

C2003 –

ENVIRONMENTAL CHEMISTRY



Course goals:

After this course, students should be able to:

- understand problems related to pollution of the environment from natural and anthropogenic sources

Week 1 (13-Mar):

Understanding pollutants

- what is pollution? What are some examples of important pollutants? Why are we concerned?

Week 2 (20-Mar):

Understand the environment (and how this relates to the pollutants)

- What are important properties of air, soil, water? How do these affect how pollutants are distributed?

Week 3 (27-Mar): No lecture – work on class project

Week 4 (03-Apr):

Understanding sampling

- How do we measure pollution in the environment? What tools do we use? How do we pick where and what to sample?

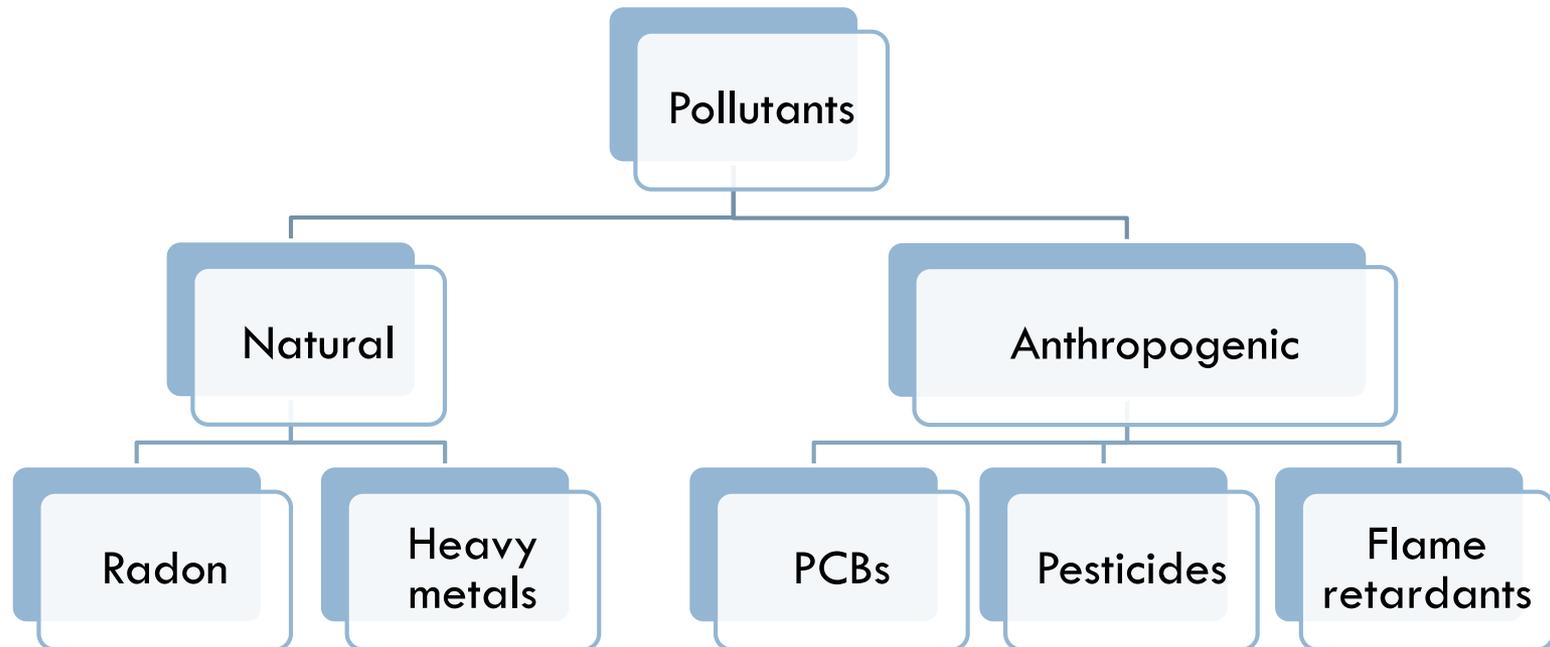
Week 5 (10-Apr):

Understanding the ways that we use environmental data

- Risk assessment and environmental policy

What is pollution?

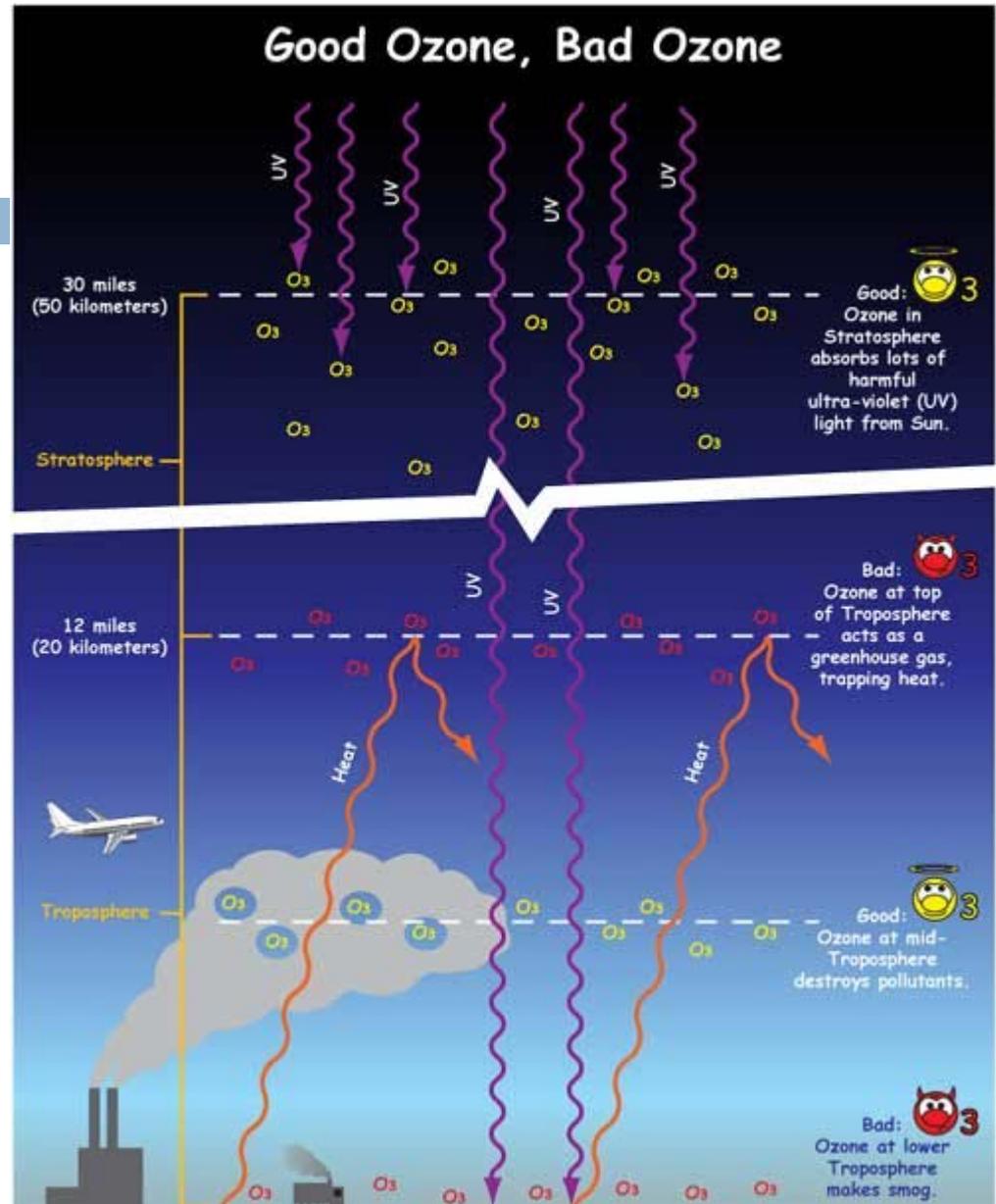
- Presence of a **substance in an environmental system** having a **harmful effect**
- The substance = *pollutant* or *contaminant*



Just a few examples...

Pollution depends on context...

- Many have both natural and anthropogenic sources (e.g., PAHs, metals...)
- Only a pollutant when unwanted adverse effect:
 - E.g., ozone, pesticides...



Environmental chemistry

- Environmental chemistry is the study of chemical processes occurring in the environment which are impacted by human activities.
- Can be local scale, e.g., urban air pollutants or toxic substances from a chemical waste site
- or-
- Can be global scale, e.g., long-range pollution transport, global warming

Why is chemistry important to understand pollution?

A chemical's *structure* dictates that compound's "*personality*,"

- provides a systematic basis to understand and predict chemical behavior in the environment
- With an understanding of the properties and behaviour of chemicals, we can better understand *what the impact of humans is* on the global environment

Types of pollutants

- Many classes and methods for classification exist – we will consider a few of the major types of pollutants:
 - Airborne particulate matter
 - Persistent organic pollutants
 - Polycyclic aromatic hydrocarbons
 - Heavy metals
 - etc.

