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MINISTRY OF EDUCATION,
YOUTH AND SPORTS



ATMOSPHERIC CHEMISTRY

Lecture No.: 9

Organisation of study

- Lecturer: Marek Staf, MSc., Ph.D., phone: +420 220 444 458
e-mail: marek.staf@vscht.cz,
web: <http://web.vscht.cz/~stafm/>
building A, Dept. 216, door No.162
e-learning:
<https://e-learning.vscht.cz/course/view.php?id=106>
- Scale of subject: winter semester
14 lectures, 14 weeks, 2 hours/week
- Classification: Exam - written + oral form (depending on result of the test)

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Scope of lecture 9

Reactions of selected pollutants and important components in atmosphere – toxic substances

- Toxic substances in atmosphere: definition, distribution, state of aggregation
- Legal definition of heavy metals and volatile organic compounds
- Persistent organic pollutants: compounds classified within POPs and their common properties
- Polychlorinated biphenyls, their congeners, history of manufacture and utilisation, atmospheric transport
- Organic chlorinated pesticides and polycyclic aromatic compounds
- Polychlorinated dibenzo dioxins and dibenzo furans: their synthesis, health and environmental effects, accidental release
- Chemical weapons: distribution into categories, history of their production and use, examples of health effects

Distribution of pollutants

- Pollutants can be divided into following fundamental groups:

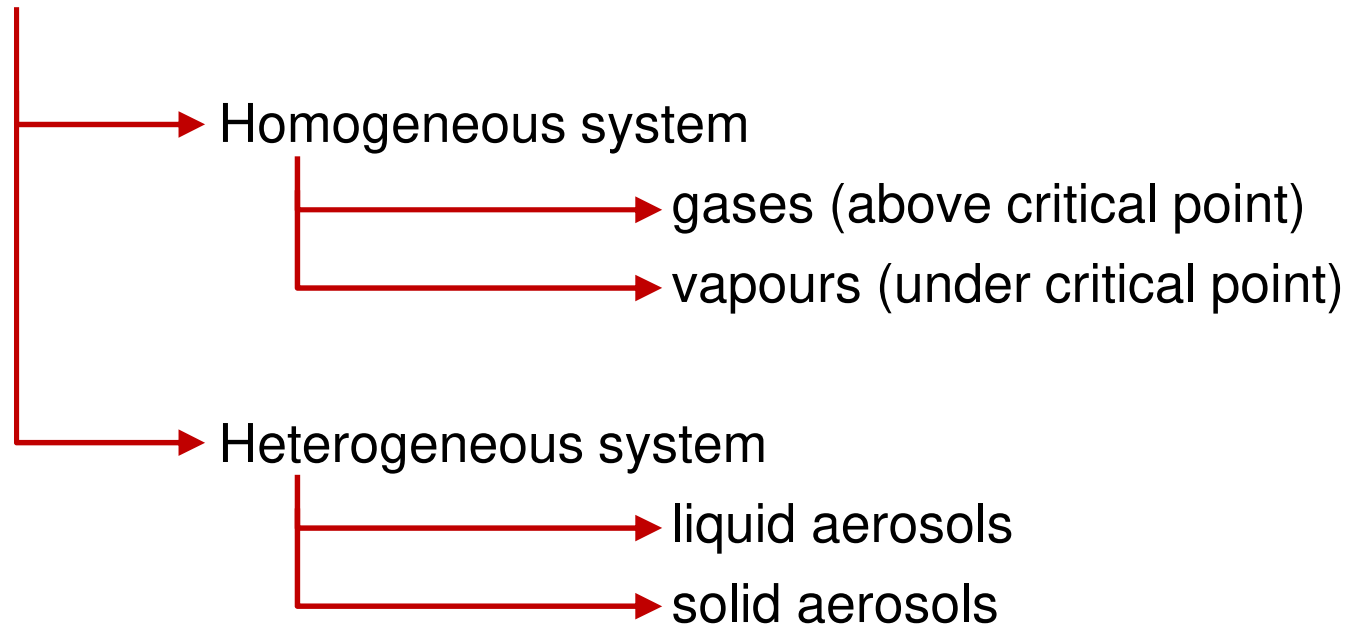
- Acidic substances
 - decrease atmospheric pH and subsequently acidify soil and water;
- Toxic substances
 - damage health of plants and animals chemically, physically or due to their radioactivity;
- Substances damaging O₃-
 - decompose the stratospheric O₃ layer;
- Greenhouse gases
 - change the balance between heat absorption and radiation from the atmosphere;
- Precursors
 - in their initial form they show no dangerous properties, but undergo changes resulting in the above mentioned properties, or allow other compounds to be transformed into dangerous substances.

Toxic substances in general

- **The largest group of toxic substances present in the air – organic compounds**
- **Presence of toxic compounds in atmosphere – big risk for health**
 - 3 main environmental factors of toxic substances for health:
 - Food
 - Drinking water
 - Air
 - 85 % of total input into the organism
 - 15 % of total input into the organism
 - Problem: Food + drinks can be chosen, air is breathed in and out spontaneously and inevitably in the volume of 15 – 20 m³/day (= 18 – 24 kg/day);
- **Terms frequently used regarding organic substances:**
 - Persistent organic pollutants POPs;
 - Persistent, bioaccumulative and toxic substances PBT;
 - Very persistent and very bioaccumulative substances vPvB;
 - Polycyclic Aromatic Hydrocarbons PAHs;
 - Volatile Organic Compounds VOC.

Toxic substances in general

- **Forms of appearance of toxic substances in nature:**



- **The biggest latent danger = liquids and solid compounds adsorbed onto particulate matter (aerosols)**

- Carrier = whichever dusty particles: soot, pollen grains, spores, and crystals, salt crystals etc.;
- Toxic substance itself, especially: POPs, heavy metals, asbestos, radionuclides etc.

Toxic substances in general

- **Definition of toxic substance – complicated**

- **Paracelsus (1493 – 1541):**

„All things are poison and nothing is without poison; only the dose makes a thing not a poison.“



- General definition:**

any substance that can impair function, cause structural damage, or otherwise injure the body, or destroys life when absorbed into the system.

- **Legal definition:**

see for example European Regulation 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures



GHS06 – Toxic substances

Note. Hazard symbols according to GHS

(Globally Harmonized System of Classification And Labeling of Chemicals; Introduced by UN)



GHS08 – Substances hazardous to health

Toxic substances – heavy metals

- **Definition – heavy metals (in atmosphere especially as aerosols)**
 - Ambiguous definition rather than historical indication (in fact all toxic metals)
 - Older definition: All metals, whose density is higher than Fe (it means $> 7.86 \text{ g/cm}^3$) \Rightarrow valid for Cd, Hg or Pb, not applicable to Se, Al, moreover As is not a metal but a semimetal;
 - Alternative definition: classification criterion is density $> 5 \text{ g/cm}^3$;
 - Universal definition: Heavy metals are all metals or semimetals, which pose any risk to environment;
 - The most discussed heavy metals: Ag, As, Cd, Co, Cr, Cu, Hg, Pb, Ni, Sb, Se, Tl, Zn.

