbic Acid 1/2



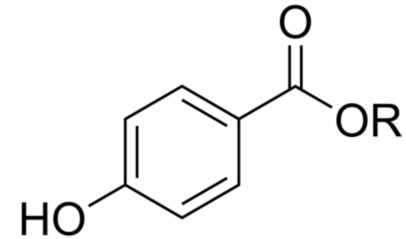
- Sorbic acid is a straight-chain, *trans-trans* unsaturated fatty acid, 2,4-hexadienoic acid
- It has low solubility in water at room temp
- The salts, sodium or potassium, are more soluble in water
- Sorbates are stable in the dry form; the are **unstable in aqueous solutions** because they decompose through oxidation
- The rate of oxidation is increased at low pH, by increased temp, and by light exposure
- Sorbic acid and other sorbates are **effective against yeasts and molds**
- Sorbates inhibit yeast growth in a variety of foods including **wine, fruit juice, dried fruit, cottage cheese, meat, and fish products**

Sorbic Acid 2/2



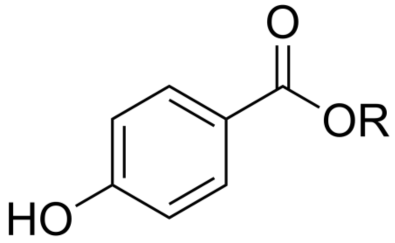
- Sorbates are most effective in products of low pH, including salad dressings, tomato products, carbonated beverages, and a variety of other foods
- Sorbates are generally used in sweetened wines or wines that contain residual sugars to prevent refermentation
- At the levels generally used, sorbates do not affect food flavor. However when used at higher levels, they may be detected by some people as an unpleasant flavor
- Sorbates can be degraded by certain microorganisms to produce off-flavors

Parabens 1/2



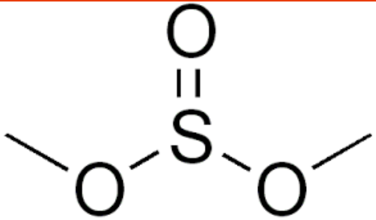
- Parabens are alkyl esters of p-hydroxybenzoic acid
- The alkyl groups may be one of the following: methyl, ethyl, propyl, butyl, or heptyl
- Parabens are colourless, tasteless, and odorless (except the methyl paraben)
- They are nonvolatile and nonhygroscopic
- Their solubility in water depends on the nature of the alkyl group
  - The longer the alkyl chain length, the lower the solubility
- They differ from benzoic acid in that they have antimicrobial activity in both acid and alkaline pH regions

Parabens 2/2



- The antimicrobial activity in parabens is proportional to the chain length of the alkyl group
- Parabens are more **active against molds and yeast** than against bacteria, and more active against gram-positive than gram-negative bacteria
- They are used in **fruitcakes, pastries, and fruit fillings**
- Methyl and propyl parabens can be used in soft drinks
- Combinations of several parabens are often used in applications such as **fish products, flavor extracts, and salad dressing**

Sulfites 1/2



- Sulfur dioxide and sulfites have long been used as preservatives
- Serving both as antimicrobial substance and as antioxidant
- Sulfur dioxide is a gas but under pressure of 3.4 atm it is liquid and can be injected directly in liquids
- Instead of sulfur dioxide solutions, a number of sulfites can be used
- The most widely used of these sulfites is potassium metabisulfite
- The bisulfite ion (HSO3-) can react with aldehydes, dextrins, pectic substances, proteins, ketones, and certain sugars to form addition compounds
- The addition compounds are known as bound sulfur dioxide

Sulfites 2/2

- SO_2 are used in: **Wine, meat products, Dried fruits, dried vegetables**
- Sulfites in wine serve a dual purpose
  - (1) antiseptic or bacteriostatic
  - (2) antioxidant

- The use of SO_2 is not permitted in foods that contain significant quantities of thiamine, because this vitamin is destroyed by SO_2
- The acceptable daily intake (ADI) is set at 1.5 mg/kg body weight
- Because SO_2 is volatile and easily lost to the atmosphere, the residual levels may be much lower than the amounts originally applied

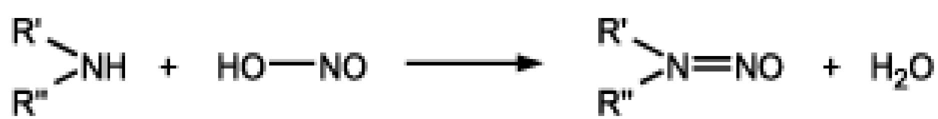
Nitrates & Nitrites 1/3

- Curing salts, which produce the characteristic color and flavor of products such as bacon and ham, have been used throughout history
- Curing salts have traditionally contained nitrate and nitrite
- The discovery that nitrite was the active compound was made in about 1890
- Currently, nitrite is not considered to be an essential component in curing mixtures
- It is sometimes suggested that nitrate may be transformed into nitrite, thus forming a reservoir for the production of nitrite
- Both nitrates and nitrites are thought to have antimicrobial action

$$\underset{\text{Nitrate}}{NO_3^-} \xrightarrow{\textit{Nitrate Reductase}} \underset{\text{Nitrite}}{NO_2^-}$$