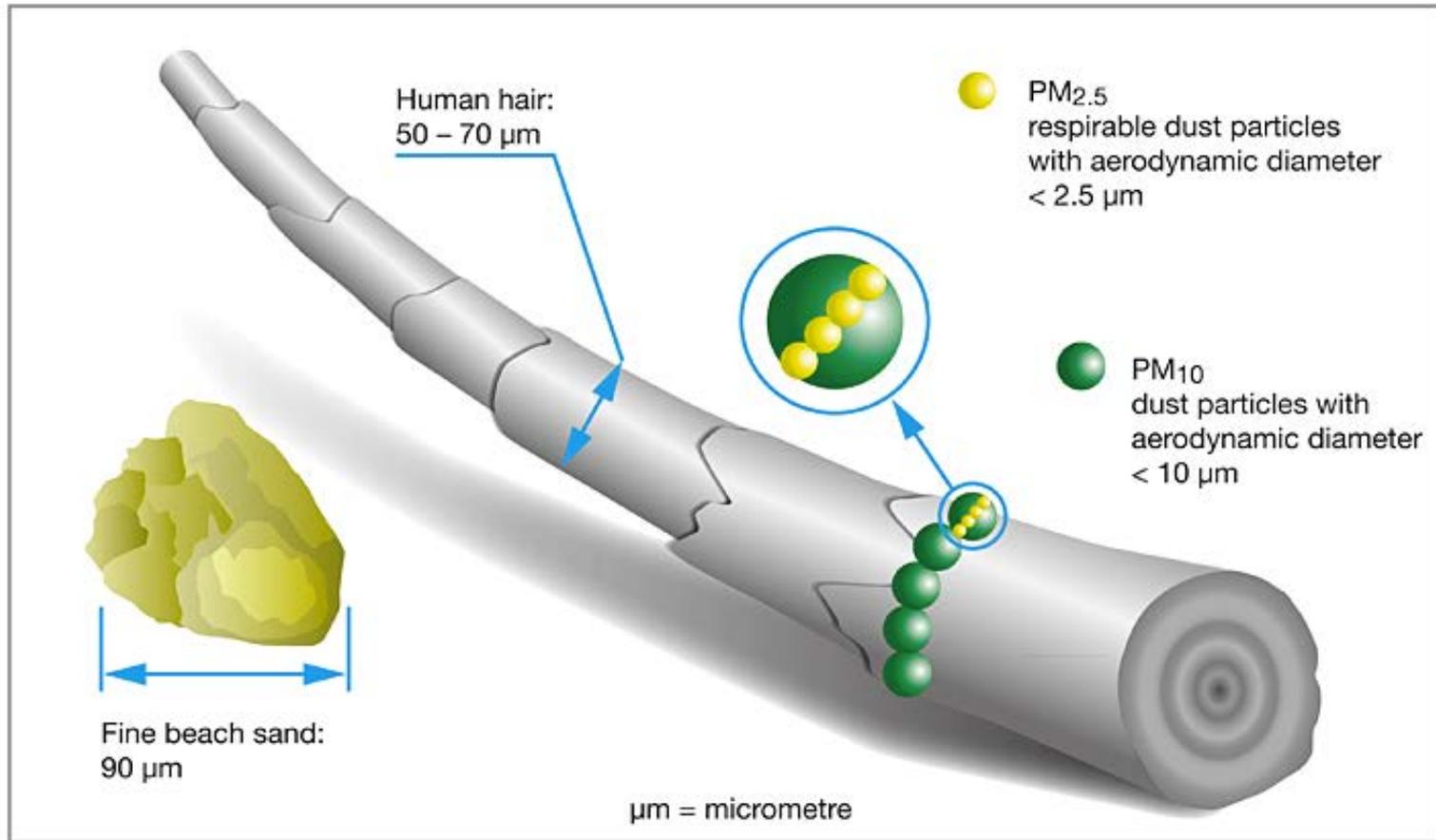
Air pollutants

- Airborne particulate matter, volatile organic compounds (VOCs) → primarily air pollutants
- 5 major air pollutants:
 - Particulate matter
 - Ozone
 - Nitrogen dioxide
 - Sulphur dioxide
 - VOCs

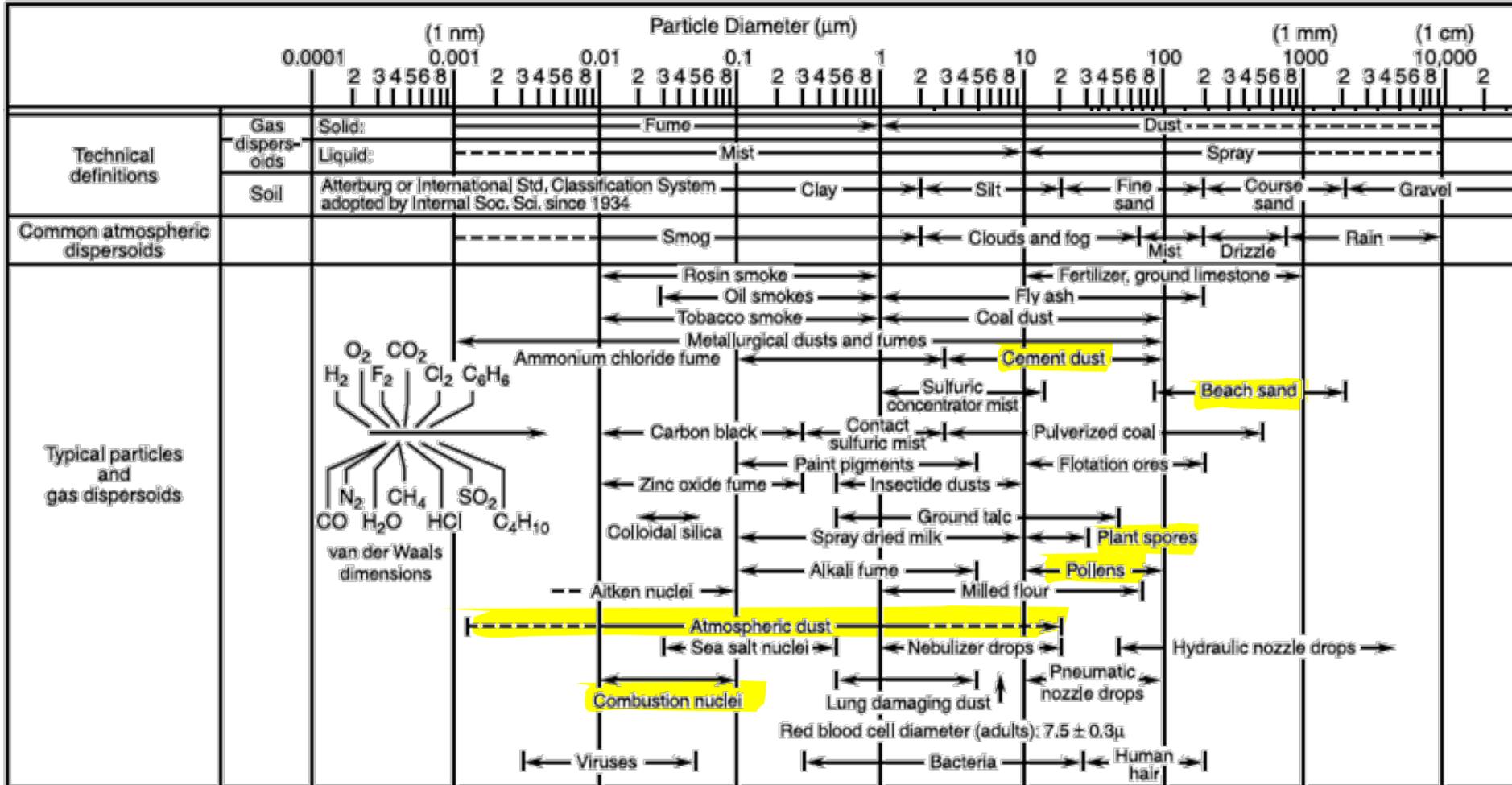
Particulate matter (PM)

- Solid and liquid particles suspended in air
- Naturally occurring and anthropogenic
- Natural sources:
 - ▣ Salt particles from sea spray, pollen, moulds, bacteria, debris from plants and animals, soil particles entrained by wind, etc.
- Anthropogenic sources:
 - ▣ Industrial processes, open burning, vehicles, agriculture, mining, etc.
- PM is not a specific chemical, but a mixture of particles with different origin, composition, size, shape, etc.
- Important itself (e.g., has negative health effects) and **as a carrier for other atmospheric pollutants**