Toxic substances – VOC

- **Definition – Volatile Organic Compounds, VOC**

- More than one acceptable definitions

- **Definition according to method ASTM D3960-90**

- Organic compounds having their vapour pressure (tension) >13.3 Pa at 25 °C

- **According to European directive 1999/13/EC „VOC Solvents Directive“**

- Organic compounds having their vapour pressure > 10 Pa at 20 °C

- **According to UN ECE (United Nations Economic Commission for Europe)**

- All organic compounds of anthropogenic origin other than methane, which are able to form photochemical oxidants by reaction with NO_x at presence of solar radiation. (the same according to directives 2001/81/EC or 2002/3/EC)

Toxic substances – VOC

- **Definition – Volatile Organic Compounds VOC**

- Other definitions (continuing from previous slide)
- **Definition according to directive 2004/42/EC** on the limitation of emissions of volatile organic compounds due to the use of organic solvents in decorative paints and varnishes and vehicle refinishing products and amending (so called Deco Paints Directive)

Organic substances having their boiling point lower or equal to 250 °C under normal pressure of 101.3 kPa .



Toxic substances – VOC

■ Emissions from industry

- Especially hydrocarbon solvents (varnishes, paints, glues, etc.)
- Emissions from high number of industrial processes – even unexpected
- Example: offset printing of newspapers, journals, books, leaflets, etc.



Dampening system in offset printing:

aqueous solution with content of 2 – 12 % vol. of isopropyl alcohol

Cleaning of printing (ink) rollers:
mixture of aliphatic hydrocarbons with flash point 40 – 60 °C

Toxic substances – POPs

- **Definition – Persistent organic pollutants POPs**

according to Protocol on POPs, agreed in Aarhus in 1998 and according to the Stockholm Convention on POPs from 2001:

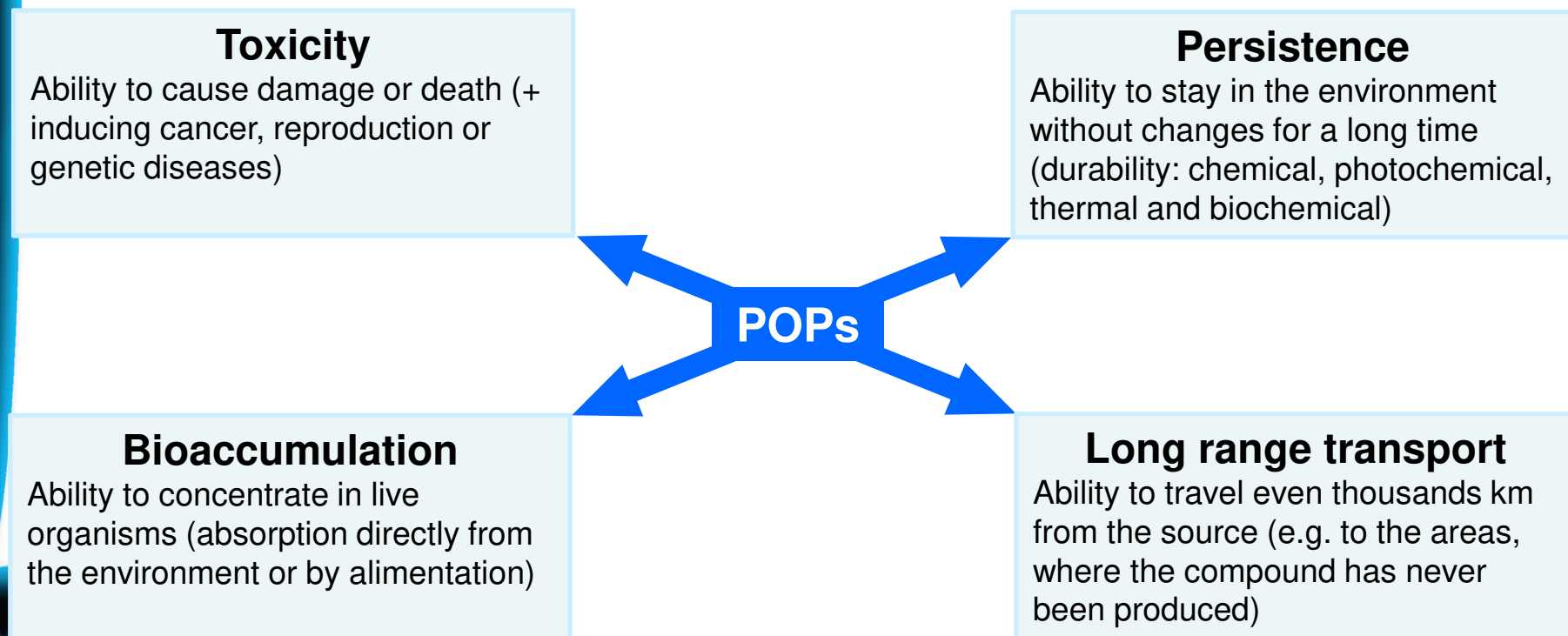
(Source: www.recetox.muni.cz)

- Persistent organic pollutants are such organic compounds, which:
 - show any toxic properties,
 - are persistent (degradation rate in the environment is slow),
 - are bioaccumulated,
 - undergo long range transport in the air, crossing state borders, and allow depositions,
 - have probable significant negative effects on human health or adverse effects on the environment.

Toxic substances – POPs

- **Completion of definition of POPs** (Source: www.recetox.muni.cz)
 - They are present as chemical individuals or as mixtures, forming specific groups. Compounds in the group:

- have similar properties and are released to the environment together;
- the mixture is available only as a certain preparation.



Toxic substances – POPs

- **Distribution of persistent organic pollutants – according to the composition**
 - Polychlorinated biphenyls (PCB);
 - Pesticides, mainly organic chlorinated pesticides (OCP);
e.g. chlorinated insecticides
 - Polycyclic aromatic hydrocarbons (PAHs);
sometimes called polyaromatic hydrocarbons
 - Polychlorinated dibenzo dioxins dibenzo furans (PCDD);
and polychlorinated dibenzo furans (PCDF);
 - Other persistent, bioaccumulative and toxic substances (PBT);
Note: Usually second generation, i.e. substitutes of the older types of highly toxic POPs.