Nitrates & Nitrites 2/3

- Nitrate is used in the production of Gouda cheese to prevent gas formation by butyric acid-forming bacteria
- The action of nitrate in meat curing is considered to involve inhibition of toxin formation by *Clostridium botulinum*, an important factor in establishing safety of cure meat products
- Major concern about the use of nitrite was generated by the realization that secondary amines in foods may react to form nitrosamines
- The **nitrosamines** are powerful **carcinogens**, and they may be **mutagenic**



sek. Amin

Nitrosamin

Nitrates & Nitrites 3/3

- The ADI of nitrite has been set at 60 mg per person per day
- It is estimated that the daily intake per person in Canada is about 10 mg
- The nitrate-nitrite intake from natural sources is much higher than that from processed foods
- It is estimated that the nitrate intake from
  - 100 g of processed meat might be 50 mg
  - and from 100 g of high-nitrate spinach, 200 mg

Sodium Chloride

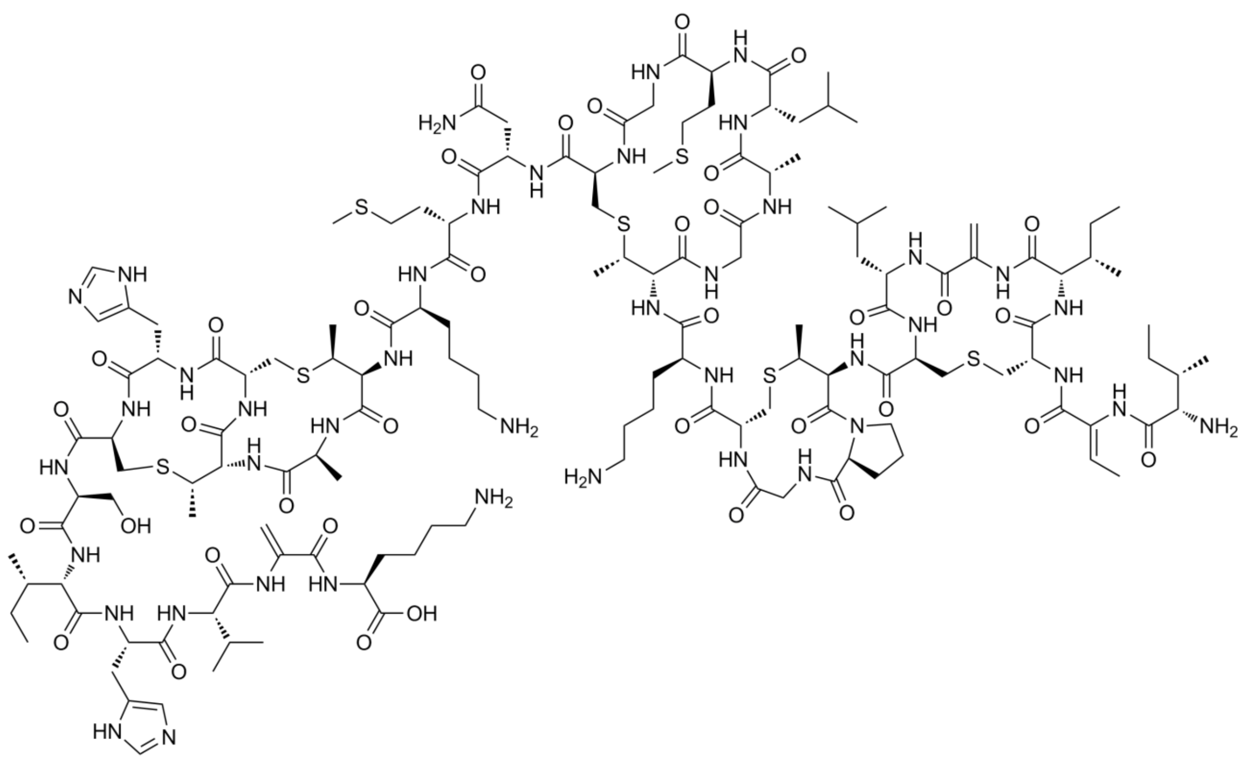
- Sodium chloride has been used for centuries to prevent spoilage of foods
- **Fish, meats and vegetables** has been preserved with salt
- Today, salt is used mainly in combination with other processing methods
- The antimicrobial activity of salt is related to its ability to reduce the water activity (a_w) thereby influencing microbial growth
- Salt has the following characteristics:
  - It produces an osmotic effect, limits oxygen solubility, changes pH
  - Sodium and chloride ions are toxic, salt contributes to loss of magnesium ions
- The use of sodium chloride is self-limiting because of its effect on taste