Particulate matter

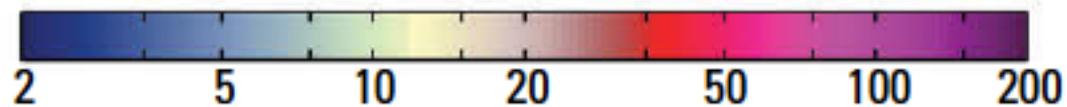
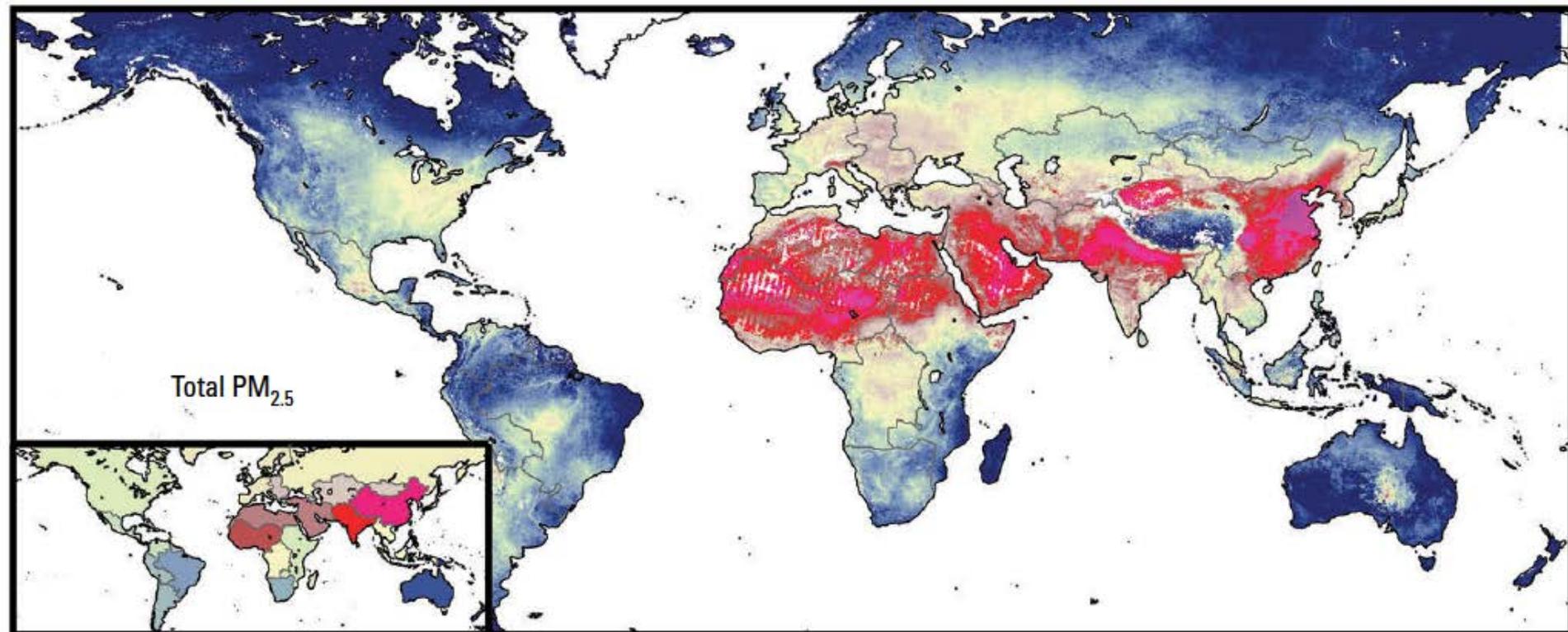


PM sizes and examples



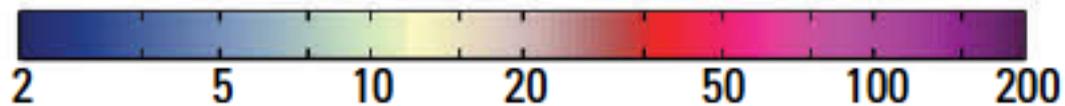
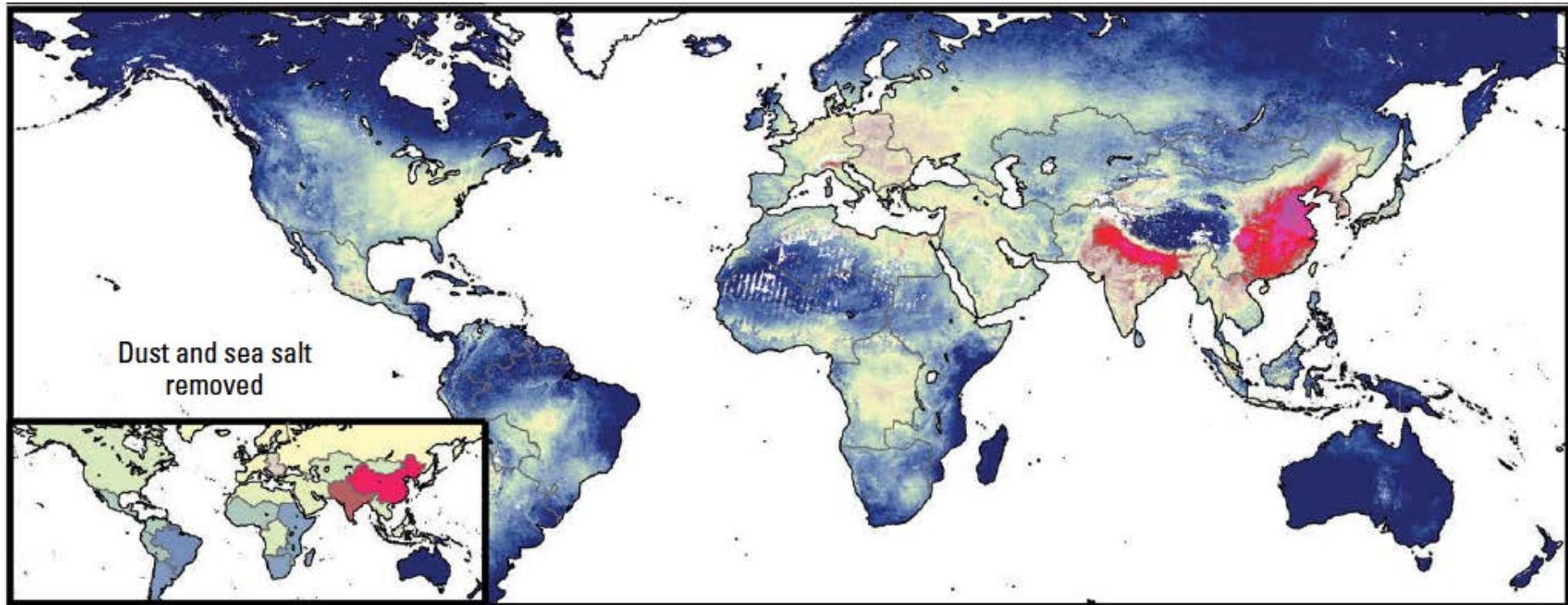
From Finlayson-Pitts and Pitts, 2000, *Chemistry of the Upper and Lower Atmosphere*

Particulate matter



PM_{2.5} ($\mu\text{g}/\text{m}^3$)

Particulate matter – excluding dust and sea spray

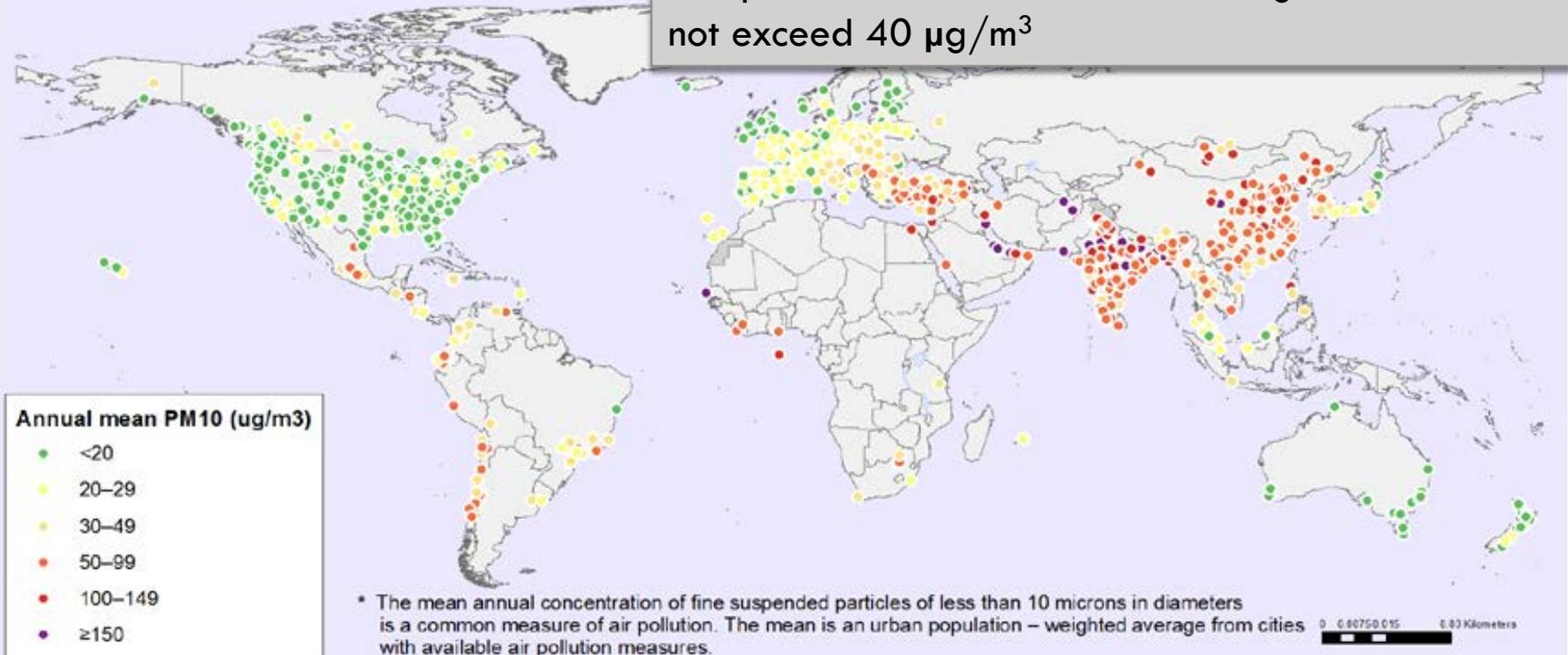


PM_{2.5} (µg/m³)

Particulate matter - exposure

Exposure to particulate matter with an aerodynamic diameter of 10 μm or less (PM10) in 1600 urban areas*, 2008–2013

European Guideline – annual average PM10 should not exceed 40 $\mu\text{g}/\text{m}^3$



European Environment Agency: "Particulate matter is the air pollutant that poses the greatest health risk to people in Europe."