Toxic substances – POPs

■ Distribution of persistent organic pollutants – according to origin

- Compounds, which were wilfully manufactured for certain purpose;

Especially:

| | |
|---|------|
| Polychlorinated biphenyls | PCB |
| Polychlorinated benzenes (solvents) | PCBz |
| Polychlorinated naphthalenes | PCN |
| Polychlorinated phenols (pentachlorophenol – wood impregnation) | PCP |
| Polybrominated diphenyl ethers (so called brominated flame retardants) | PBDE |
| Chlorinated paraffins (lubricants, solvents etc.) | CP |

- Compounds, which are formed as by-products of other processes;

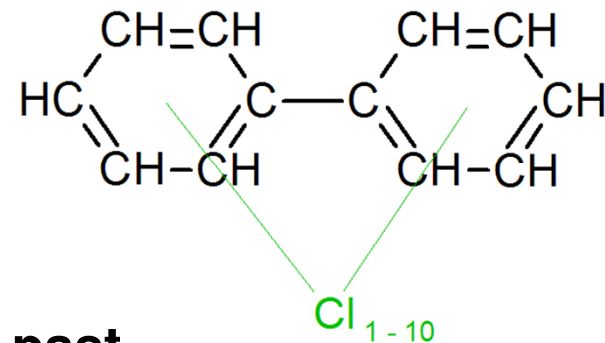
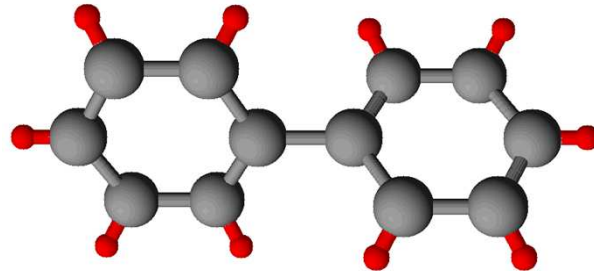
Especially:

| | |
|--|--------|
| Polychlorinated dibenzo dioxins and furans | PCDD/F |
|--|--------|

Polychlorinated biphenyls

■ General characteristics

- Number of chlorine atoms in the biphenyl molecule is 1 – 10;
- Molecules can be differently substituted, 209 congeners were identified in total ;
- Highest toxicity – in so called coplanar arrangement



■ Production – massive manufacture in the past

- At present, their production (with some exceptions) stopped;
- Basic historical applications: heat exchanging media;
hydraulic liquids (vacuum pumps,
drilling systems);
cooling liquid in transformers;
dielectric liquid in capacitors.

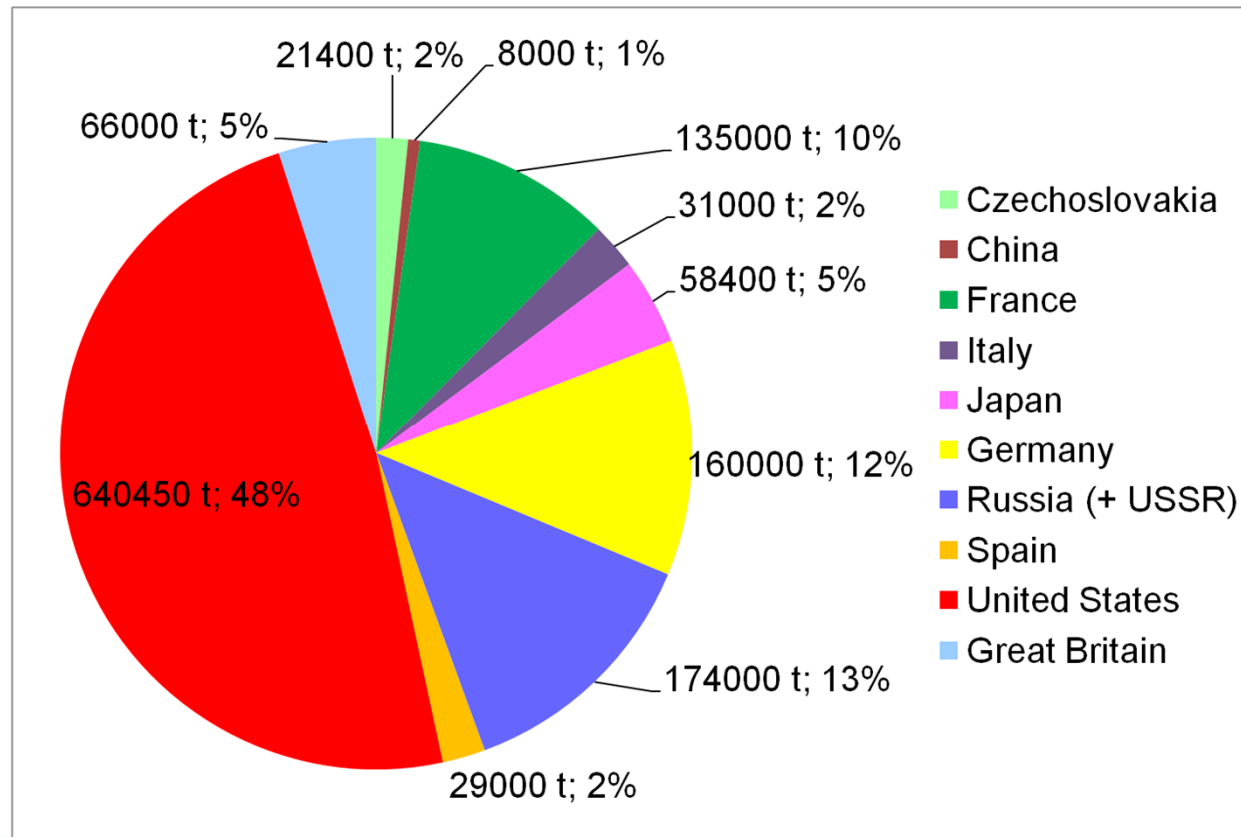
Polychlorinated biphenyls

■ Production

- Totally produced ca. $1.7 \cdot 10^6$ metric tons

■ Transport in atmosphere

- high boiling point \Rightarrow particularly aerosol in the air, e.g. PCB sorbed on dusty particles.



Organic chlorinated pesticides

■ Characterization of OCP

- almost without exceptions: persistent, bioaccumulative and toxic;
- majority of OCP belongs to organochlorinated insecticides;
- production and selling is generally banned.

■ Atmospheric appearance

- usually present in soil and water \Rightarrow in the air they are present as aerosols (and on the surface of dusty particles etc.).