Bacteriocins – Nisin 1/2

- Nisin is an antimicrobial polypeptide produced by some strains of *Lactococcus lactis*
- Nisin-like substances are widely produced by lactic acid bacteria
- These inhibitory substances are known as bacteriocins
- Nisin has been called an antibiotic, but this term is avoided because nisin is not used for therapeutic purposes in humans or animals
- Nisin-producing organisms occur naturally in milk
- Nisin can be used as a processing aid against gram-positive organisms

Bacteriocins – Nisin 2/2

- It has been used effectively in preservation of processed cheese
- It is also used in the heat treatment of nonacid foods and in extending the shelf life of sterilized milk



Classes	Examples	Use	Origins	Functions
Natural	Sugar Salt Vinegar Alcohol Smoke	Jam, sweets Bacon, pickles Pickles, chutney Fruit, cake Fish, meat, cheese	Beet/cane Rock, sea Fermentation Fermentation Burning wood	• Prevents spoilage by preventing microbial growth. • Extend shelf life. • Prevents food poisoning. • Reduces waste. • Greater variety foods available
Artifical	Sulphur dioxide (E220) Sorbic acid (E200) Diphenyl	Sausages, fruit juice, dried fruit & veg. Soft fruit, fruit yoghurt, processed cheese. Citrus fruit, bananas	Made in labs	
Not permitted in baby foods				

UCT PRAGUE

Antioxidants E 300 – E 399

- Antioxidants are used to protect oils, fats, and shortening against oxidative rancidity and to prevent the formation of toxic degradation of products and polymers.
- Many foods may undergo oxidation, but particularly those containing fats are susceptible to changes in color, odor, taste, and nutritional value.
- Unsaturated fatty acids are readily peroxidized in the presence of molecular oxygen.
- The peroxidation products may induce toxic effects.
- Also, in biological systems peroxidation of lipids may have severe adverse consequences.

Antioxidants – occurrence and importance

- Organic compounds
- Natural (tea, fruit, wine) x synthetic
- Defense against oxidation reactions
- They lower the activity of the oxygen radicals
  - Prevent their occurrence
  - less reactive or non-reactive forms
- In food
  - avoidance of oxidation damage
  - maintaining the integrity of cell structures and macromolecules from free radical damage
  - prolonging of shelf life

Oxidation in food

- Destructive process
- Loss of nutritional value of food
- Changes in chemical composition
- The formation of undesirable aromatic substances
- Unwanted color changes
- Potential emergence of toxic substances

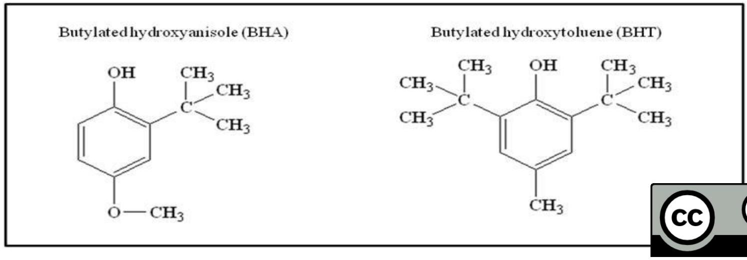
Antioxidants - classification

- Food antioxidants in the broadest sense are all of the substances that have some effect on preventing or retarding oxidative deterioration in foods
- They can be classified into a number of groups:
- ***i) Primary antioxidants -*** Terminate free radical chains and function as electron donors

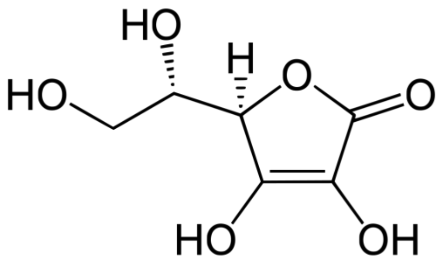
ArOH + R-O-O• → ArO• + R-O-OH

R-O-O• + ArO• → R-O-Ar + O_2

- They include **phenolic antioxidants, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) tertiary butyl hydroquinone (TBHQ), propylgallate (PG) and natural synthetic tocopherols**

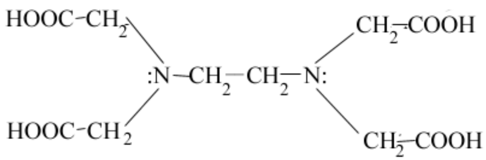


Antioxidants - classification



Vit C

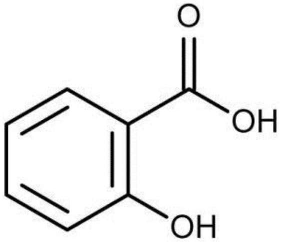
- *ii) Oxygen scavengers*
  - Can remove oxygen in a closed system
  - Most widely used compounds are **Vit C, and related substances, ascorbyl palmitate, and erythorbic acid (D-isomer of ascorbic acid)**
- *iii) Chelating agents or sequestrants*
  - They remove metallic ions, especially copper and iron, which are powerful pro-oxidants
  - Citric acid is widely used for this purpose
  - **Amino acids and ethylene diamine tetraacetic acid (EDTA) are examples of chelating agents**