Data Source: World Health Organization
Map Production: Health Statistics and Information Systems (HSI)
World Health Organization



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Types of pollutants

- Many classes and methods for classification exist – we will consider a few of the major types of pollutants:

- Airborne particulate matter ✓

- Persistent organic pollutants

- Polycyclic aromatic hydrocarbons

- etc.

} + others = **SEMI-VOLATILE**
ORGANIC
COMPOUNDS

What are semivolatile organic compounds (SVOCs)?

- Generally determined by vapour pressure
 - ▣ typically between ~ 1 and 10^{-10} Pa
- Not a firm grouping though

Why are they important?

- Can distribute in multiple media (gas-phase air, particle-phase air, soil, water, plants, lipids, floor dust, window films...)
- Many are persistent, lipophilic, bioaccumulative
- Many **chemicals of concern** are in this group.

Examples of SVOCs

- Pesticides
- Industrial chemicals
- By-products
- Additives in consumer products

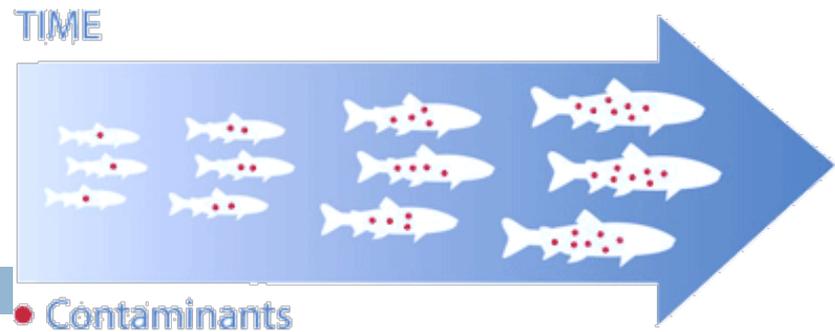
POPs / PBT

- Many SVOCs are classified as “persistent organic pollutants” (POPs) or “persistent, bioaccumulative and toxic” (PBT)
- 3 key terms to understand:
 - Persistence
 - Bioaccumulation
 - Toxicity

Environmental Persistence

- The length of time a chemical remains in environmental system or media
- Governed by **the rates at which the compound is removed from the system** by biological and chemical processes, such as environmental transport, biodegradation, hydrolysis, atmospheric reactions
- Measured as the **half-life of the substance in the medium**
- A chemical is considered persistent if it has a half-life of:
 - ▣ >2 days in air
 - ▣ ~2-6 months or more in water, sediment or soil

Bioaccumulation



- The accumulation of a chemical in tissues of an organism through any route, including respiration, ingestion, or direct contact with the contaminated environment
i.e. *Rate of chemical uptake* \gg *rate of chemical loss*
- If a chemical is “bioaccumulative” this means that the concentration of the chemical in the tissues of an organism can be significantly higher (e.g., several orders of magnitude) than the concentration of the chemical in the surrounding environment
- Measured by bioaccumulation factor (BAF)
 - ▣ $BAF > \sim 1000$ means a chemical is considered “bioaccumulative”

$$BAF = \frac{\text{Conc. on contaminant in organism}}{\text{Conc. on contaminant in ambient environment}}$$

Toxicity (1)

- A measure of the amount which a substance can cause harm to an organism
- Related to the dose of a chemical received by an organism
 - ▣ Moderately toxic substance can cause harm if an organism receives a higher dose
 - ▣ Highly toxic substances can cause harm at low doses

Toxicity (2)

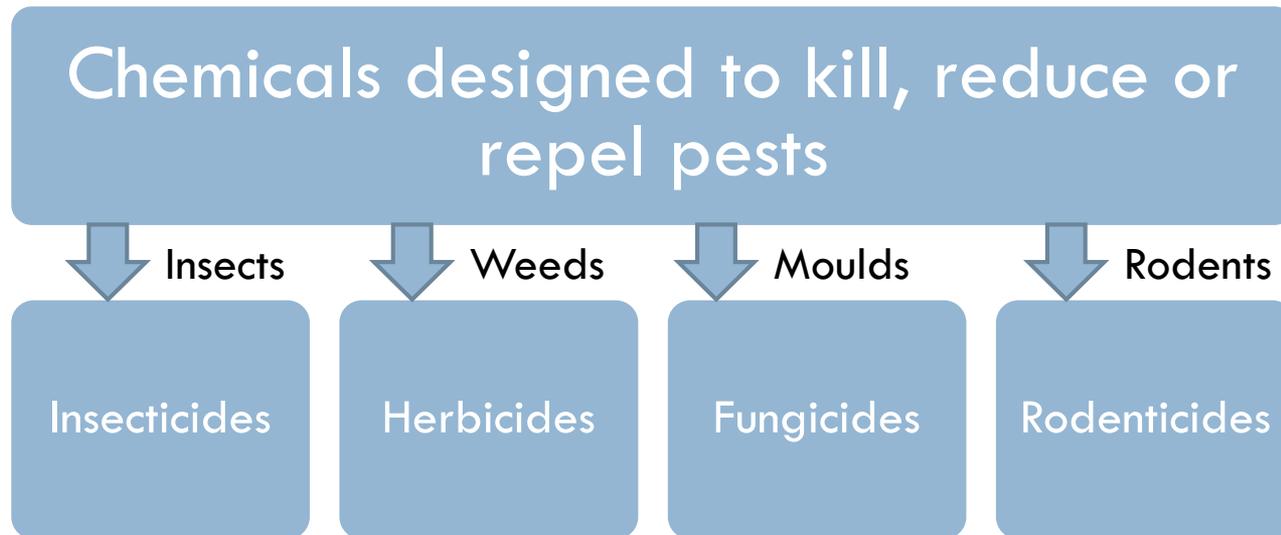
- It is all about the dose
- Even mundane substances can be toxic

Substance	Animal, Route	LD ₅₀ : g/kg	Substance	Animal, Route	LD ₅₀ : g/kg
		{LC ₅₀ : g/L}			{LC ₅₀ : g/L}
Water	rat, oral	>90	Sodium fluoride	rat, oral	0.052
Sucrose (table sugar)	rat, oral	29.7	Pentaborane	human, oral	<0.05
Monosodium glutamate (MSG)	rat, oral	16.6	Capsaicin	mouse, oral	0.0472
Vitamin C (ascorbic acid)	rat, oral	11.9	Mercury(II) chloride	rat, dermal	0.041
Urea	rat, oral	8.471	Lysergic acid diethylamide (LSD)	rat, intravenous	0.0165
Cyanuric acid	rat, oral	7.7	Arsenic trioxide	rat, oral	0.014
cadmium sulfide	rat, oral	7.08	Metallic Arsenic	rat, intraperitoneal	0.013
ethanol (Grain alcohol)	rat, oral	7.06	Nicotine	human, oral	0.0065-0.013
sodium isopropyl methylphosphonic acid (IMPA, metabolite of sarin)	rat, oral	6.86	Sodium cyanide	rat, oral	0.0064
Melamine	rat, oral	6	White phosphorus	rat, oral	0.00303
Melamine cyanurate	rat, oral	4.1	Strychnine	human, oral	0.001
Sodium molybdate	rat, oral	4	Cantharidin	human, oral	0.0005
Sodium chloride (table salt)	rat, oral	3	Aflatoxin B1 (from Aspergillus flavus)	rat, oral	0.00048
Paracetamol (acetaminophen)	rat, oral	1.944	Venom of the Brazilian wandering spider	rat, subcutaneous	0.000134
Delta-9-tetrahydrocannabinol (THC)	rat, oral	1.27	Venom of the Inland Taipan (Australian snake)	rat, subcutaneous	0.000025
Metallic Arsenic	rat, oral	0.763	Ricin	rat, intraperitoneal	0.000022
	rat, oral	0.3045		rat, oral	0.02
Alkyl dimethyl benzalkonium chloride (ADBAC)	fish, immersion	{0.00028}	2,3,7,8-Tetrachlorodibenzodioxin (TCDD, a dioxin)	rat, oral	0.00002
	aq. invertebrates, imm.	{0.000059}	Sarin	mouse, subcutaneous injection	0.0000172
Coumarin (benzopyrone, from Cinnamomum aromaticum and other plants)	rat, oral	0.293	VX	human, oral, inhalation, absorption through skin/eyes	0.0000023
Aspirin (acetylsalicylic acid)	rat, oral	0.2	Batrachotoxin (from poison dart frog)	human, subcutaneous injection	0.000002
Caffeine	rat, oral	0.192	Abrin	mice, intravenously	0.0000007
Arsenic trisulfide	rat, oral	0.185-6.4		human, inhalation	0.0000033
Sodium nitrite	rat, oral	0.18		human, oral	0.00001-0.001
uranyl acetate dihydrate	mouse, oral	0.136	Maitotoxin	mouse, intraperitoneal	0.0000013
Bisoprolol	mouse, oral	0.1	Polonium-210	human, inhalation	0.00000001
Cobalt(II) chloride	rat, oral	0.08	Botulinum toxin (Botox)	human, oral, injection, inhalation	0.000000001
Cadmium oxide	rat, oral	0.072	Ionizing radiation	human, irradiation	