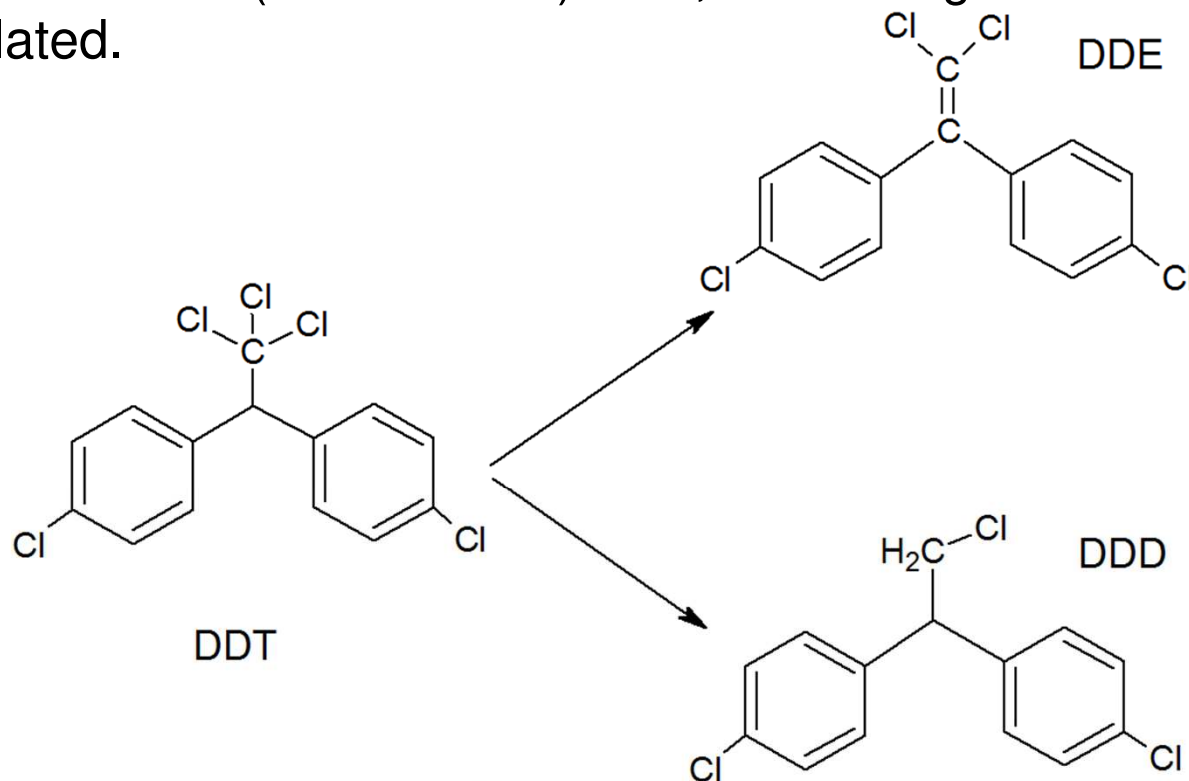
■ Historically most produced OCP

- DDT 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
 - γ -HCH 1,2,3,4,5,6-hexachlorocyclohexane lindane
(totally 5 stereoisomers, which the most important α -HCH + β -HCH)
 - CHL cis/trans-1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-
hexahydro-4,7-methano-1H-indene chlordane
 - Aldrine
 - Dieldrine
- } chlorinated cyclodiene-based insecticides named after famous chemists Diels and Alder.

Organic chlorinated pesticides

■ DDT – possibilities of natural decomposition

- very slow process (e.g. in Czechoslovakia, DDT production stopped in 1974, in Russia in 1993), however, significant concentrations are still detected in the environment;
- natural decay possible by dehydrogenchlorination and dechlorination
- from the concentration ratio (DDE + DDD)/DDT, the biodegradation rate can be calculated.



Organic chlorinated pesticides

■ DDT



INSECTICIDAS
ORION

D.D.T.
Y PELITRE

EXTERMINAN LOS INSECTOS DEL HOGAR

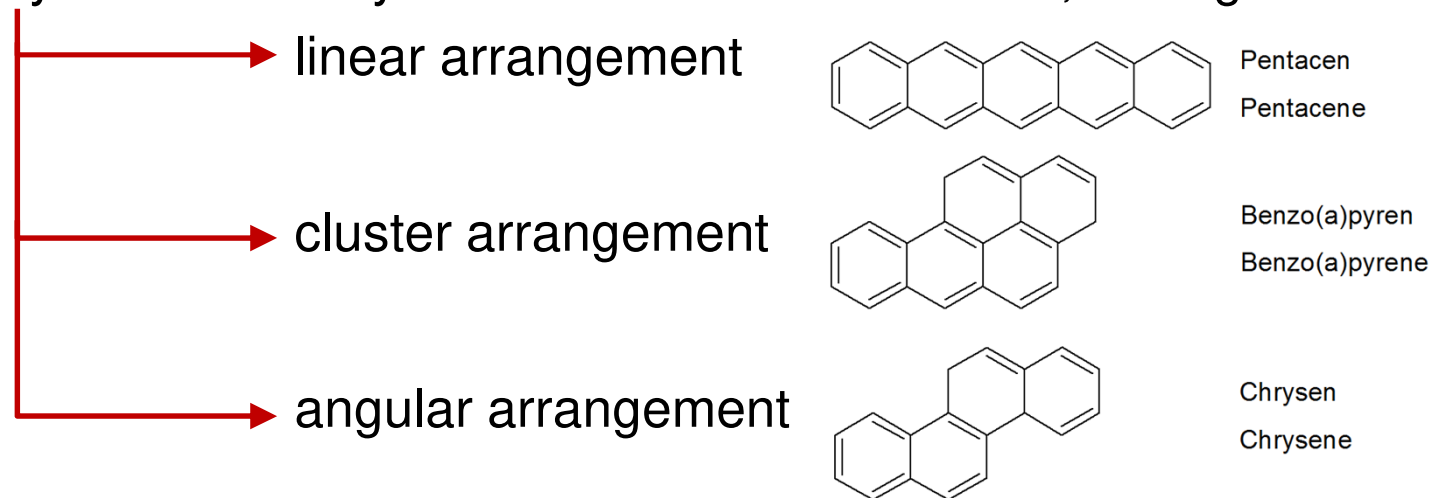
Shortly after its invention in 1939, DDT was promoted as a miracle pesticide all around the world.

The advertisement features a cartoon elephant holding a bottle of Orion insecticide. The bottle is labeled 'INSECTICIDA ORION'. A syringe and a fly are also visible. The text is in Spanish and English.

Polycyclic aromatic hydrocarbons

■ PAHs

- less frequent synonym is also PAC polycyclic aromatic compounds
- or, sometimes PNA polynuclear aromatics
- they are formed by two or more benzene cores, arranged in:



- Also, their following derivatives are PAHs too: alkyl-, halogen-, nitro-, amino-, hydroxy-
- Extraordinary toxic compound: benzo(a)pyrene – strongly carcinogenic and mutagenic:
formed by incomplete combustion (300 up to 600 °C)
discovered in black coal tar in 1933 (one of the first carcinogenes)

Polycyclic aromatic hydrocarbons

- **PAHs – Emissions into the air:**

Combustion processes – present in tar and soot (carbon black) e.g. from steelworks and heat plants

Combustion engines - especially diesel

Household sources (danger to homes - candles, grilled and fried food, fireplaces, and so on).