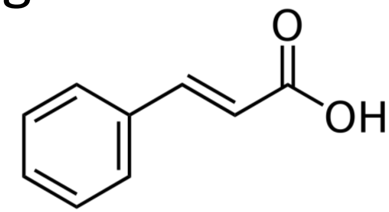
structure of EDTA

Antioxidants - classification

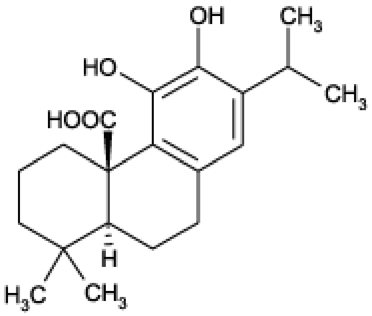
- ***Natural antioxidants***
  - Present in many spices and herbs
  - Rosemary and sage are the most potent antioxidant spices
  - The active principles in rosemary are carnosic acid and carnosol. Antioxidants from spices can be obtained as extracts or in powdered form.
  - Phenolic acids – cinnamic acid, benzoic acid, salicylic acid……
  - Curcuminoids, terpenoids and lignans



salicylic acid



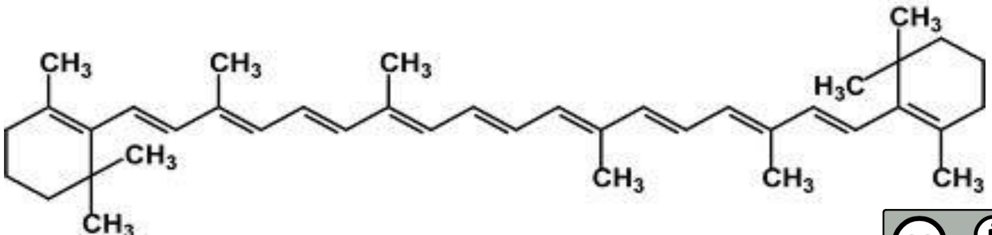
cinnamic acid



carnosic acid

Most important antioxidants in food

- Carotenoids
  - Naturally; lipophilic pigments
  - The antioxidant properties are probably due to chemical structure (the backbone of the molecule is a 40 carbon polyene chain)
  - UV protection, inhibition of the development of some types of cancer (?)
  - Important β-carotene
  - The most effective lycopene (tomatoes, 80% of the intake)
  - Isomers lutein and zeaxanthin (yellow pigments)



Most important antioxidants in food

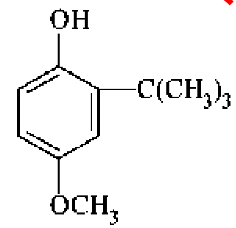
- Phenolic compounds
  - Simple phenols, hydroxybenzoic and hydroxycinnamic acid derivatives, flavonoids, stilbens, lignans and tannins

- The most important **flavonoids**
  - Edible fruits, leafy vegetables, roots, bulbs of onions, herbs, spices, legumes, tea, coffee, cocoa, chocolate and red wine

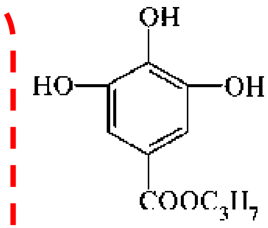
- Diet rich in flavonoids → possible protection against cardiovascular disease, neurodegenerative disorders and some types of cancer

Most important antioxidants in food

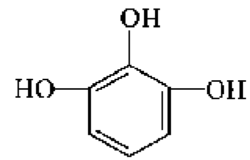
- **BHA (butylhydroxyanisol)**
  - E320
  - oils, margarines, cheeses



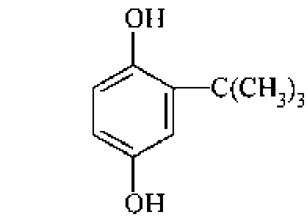
Butylated Hydroxyanisole (BHA)



Propyl Gallate (PG)

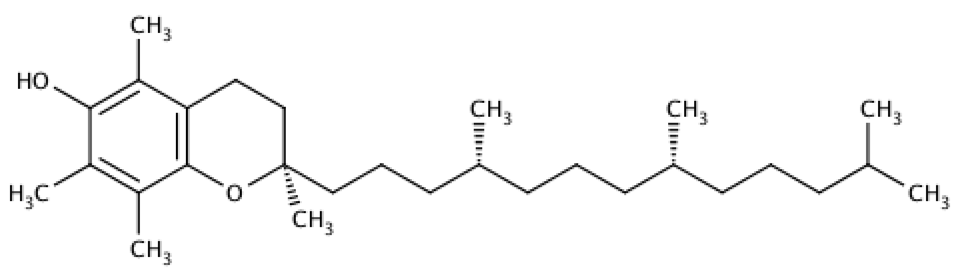


Pyrogallol (PY)