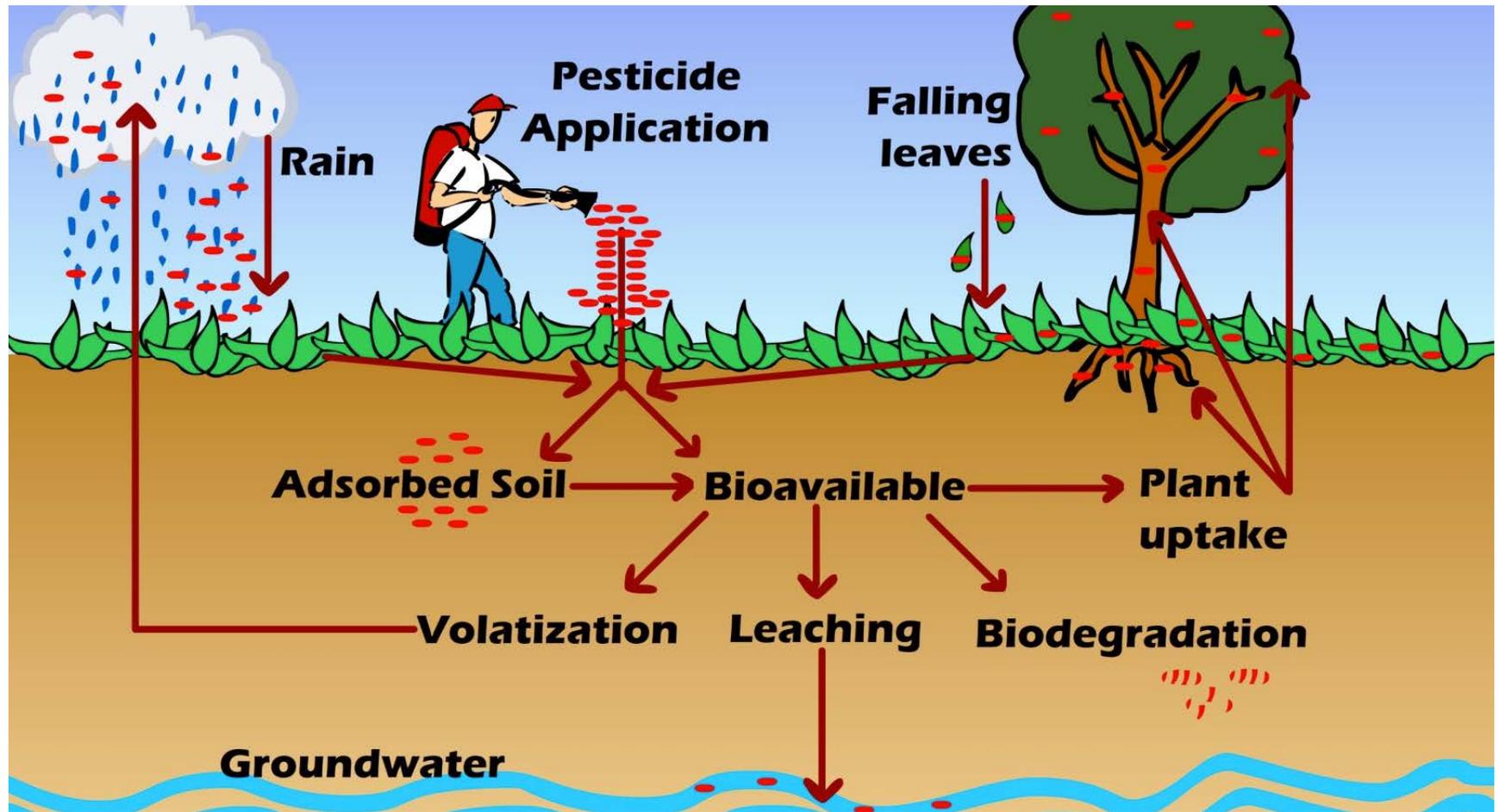
Examples of SVOCs

- **Pesticides**
- Industrial chemicals
- By-products
- Additives in consumer products

Pesticides – intentionally toxic!



How pesticides enter the environment



Global pesticide use

2.5 million tonnes per year (Alavanja, 2009)



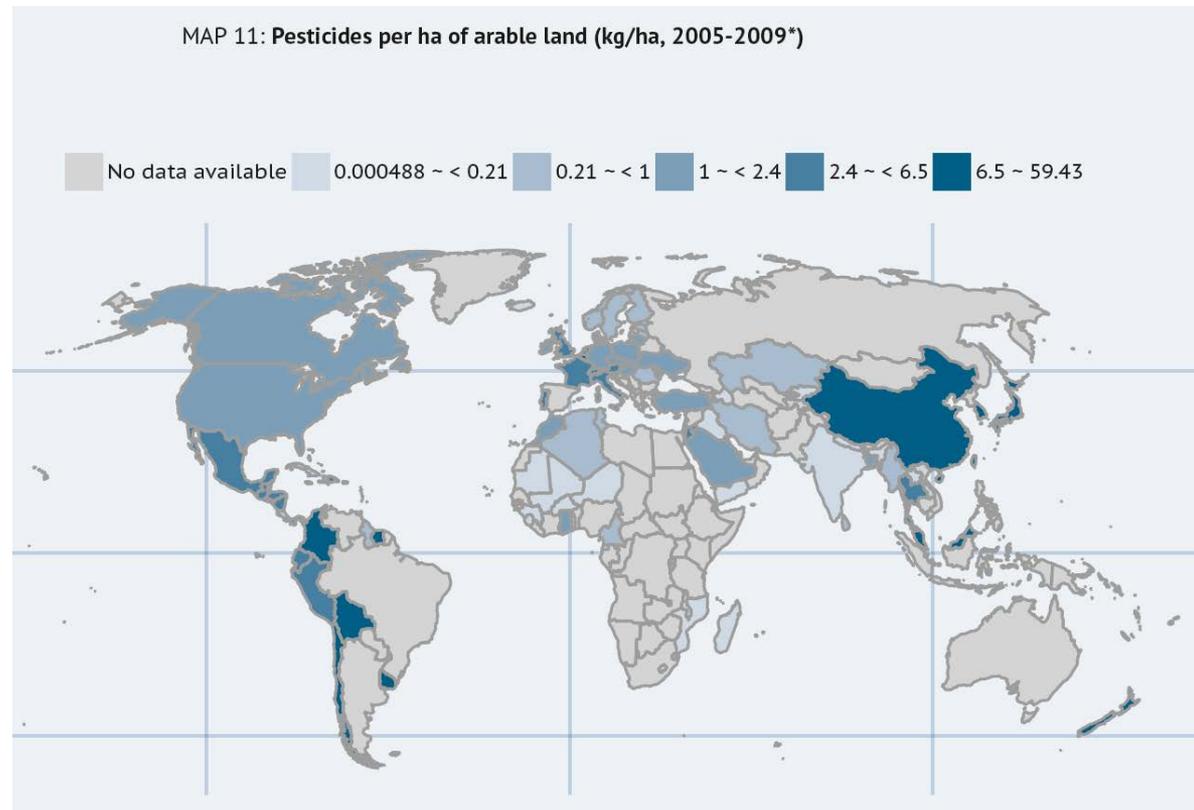
Insecticide



Herbicide



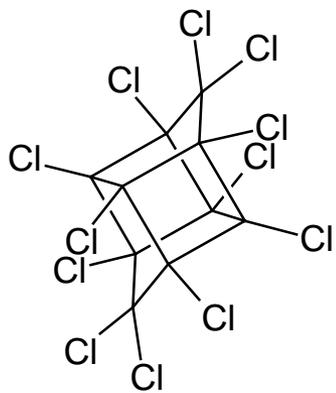
Fungicide



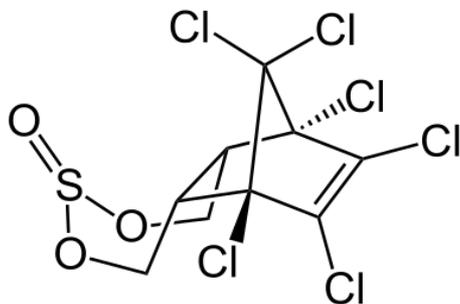
From FAO Statistical Yearbook, UN 2013

Organochlorine pesticides

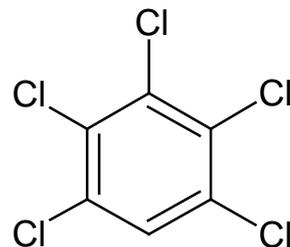
- OCPs = organochlorine pesticides
- What are the OCPs?
 - DDT
 - Hexachlorobenzene (HCB)
 - Pentachlorobenzene (PeCB)
 - Hexachlorocyclohexanes (multiple isomers)
 - Heptachlor/heptachlor epoxide
 - Aldrin/dieldrin/endrin
 - Chlordane (multiple isomers)
 - Endosulfan
 - Mirex
 - ...