PCDDs and PCDFs

- **Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans**

- Example: tetrachlorodibenzoparadioxin ($LD_{50} = 10^{-9}$ x body weight)
- Illustrative example of accidental leakage to the atmosphere:

Seveso 1976 – accident in the premises of the company Givaudan (part of concern Hoffmann-La Roche)

Manufacture of herbicide TCP (trichlorophenol) \Rightarrow failure in production process with accumulation of TCDD in the reactor and subsequent release of 2 kg TCDD into the air via a security valve;

Error repaired within 20 minutes, but the leakage officially confessed after 17 days \Rightarrow

Transfer of TCDD to soil by rain

Contamination of wide area

250 people hospitalized

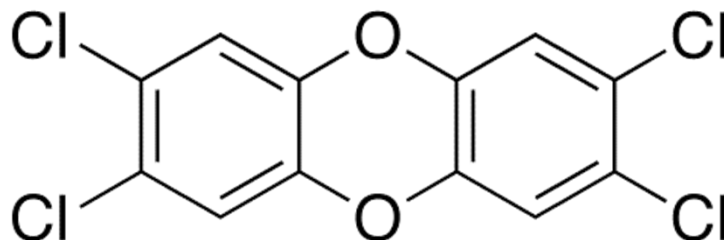
Evacuation of 600 persons + subsequent health damage

PCDDs and PCDFs

- **Polychlorinated dibenzo dioxins and polychlorinated dibenzo furans**

- **Course of the accident:**

- Production of herbicide TCP (2,4,5 – trichloro phenol) for wood knapweed control
- 2,3,7,8-tetrachloro dibenzo dioxin (TCDD) is a by-product of the TCP synthesis



- The reactor must be stirred permanently to avoid overheating.
- Saturday, 10th July, 1976: weekend shutdown ordered according to the Italian law.
- The prescribed correct shut down sequence was not accomplished – the stirrer was disabled before the tank was cooled down completely
- In the tank, a mixture of TCP + NaOH started to react exothermally = raising pressure

PCDDs and PCDFs

- **Polychlorinated dibenzo dioxins and polychlorinated dibenzo furans**
- **Course of the accident:**
 - Pressure exceeded the value set up on the safety valve = emergency opening
 - Leakage of up to 6 tons of the mixture containing ca. 1 – 2 kg TCDD
 - Dispersion of a hot aerosol over the area of 18 km²
 - Due to adverse wind conditions, a toxic cloud was transferred near the city.
 - The malfunction in the factory was removed in 20 – 30 minutes.
 - Legal authorities were not informed about TCDD content in the released aerosol by the management = no immediate measures were adopted.
 - Only after health problems reported by the inhabitants (14 days after the accident), the government established a committee and evacuated all the people living within 4 km around the factory.
 - 1,000 ha of fields were contaminated, the factory closed and after 5 years it was demolished.

PCDDs and PCDFs

- Seveso – a city located in the north Italy: Givaudan company



14,000 inhabitants

Location:

20 km north of Milan

PCDDs and PCDFs

- **PCDD – consequences of the Seveso accident**

Immediate decease of birds exposed to the aerosol during their flight!

Within the area of 5 x 0.7 km, decease of 3,000 animals (especially sheep)

Subsequently, 80,000 exposed farm animals were euthanized.



PCDDs and PCDFs

- PCDD – illustrative photos from the Seveso accident



Typical skin injury, caused
by PCDD

– expansion of
chloracne



PCDDs and PCDFs

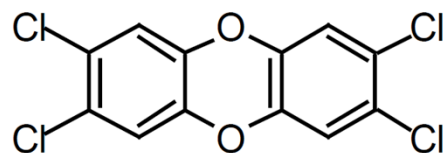
■ PCDD – consequences of the Seveso accident

- Exposed inhabitants suffered by acute intoxication: headache, respiratory difficulties and skin itching
- Later symptoms: severe rash and blistering - development of chloracne in several hundred people, after a certain time, about 200 people suffered from severe hepatic and renal damage (cirrhosis, liver cancer)
- 600 people sterile permanently, tens of pregnant women had to undergo interruption due to seriously damaged fetuses.

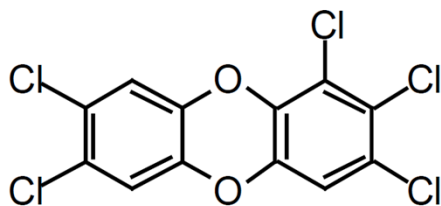
PCDDs and PCDFs

- **Generation of PCDD and PCDF during incineration (esp. wastes)**

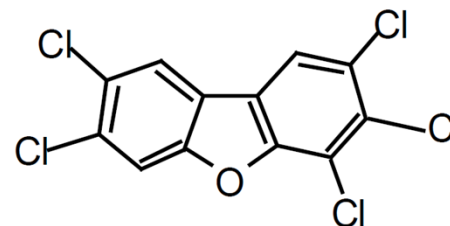
- Highly toxic, carcinogenic, mutagenic and teratogenic compounds \Rightarrow very low emission limit 0.1 ng.m_n^{-3} TEQ (3 most toxic depicted):



2,3,7,8,-TCDD



1,2,3,7,8,-pentaCDD



2,3,4,7,8,-pentaCDF

- During combustion, decomposition of halogen derivatives and subsequent synthesis of PCDD/F during cooling down the flue gas \Rightarrow temperature window $200 - \text{ca. } 450^\circ\text{C}$ (sometimes up to 600°C).