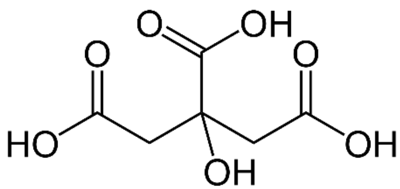
tert-Butylatedhydroquinone (TBHQ)

- **Tocopherols**
  - E306
  - oils, meat pates
  - they are obtained from soybeans and corn



Most important antioxidants in food

Citric acid



- E330
- Jams, canned fruits, biscuits, beverages, cheeses, instant sauces
- Naturally in citrus fruits
- Helps increase the antioxidant effect of other compounds
- Prevents reactions that can lead to color changes in fruit
- Possible use as a pH regulator in jams and jellies

Antioxidants

- Sometimes the antioxidant are incorporated in the packaging materials rather than in the food itself

Classes	Examples	Use	Origins	Functions
Natural	Ascorbic acid Tocopherol (E306)	Fruit drinks Vegetable oils	Fruit & veg. Nuts & seeds	Prevents oxidation where food is spoiled by reacting with oxygen
Artificial	BHA (E320) BHT (E321)	Stock cubes, cheese spread Chewing gum	Made in lab	
BHA and BHT **not permitted in baby food**				

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Food and Biochemical Technology
Department of Food Analysis and Nutrition

Practice 1: Chemical Food Safety, Definitions, Legislative Aspects

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

Students´ short presentation

- **In pairs, prepare a short presentation on a selected topic**
- **The length of the presentation will be at maximum 20 minutes**
- **Presentation outline**
- Brief introduction to the topic (properties of the compounds)
- Health risk
- Penetration into environment / food chains, or formation mechanism in food
- Occurrence in food and legislation
- Prevention options / Protection against contamination

Topics of the presentations

1	Re-evaluation of titanium dioxide (E 171) as a food additive
2	Assessment of dietary exposure to pyrrolizidine alkaloids in the European population
3	Malachite green in food
4	Testing a procedure for the identification of emerging chemical risks in the food chain
5	Pesticide residues in food and feed according to Regulation (EC) No 396/2005 (2015 data collection)
6	Aspartam
7	Review and analysis of occurrence, exposure and toxicity of cyanobacteria toxins in food
8	Evaluation of allergenic foods and food ingredients for labelling purposes
9	Pesticide risk assessment of the active substance glyphosate
10	Monitoring of veterinary medicinal product residues and other substances in live animals and animal products
11	Public health risks related to the presence of chlorate in food
12	Presence of perchlorate in food, in particular fruits and vegetables
13	Presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food
14	Acrylamide in food
15	Food contact materials