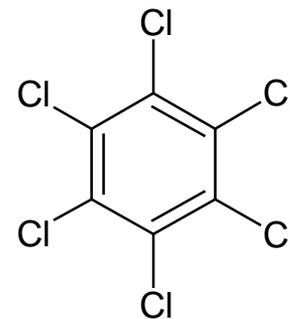
Mirex



Endosulfan

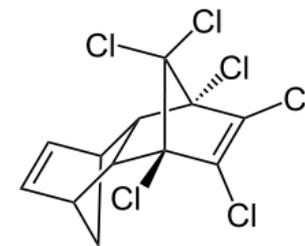


PeCB

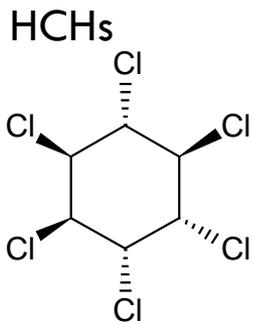


HCB

Chlorinated molecules – highly stable – therefore environmentally persistent



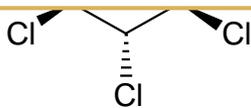
Aldrin



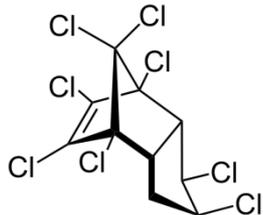
α



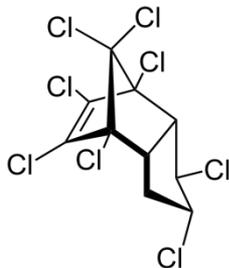
β



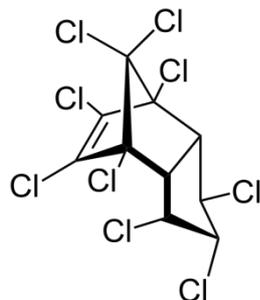
γ



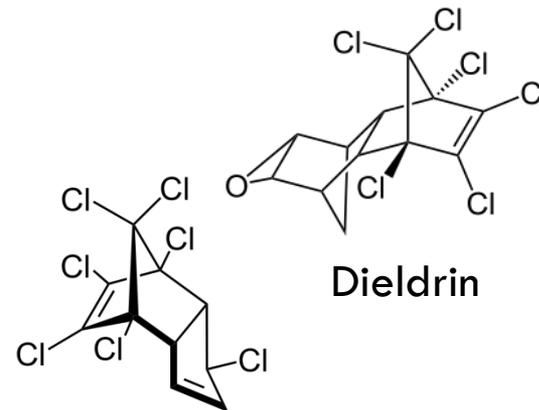
cis-chlordane



trans-chlordane



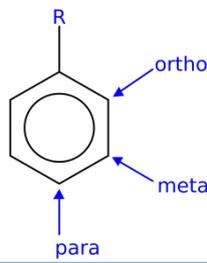
trans-nonachlor



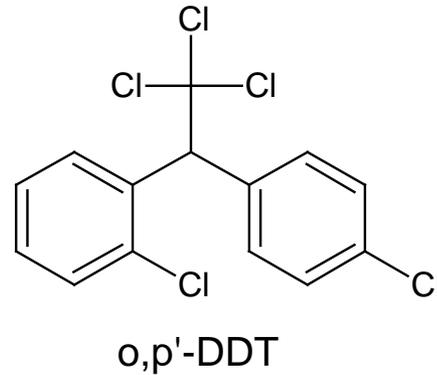
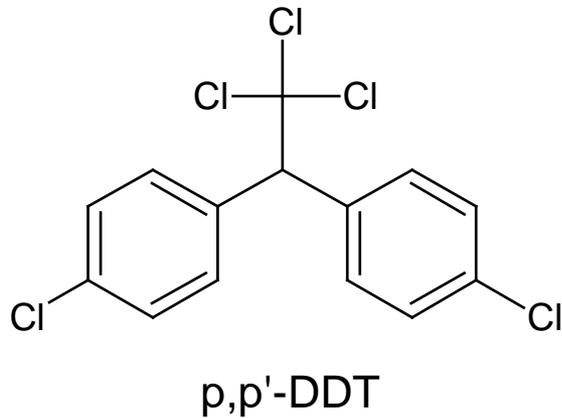
heptachlor

Dieldrin

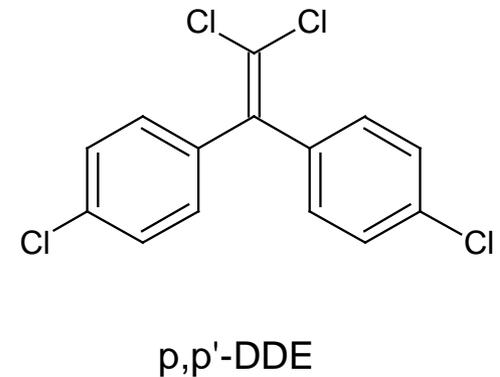
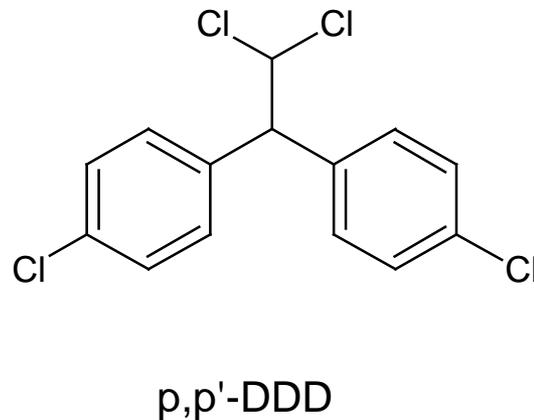
Case study 2: DDT



□ DDT – dichlorodiphenyl trichloroethane



Degradation products/metabolites are often also considered:



DDT – a brief history

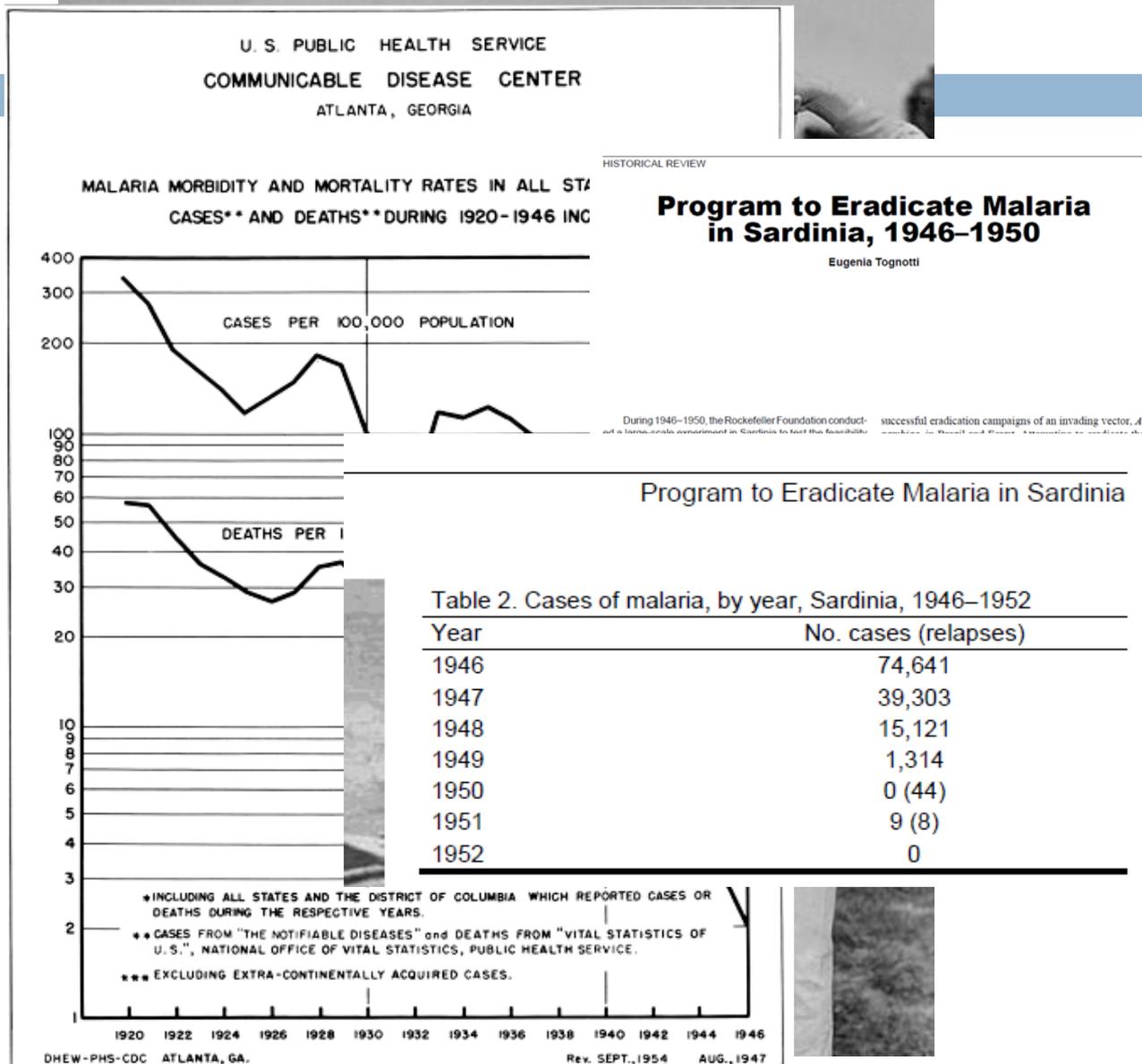
1872 – DDT was first synthesized by Austrian chemistry student

1939 – insecticidal properties discovered

WW2– global use of DDT against typhus, malaria

1945 – DDT available to public

1940s, 1950s – WHO and country-specific programs targeting elimination of malaria – successful in Europe and North America, and large reduction in cases in India, southeast Asia



DDT – a brief history

1959 - More than 36 million kg of DDT was sprayed over the US

1961 - DDT use reaches its peak.