PCDDs and PCDFs

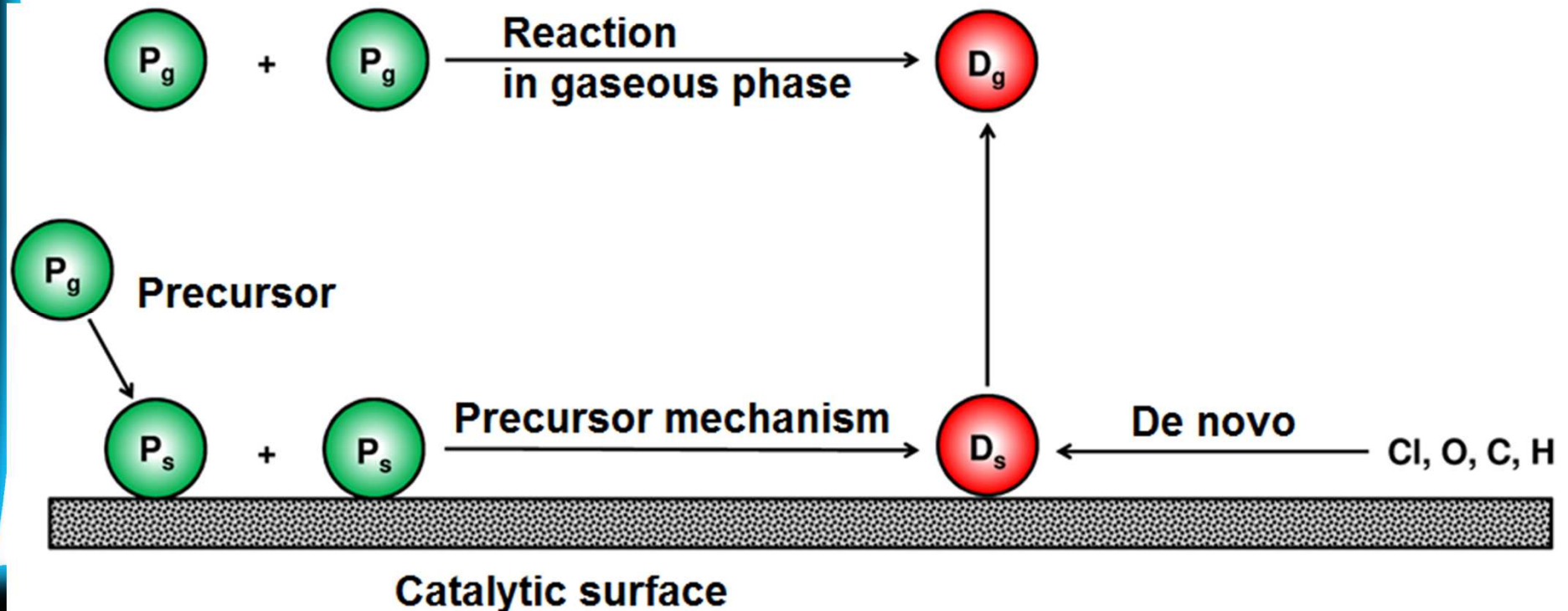
- **Generation of PCDD and PCDF during combustion** (Source: Konduri & Altwicker 1994)
 - Formed both in gaseous phase or catalytically on solid surfaces.
 - Reaction on surfaces considered as main source for combustion processes.
 - For the catalytic surface process two mechanisms were proposed:
 - Mechanism through precursors;
 - Synthesis de novo;
 - Precursor mechanism is based on the reaction of chlorinated hydrocarbons (chlorobenzenes and chlorophenols).
 - De novo synthesis estimates the recombination of carbon, oxygen, hydrogen and chlorine.
 - Ratio of pyrosynthetic mechanism in gas, precursor mechanism and de novo synthesis are not accurately defined.

PCDDs and PCDFs

■ Formation of PCDD and PCDF during incineration

(Source: Konduri & Altwicker 1994)

- General rules: Precursor mechanism is primary and runs at higher temperatures.
Synthesis de novo continues at lower temperatures.

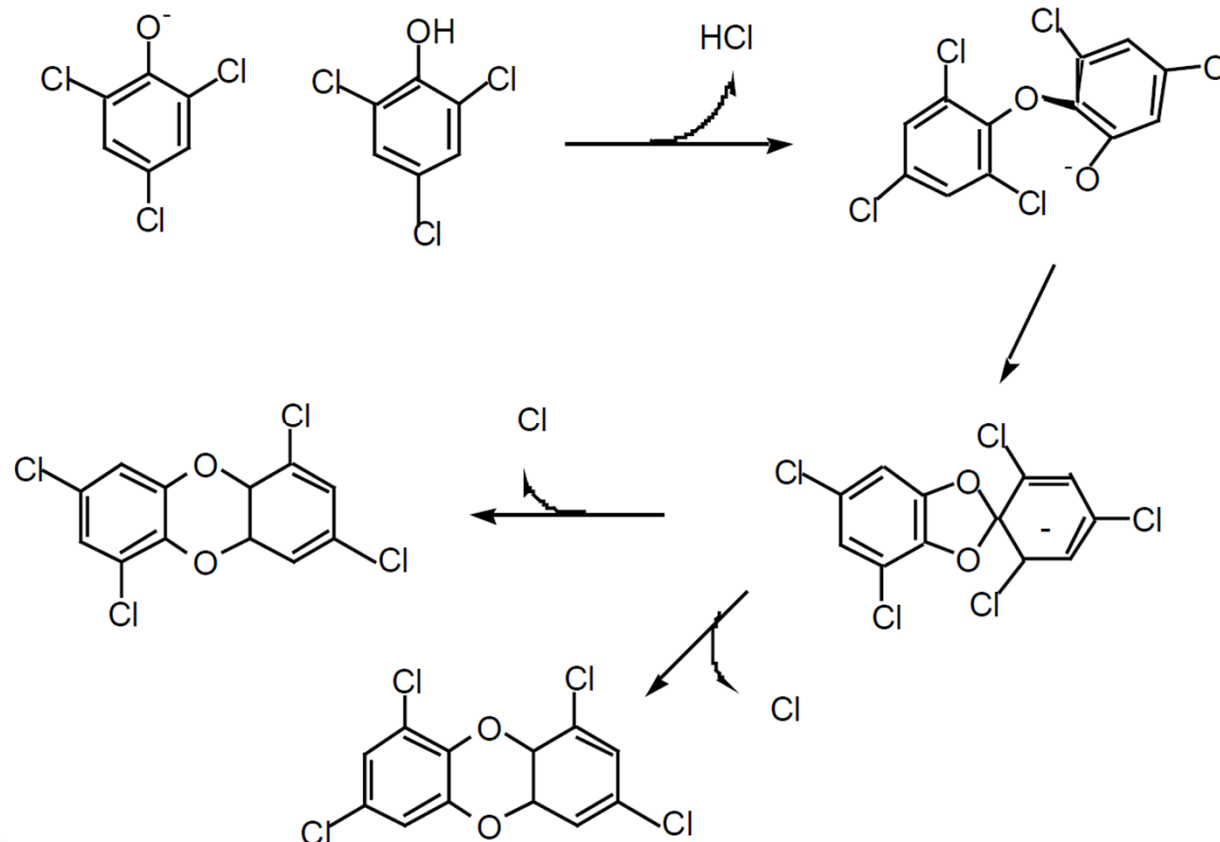


PCDDs and PCDFs

■ Formation of PCDD and PCDF during incineration

- Precursor mechanism includes more alternatives.
- Reaction running via chlorinated phenolate intermediate (Source: Tuppurainen et al 1998):