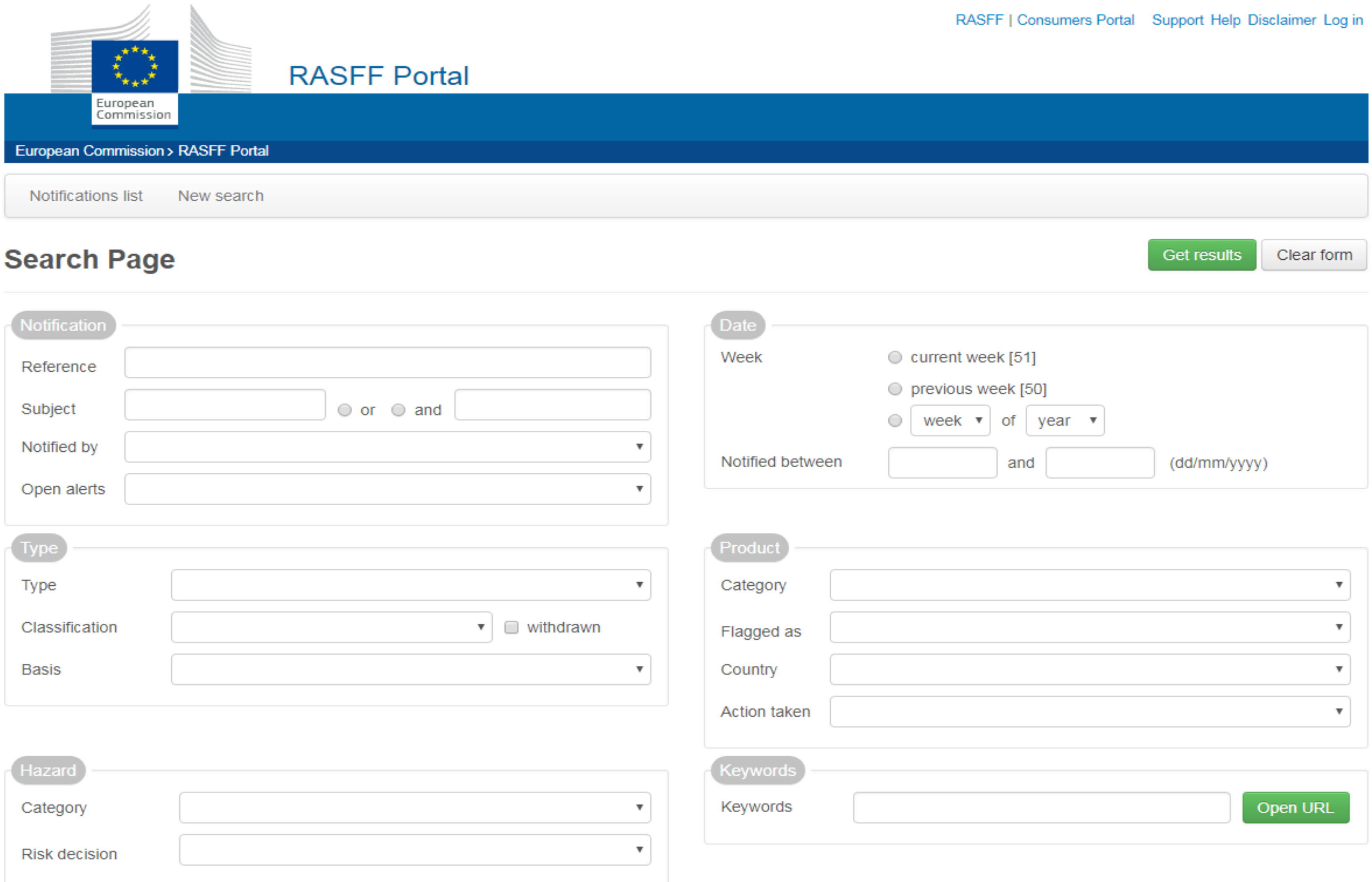
Topics of the presentations

16	Nanoparticles in food
17	Health benefits of seafood (fish and shellfish) consumption in relation to health risks associated with exposure to methylmercury
18	Dietary exposure to inorganic arsenic in the European population
19	Mineral Oil Hydrocarbons in Food
20	Endocrine active substances
21	Risks to human and animal health related to the presence of beauvericin and enniatins in food and feed
22	Ergot alkaloids in food and feed
23	Risks to animal and public health related to the presence of T-2 and HT-2 toxins in food and feed
24	Risks to animal and public health related to the presence of Alternaria toxins in feed and food
25	Risks to public health related to the presence of zearalenone in food
26	Presence of dioxins (PCDD/Fs) and dioxin-like PCBs (DL-PCBs) in commercially available foods for infants and young children
27	Update of the monitoring of levels of dioxins and PCBs in food and feed
28	Emerging and Novel Brominated Flame Retardants (BFRs) in Food
29	Brominated Flame Retardants (BFRs) in Food: Brominated Phenols and their Derivatives
30	Tetrabromobisphenol A (TBBPA) and its derivatives in food

Rapid Alert System for Food and Feed RASFF

- What is RASFF?

- Demonstration of work with RASFF portal:
- https://webgate.ec.europa.eu/rasff-window/portal/?event=SearchForm&cleanSearch=1


RASFF | Consumers Portal Support Help Disclaimer Log in
European Commission
RASFF Portal
European Commission > RASFF Portal
Notifications list
New search
Search Page
Get results
Clear form
Notification
Reference
Subject
or
and
Notified by
Open alerts
Date
Week
current week [51]
previous week [50]
week
of
year
Notified between
and
(dd/mm/yyyy)
Type
Type
Classification
withdrawn
Basis
Product
Category
Flagged as
Country
Action taken
Hazard
Category
Risk decision
Keywords
Keywords
Open URL

HACCP

- Hazard analysis and Critical Control Points - **HACCP system**

- What is HACCP?
- What is the system of critical points for?
- What the Critical Points System looks like

HACCP

- However, in accordance with the legal requirements, each system must:
- 1. Conduct Hazards Analysis
- 2. Determine Critical Control Points
- 3. Establish Critical Limits
- 4. Establish Monitoring System
- 5. Establish Corrective Action
- 6. Establish Verification Procedures
- 7. Establish Documentation

The published materials are intended for students of the University of Chemistry and Technology, Prague as a study material. Some text and image data contained herein are taken from public sources. In the case of insufficient quotations, the author's intention was not to intentionally infringe the possible author(s) rights to the original work.

If you have any reservations, please contact the author(s) of the specific teaching material in order to remedy the situation.