1940s, 1950s – Gradual increase in number of scientific studies identifying negative effects of DDT on wildlife

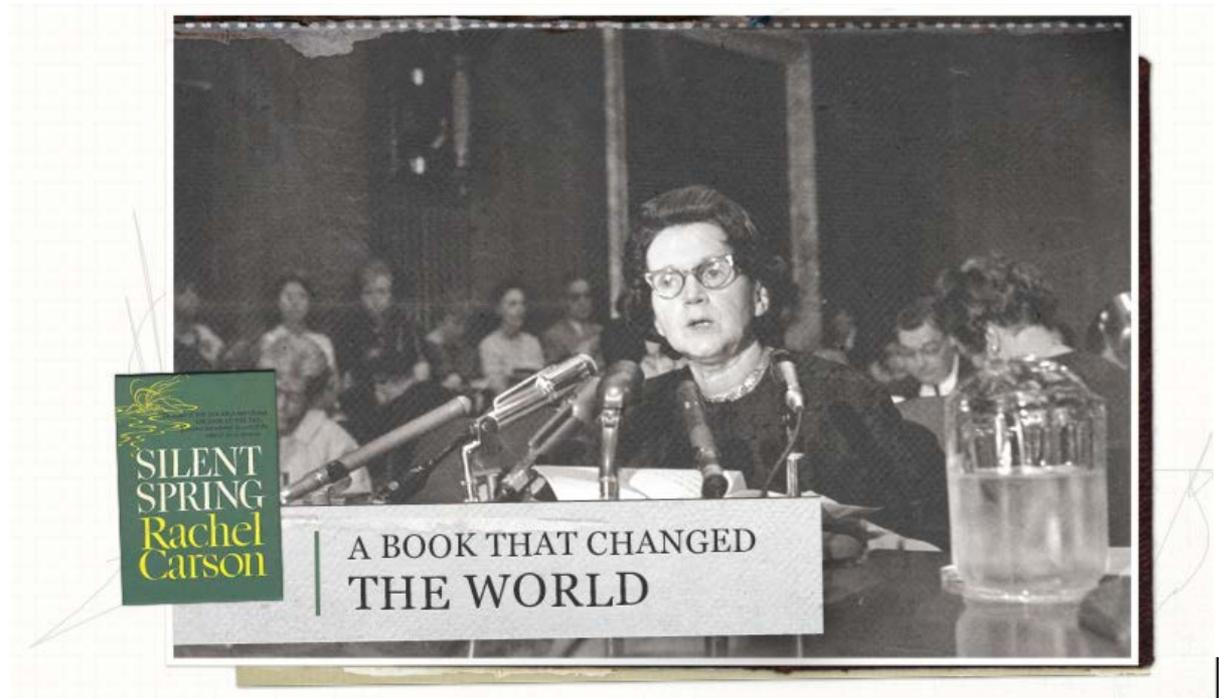
1962 - Rachel Carson's book *Silent Spring* blamed environmental destruction on DDT.

492

1946.

HILDREN

ts!



preliminary and served as a basis for subsequent field work on mosquitoes pending more detailed studies by the Fish and Wildlife Service and various State agencies to determine more fully the relation of various formulations of DDT to wildlife in general.

heavy rains shortly after application.

Another small pond was treated at the rate of 2.0 p.p.m. with a suspension containing 10 per cent each of DDT and Nopco 1216 (sulfonated sperm oil) in Cellosolve (ethyl ether of ethylene glycol). This pond was full of water lilies and at the shallow end there

Another Product of TRIMAX CO., INC., Division of UNITED WALLPAPER

World's Leading Designer and Largest Manufacturer, Merchandise Mart, Chicago 54, Illinois

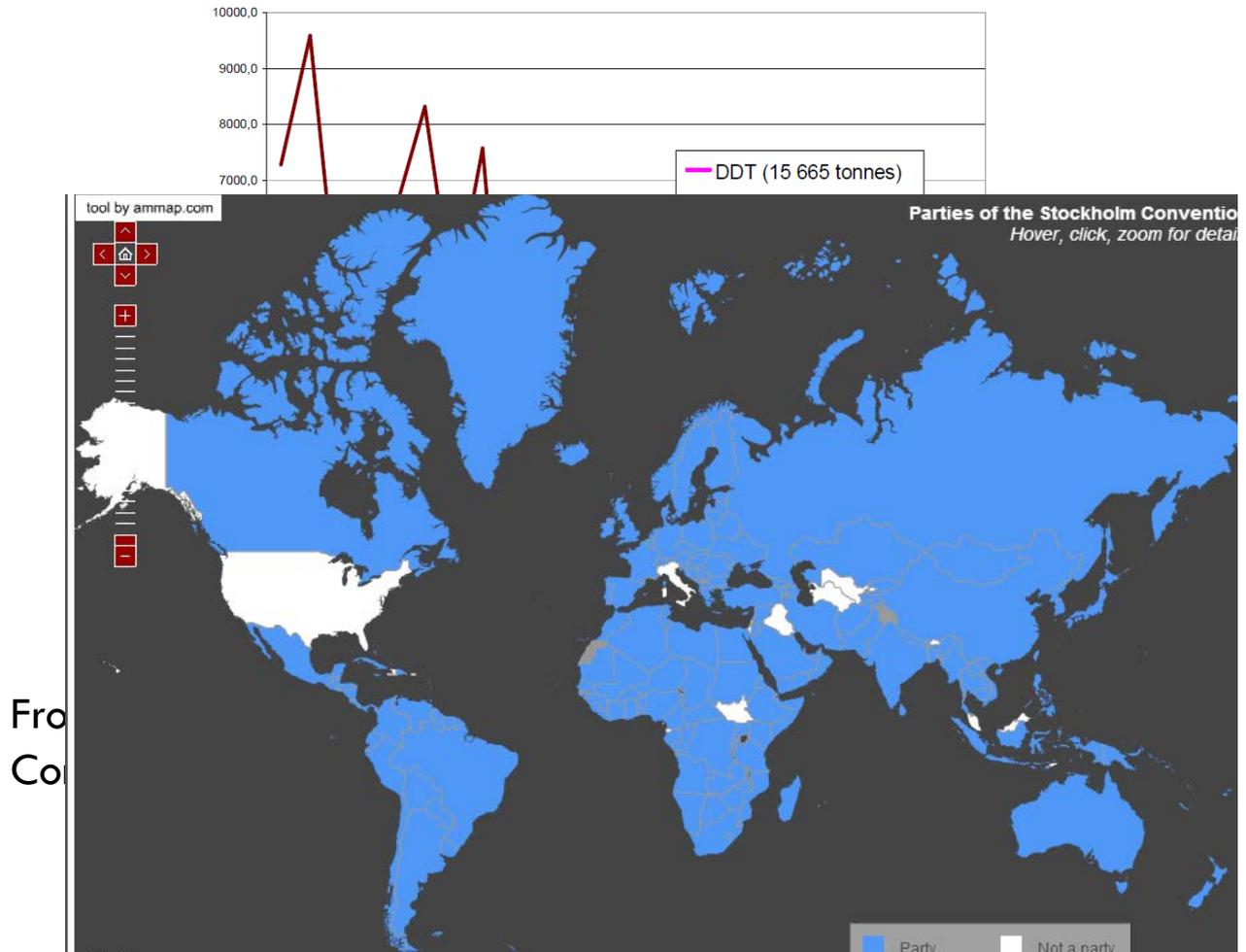


©1947, TRIMAX CO., INC.

DDT – a brief history

1972 – DDT ban in USA and Canada
1974 – DDT ban in Czechoslovakia
1970s, 1980s –ban on DDT in many countries
2001 – Stockholm Convention on POPs – DDT is banned with limited exceptions for malaria control
Currently

Figure 2: The use of selected POPs pesticides in the former Czechoslovakia (values after the name indicate the production figures during the production period)



From
Co

Where is DDT still used?

Legally – for malaria control:

- Botswana, Eritrea, Ethiopia, India, Madagascar, Marshall Islands, Mauritius, Morocco, Mozambique, Namibia, Senegal, South Africa, Swaziland, Uganda, Venezuela, Yemen, Zambia
- Illegal use continues in limited locations? Sometimes, especially if previously stockpiled.

DDT – What are the concerns?

Persistence, toxicity, long-range transport and bioaccumulation/biomagnification!

What are typical trends in DDTs?

SumDDT compounds in ice core from Mt. Everest glacier

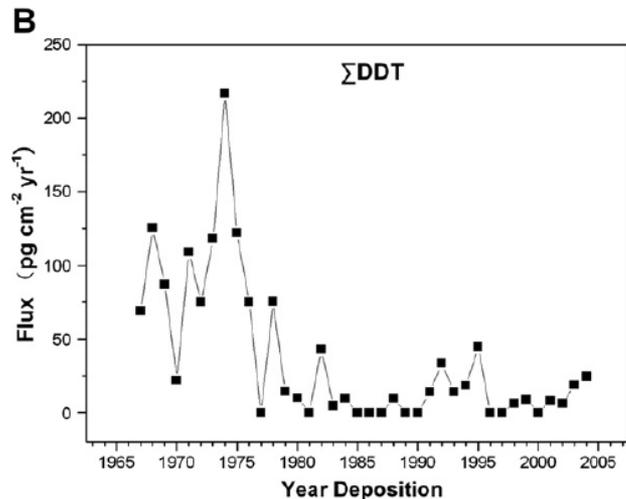
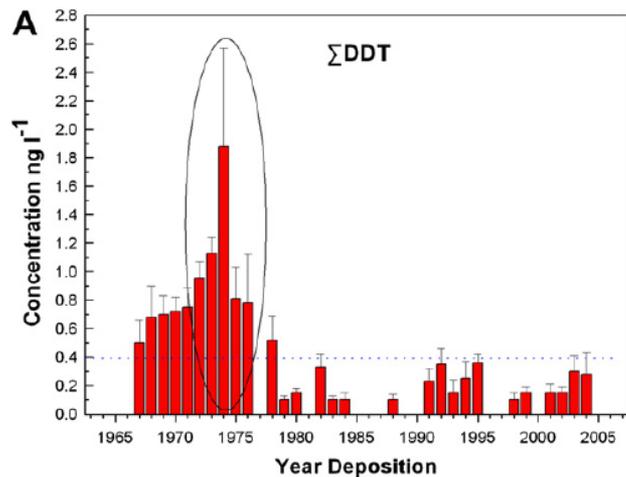


Fig. 4. Concentration (A) and deposition flux (B) of DDT in the ice core from East Rongbuk glacier (Mt. Everest, The Himalayas).