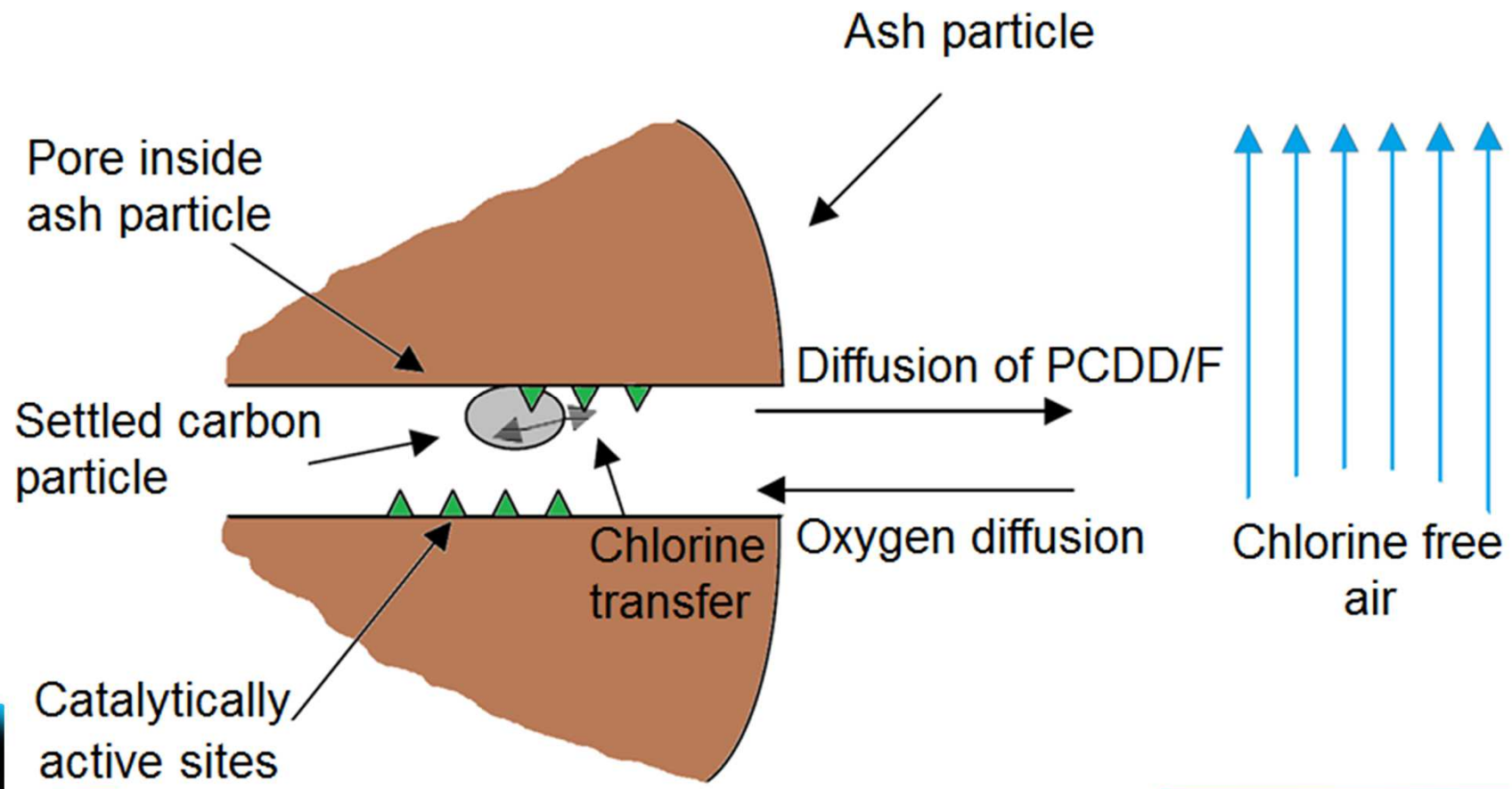
Note. PCDDs are also formed during some chemical processes like pentachlorophenol production etc.



PCDDs and PCDFs

■ Formation of PCDD and PCDF during incineration

- De novo synthesis;
- Strong catalytic activity of Cu
- Maximum reaction yield at 325 °C (Source: Milligan and Altwicker 1995):



Chemical weapons - introduction

■ History of chemical warfare

- Written sources available from antiquity (Source: www.population-protection.eu)

Example: In 178 A. D. suppression of a rebellion of peasants in China using unspecified arsenic-containing mist (As_2O_3);

- Massive application during WW1 (Source: www.valka.cz)

Estimated number of exposed people: 1,297,000, with 91,200 soldiers dying on exposure

Totally applied:

| | | | |
|---------------|-------------|---|---|
| Germany | 68 000 tons |  |  |
| France | 36 000 tons |  |  |
| Great Britain | 25 000 tons |  |  |

- Ban of chemical weapons: Geneva protocol (1925) and subsequent international agreement (1993).

Chemical weapons - overview

| Group | Examples | | |
|-----------------------------|---|---|--|
| Tear-forming | bromobenzylcyanide (BA) chloropicrin (PS) 2-chloro-benzalmalononitrile (CS) | | chloroacetophenone (CN) 1-bromo-2-propanone (BA) dibenz[b,f][1,4]oxazepine (CR) |
| Causing vomiting | adamsit diphenylcyanoarsane | | diphenylchloroarsane |
| damaging haematopoiesis | arsane (AsH ₃) hydrogen chloride | | cyanogen chloride hydrogen cyanide |
| Causing respiratory damages | chlorine diphosgene nitrogen dioxide perfluoroisobutylene | | phosgene red phosphorus chlorosulphonic acid TiCl ₄ ZnO ₂ |
| Oxygen transport inhibitors | hydrogen cyanide | | sulphane |
| Blistering agents | yperite lewisite phosgene | ethyl dichloroarsane nitrogen yperite phosgene oxim | methyl dichloroarsane phenodichloroarsane sesquiyperite |
| Neurotoxic | sarin soman | cyklohexylsarin tabun | diisopropyl-phosphofluoridate GE, VE, VG, V-Gas, VM, VX |

Chemical weapons – production

| Period | | Compound |
|--------------|-------------|--|
| WW1 | 1915 | chlorine, phosgene, benzylbromide |
| | 1916 | diphosgene, dibromo methyl-ethylketone, chloropicrine, yperite |
| | 1917 | diphenyl chloroarsane |
| | 1918 | diphenyl-cyanoarsane, ethyl-dichloroarsane, dichloromethyl ether |
| Between wars | 1930 | First nervously paralytic agents (Germany) |
| WW2 | 1941 – 1945 | CO, HCN concentration camps |
| | 1942 – 1945 | produced 12,000 tons of tabun, not used |
| | 1944 – 1945 | sarin, soman + 200 other organophosphates, not used |
| After WW2 | 1955 | group of compounds type agent V (USA) |
| | 1958 | VX (USA) |
| | 1979 - 1988 | yperite, Iran vs. Iraq |
| | 2013 (?) | yperite, sarin Syria (?) |