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

2 Overview of important groups of compounds associated with chemical food safety

1. **List three symptoms of foodborne illnesses.**

2. **List three ways that food commonly becomes contaminated.**

3. **What are the five ways to prevent foodborne illnesses?**

4. **What is the proper temperature to which meat should be cooked?**

5. **Describe two ways to prevent cross-contamination.**

6. **What is the proper temperature for your freezer?**

7. T/F: Large volumes of food should be separated in the refrigerator so that they cool more quickly.

8. What does the HACCP system stand for, and what is it?

9. Name five foods that should be thoroughly washed before being cut.

10. What are the seven HACCP principles?

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

3. Substances produced in the production of food - process contaminants

1) **Draw the structure of each process contaminant:**

Acrylamide　　　　Furan　　　　3-MCPD

2) **Which other group of substances also belongs to processing contaminants? Describe their properties.**

3) How is acrylamide formed? Describe the reaction:

4) Which foods are typical for the occurrence of the following substances and why?

Acrylamide

3-MCPD

Polycyclic aromatic hydrocarbons

5) How do these substances affect our health?

6) **Short students´ presentations:**

Presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food

Acrylamide in food

4. Natural toxic substances - the most important groups, legislative aspects

1) Which groups of compounds belong to Natural toxins? Write down the list.

2) To which group of Natural toxins do the following substances belong and where can you find them?

Contaminant	Category	Where you can find them
caffeine		
ergometrine		
solanine		
amygdalin		
glucoraphanin		
histamine		
amanitin		
tetrodotoxin		
genistein		
nicotine		
erucine		
muscarine		
isoflavones		
SECO		
quinine		

3) Short students´ presentations

Review and analysis of occurrence, exposure and toxicity of cyanobacteria toxins in food

Assessment of dietary exposure to pyrrolizidine alkaloids in the European population

Ergot alkaloids in food and feed

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

5. Mycotoxins and bacterial toxins

1) What are mycotoxins and which groups of these substances do you know?

2) To which group of mycotoxins do the following substances belong and where can you find them?

Contaminant	**Category**	**Where you can find them**
T-2 toxin		
Patulin		
Deoxynivalenol		
Aflatoxin B1		
Zearalenone		
FB1		
Aflatoxin M1		
Alternariol		
Ergotamine		
Ochratoxin A		

3) Short students´ presentations

Risks to human and animal health related to the presence of beauvericin and enniatins in food and feed

Risks to animal and public health related to the presence of T-2 and HT-2 toxin in food and feed

Risks to animal and public health related to the presence of Alternaria toxins in feed and food

Risks to public health related to the presence of zearalenone in food

6. "New" risky groups of chemical compounds, the global protection of the food chain

1) What kinds of emerging contaminants are occurring in the environment?

2) What are the sources of emerging contaminants? Where do they come from?

3) What are the environmental fate and effect of these emerging contaminants?

4) What are the pollution prevention strategies to minimize the loading of emerging contaminants into the environment?

5) What are the treatment techniques for removal of emerging contaminants in contaminated environment?

6) Short students´ presentations:

Testing a procedure for the identification of emerging chemical risks in the food chain

Risks to public health related to the presence of chlorate in food

Presence of perchlorate in food, in particular fruits and vegetables

Emerging and Novel Brominated Flame Retardants (BFRs) in Food

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

7. Characterization of properties of exogenous contaminants, penetration into food chains

1) How can pollutants be classified?

2) Which types of pollution do you know?

3) What is biomagnification?

4) Short students´ presentations:

Evaluation of allergenic foods and food ingredients for labelling purposes

Mineral Oil Hydrocarbons in Food

Endocrine active substances

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

8. Persistent organic pollutants

1) Which statement is correct and why?

a) PCBs are found mainly in foods of plant origin, where they accumulate.
b) Fish is an important dietary source of these contaminants for the population.
c) PCBs were used as dielectrics in transformers
d) PCBs are very persistent and may accumulate in human milk

What do you know about polycyclic aromatic hydrocarbons?

What do you know about brominated flame retardants?

3) Short students´ presentations:

Presence of dioxins (PCDD/Fs) and dioxin-like PCBs (DL-PCBs) in commercially available foods for infants and young children

Update of the monitoring of levels of dioxins and PCBs in food and feed

Brominated Flame Retardants (BFRs) in Food: Brominated Phenols and their Derivatives

Tetrabromobisphenol A (TBBPA) and its derivatives in food

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

9. Modern pesticides and veterinary drugs, organic products

1) What do these acronyms mean?

RASFF

ADI

WHO

NOAEL

EFSA

MRL

2) Which statement is correct and why?

a. Organochlorine pesticides are the most often used group of pesticides.
b. The control of pesticides residues in food is done via the law.
c. Pyrethroids are more hazardous to humans and environment than organochlorine pesticides.
d. Following application, the residues of modern pesticides are dropping, no residues are found at harvest time.