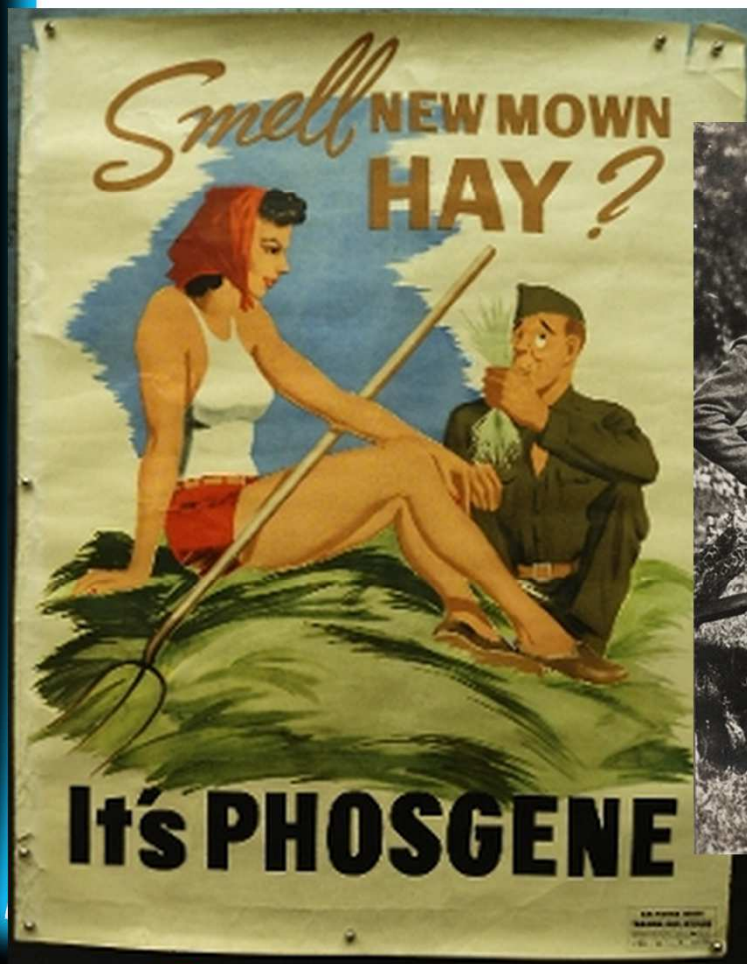
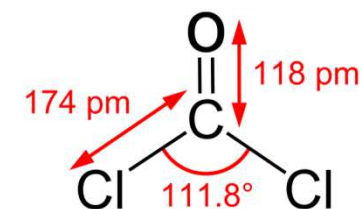
Chemical weapons - examples

■ Phosgene (carbonyl dichloride)

- Suffocating and toxic colourless gas;
- After high dilution the smell of hay or rotten potatoes;
- Manufacture via direct synthesis $\text{CO} + \text{Cl}_2$ at 130 – 150 °C and catalysis by active coal or Pt sponge;
- Atmospheric formation by photolysis of chlorinated hydrocarbons (CH_2Cl_2 , CCl_4 etc.);
- Mechanism of intoxication: hydrolysis in lungs to $\text{H}_2\text{CO}_3 + \text{HCl} \Rightarrow$ subsequently damaging membranes of lung alveoli and progression of oedema;
- Immediately life endangering concentrations $> 50 \text{ ppm}_v$, where the content of 500 – 800 ppm is lethal during exposition $< 1 \text{ min}$.
- Civil utilisation: raw material for organic syntheses;
- Military application: WW1, especially cannon ammunition filled with the compound.

Chemical weapons - examples

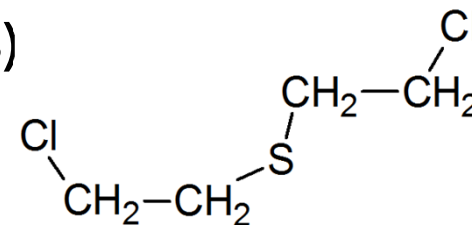
- Phosgene (carbonyl dichloride)
 - Contemporary pictures:



Chemical weapons - examples

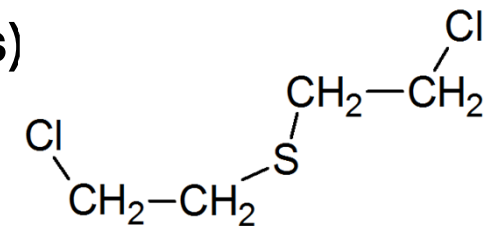
■ Yperite; bis(2-chloroethyl)sulphide (mustard gas)

- At 20 °C, colourless oily liquid without smell (characteristic mustard odour due to insufficient purity during production)
- Mechanism of intoxication: penetration into organism through skin, respiratory tract or other mucous membranes; the surface exposed shows morphological changes, inflammation and necrosis;
- Symptoms: it does not irritate immediately
The effect comes after a latency time; depression, headache, weakness, raised temperature, fluctuating blood pressure and pulse;
After certain time skin is reddish and swelling is visible; within 24 hours blisters appear with subsequent development during up to 6 days (risk of infection);
In case of intrusion into eyes large swelling of eyelids, damage to the cornea.
- War application: dispersion of aerosol by grenade explosion etc.
- Civil application: not manufactured or used.



Chemical weapons - examples

- Yperite; bis(2-chloroethyl)sulphide (mustard gas)
 - Contemporary pictures:



Affected skin

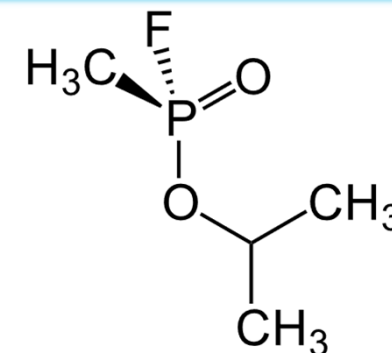


protective clothing

Chemical weapons - examples

■ Sarin; O-isopropylmethyl fluorophosphonate

- organophosphates-based neurotoxin
- At 20 °C colourless volatile liquid with fruity scent
- In 1939 synthesised in Germany by the team:
Schrader, Ambros, Ritter, Van der Linde.
- Production: synthesis of isopropanol with methyl difluorophosphate (CH_3POF_2).
- Mechanism of intoxication: penetration into organism through skin, respiratory tract or other mucous membranes; exposed surface without local symptoms; subsequently inhibition of choline esterase causing accumulation of acetyl choline \Rightarrow interruption of signal transfer via neurons;
- Symptoms: headache, then salivation and respiratory insufficiency, convulsions, at the last stage loss of consciousness, vomiting, defecation, paralytic of respiratory muscles and death
- War application: dispersion of aerosol (possible synthesis in situ)
- Civil application: not produced or used

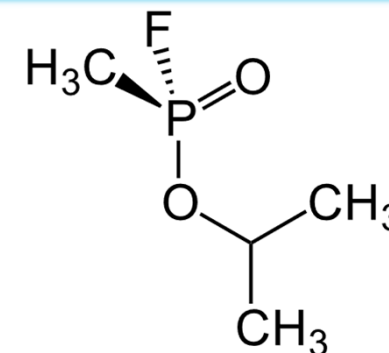


Chemical weapons - examples

- **Sarin; O-isopropylmethyl fluorophosphonate**

Contemporary footage: (1995, Tokyo attacked by the sect

Aum Shinrikyo)



Shoko Asahara (leader)



first aid for victims (12 people died
5,500 poisoned)