3) Short students´ presentations:

Pesticide residues in food and feed according to Regulation (EC) No 396/2005 (2015 data collection)

Pesticide risk assessment of the active substance glyphosate

Monitoring of veterinary medicinal product residues and other substances in live animals and animal products

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

10 Toxic metals, nitrates and radionuclides

1) To which group of contaminants do the following compounds belong? Give one most typical example where they occur.

a) furan
b) tetracyclines
c) DDT
d) methylmercury
e) carbon dioxide
f) dadzein
g) morphine
h) histamine
i) DON
j) tetrodotoxin

2) For which contaminants would you look for in the following foods? *(Write at least 3 groups)*

smoked mackerel

bread

baby food

olive oil

strawberry müesli bar

3) Short students´ presentations:

Health benefits of seafood (fish and shellfish) consumption in relation to health risks associated with exposure to methylmercury

Dietary exposure to inorganic arsenic in the European population

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

11. Food Additives - Important groups – E numbers

1) For what purpose are the following food additives used?

a) BHA
b) Monosodium glutamate
c) Nisin
d) Sucralose
e) Sulphite

2) Which groups of food additives do you know? Write down the list.

3) For what purpose are emulsifiers used?

4) Short students´ presentations:

Re-evaluation of titanium dioxide (E 171) as a food additive

Malachite green in food

Aspartame

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

12. Nanotechnologies and their use as additives in food production

1) Do you know any products where nanotechnology could be used?

2) Do you know any naturally occurring nanostructures?

3) What does “Smart“ packaging mean?

4) Short students´ presentations:

Evaluation of allergenic foods and food ingredients for labelling purposes

Food Contact Materials

Nanoparticles in Food

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

13. Substances regulating sensory quality - properties and use

1) To which group of food additives do MSG belong?

A. preservatives
B. flavour enhancers
C. flavourings
D. antioxidants
E. sweeteners

2) **Where can you find sulphites, and to which group of food additives do they belong?**

A. flavourings in beverages
B. antioxidants in oils
C. sweeteners in baked goods
D. antioxidants in wine
E. preservatives in wine

3) **Where can you find aspartame and to which group of food additives does it belong?**

A. preservatives – candies
B. preservatives – baked goods
C. sweeteners – candies
D. sweeteners – baked goods
E. colours – candies

4) **Where can you find lecithin and to which group of food additives does it belong?**

A. emulsifiers – margarines
B. colours – dairy products
C. acidity regulators - soup
D. colours – alcoholic beverages
E. flavour enhancers – soup

5) **Where can you find curcumin and to which group of food additives does it belong?**

A. sweeteners - candies
B. colours - curry
C. bitter substances – soft drinks
D. antioxidants - candies
E. emulsifiers – margarines

6) **Which one is incorrect?**

A. acesulfame K, neotame, saccharin, stevioside
B. BHT, vitamin C, EDTA, benzoic acid
C. benzoic acid, citric acid, sulfites, nisin
D. anthocyanins, riboflavin, cochineal, MSG
E. pectins, arabic gum, agar, starch

7) **Which statement is correct?**

A. EFSA established TDI for each food additive.
B. Aspartame is mainly used as a sweetener in baked goods.
C. BHT and BHA belong to the group of preservatives.
D. Nisin-producing organisms occur naturally in meat.
E. Nitrosamines are powerful carcinogens.

8**) To which group of contaminants does histamine belong and where can you find it?**

A. processing contaminant – fish
B. mycotoxins – milk
C. biogenic amines – fish
D. veterinary drugs – meat
E. phytoestrogens - vegetable

9) **Which group of contaminants doesn‘t belong to the group of natural contaminants**

A. alkaloids
B. heavy metals
C. mycotoxins
D. phytoestrogens
E. biogenic amines

10) Which one is incorrect?

A. ADI – Acceptable Daily Intake
B. WHO – World Health Organization
C. EFSA – The European Food Safety Authority
D. POPs – Polychlorinated Organic Pollutants
E. BFRs – Brominated Flame Retardants

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

14. Substances used for preservation - properties and use

1) Please explain what the following abbreviations mean *(Give full name)***:**

a) RASFF
b) EFSA
c) ADI
d) MRL
e) BFR
f) WHO
g) NOAEL
h) PCB
i) BHA
j) PAH
k) PFOS

2) For what purpose are the following food additives used?

a) BHA
b) Monosodium glutamate
c) Nisin
d) Sucralose
e) Sulphite
f) Curcumin
g) Benzoic acid
h) Ethyl vanillin
i) Citric acid
j) Lecithin

3) Which category are the following compounds? Give one most typical example where they occur.

a) Methyl mercury
b) Benzo[a]pyrene
c) 3-MCPD esters
d) PBDE
e) T-2 /HT-2
f) DDT /DDE
g) Aflatoxin M1
h) Botulinum toxin
i) Histamine
j) Patulin
k) Acrylamide