(Wang et al., Atmospheric Environment, 2008)

DDT compounds in precipitation from North America, 1995-2005

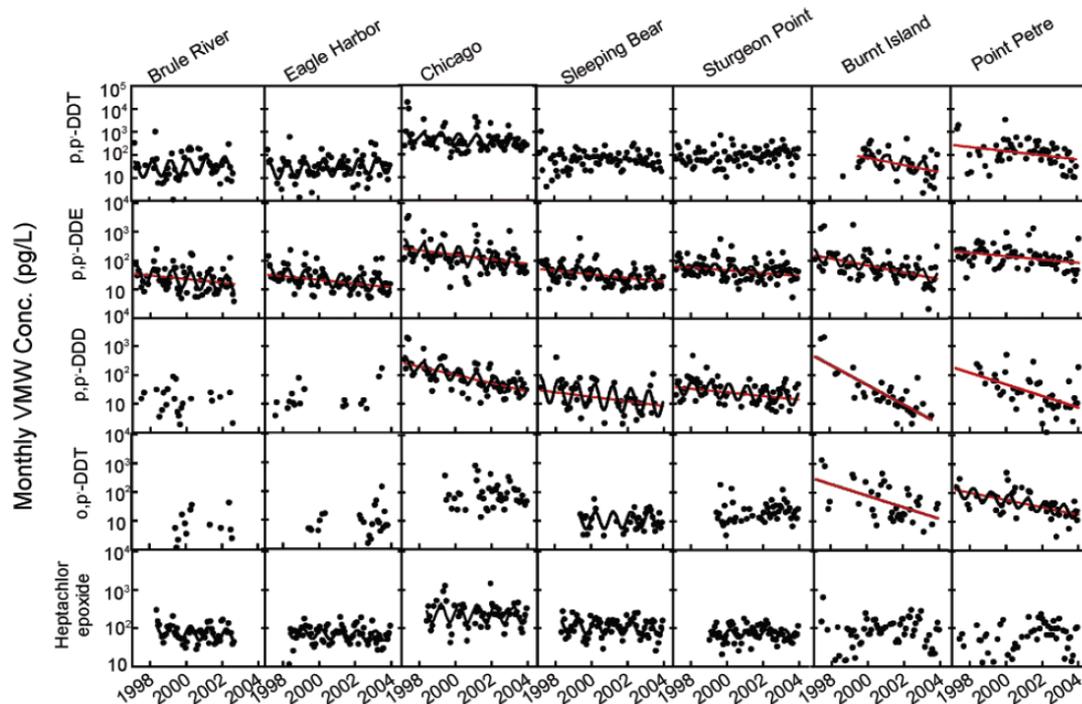


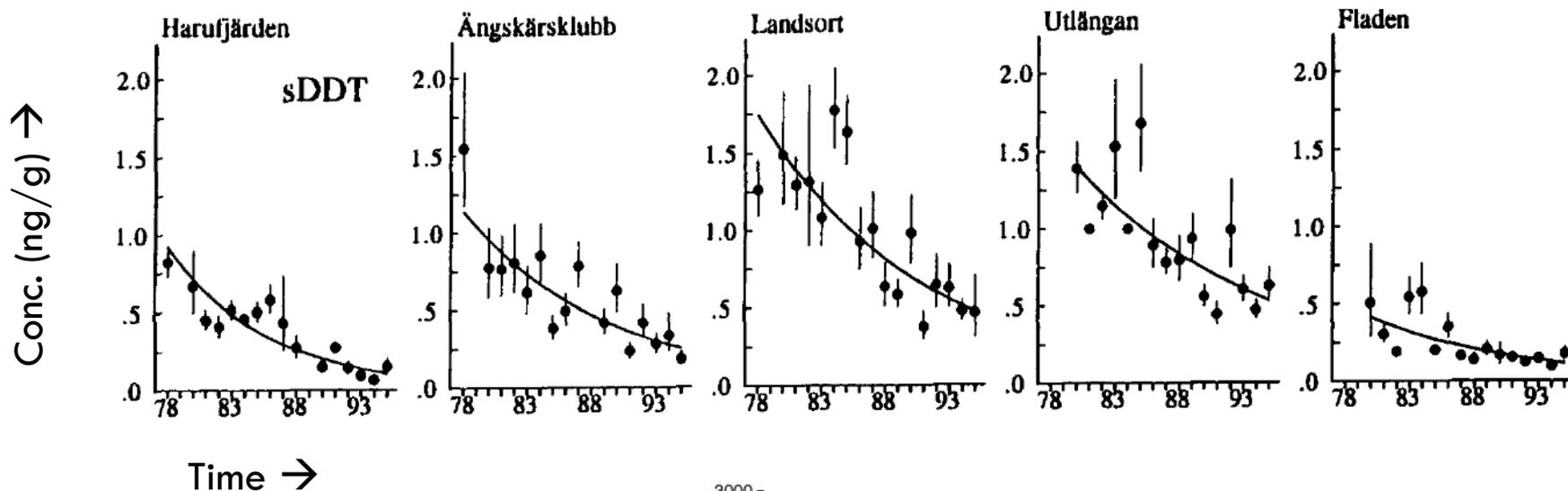
FIGURE 4. Organochlorine pesticide concentrations in precipitation collected at 7 IADN sites near the Great Lakes. The black curve is the fitted line of the sinusoidal model with the period length (a_2) set to one year. The red lines indicate long-term significant decreasing or increasing trends. Detailed information on the fitted parameters is in the Supporting Information.

(Sun et al., Environmental Science and Technology, 2006)

What are typical trends in DDTs?

SumDDT compounds in herring fish from Sweden from 1977-1995

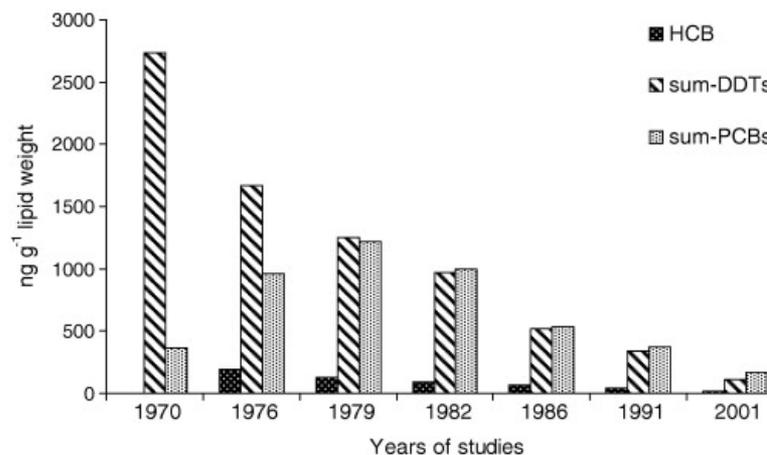
A. Bignert et al./Environmental Pollution 99 (1998) 177-198



A. Polder, C. Thomsen, G. Lindström, K.B. Løken, J.U. Skaare

Levels and temporal trends of chlorinated pesticides, polychlorinated biphenyls and brominated flame retardants in individual human breast milk samples from Northern and Southern Norway

Chemosphere, Volume 73, Issue 1, 2008, 14 - 23



Time trend of levels of HCB, sum-DDTs and sum-PCBs in breast milk

DDT – remaining questions?

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Should DDT Be Used to Combat Malaria?

DDT should be used "with caution" in combating malaria, a panel of scientists recommended today that the spraying of DDT in malaria-plagued Africa and Asia should be greatly reduced because people are exposed in their homes to high levels that may cause serious health effects.

May 4, 2009 | By Marla Cone and Environmental Health News

A panel of scientists recommended today that the spraying of DDT in malaria-plagued Africa and Asia should be greatly reduced because people are exposed in their homes to high levels that may cause serious health effects.

The scientists from the United States and South Africa said the insecticide, banned decades ago in most of the world, should only be used as a last resort in combating malaria.



If Malaria's the Problem, DDT's Not the Only Answer

By May Berenbaum
Sunday, June 5, 2005

In the pantheon of poisons, DDT occupies a special place. It's the only pesticide celebrated with a Nobel Prize: Swiss chemist Paul Mueller won in 1948 for having discovered its insecticidal properties. But it's also the only pesticide condemned in pop song lyrics -- Joni Mitchell's famous "Hey, farmer, farmer put away your DDT now" -- for damaging the environment. Banned in the United States more than 30 years ago, it remains America's best known toxic substance. Like some sort of rap star, it's known just by its initials; it's the Notorious B.I.G. of pesticides.

Now DDT is making headlines again. Many African governments are calling for access to the pesticide, believing that it's their best hope against malaria, a disease that infects more than 300 million people worldwide a year and kills at least 3 million, a large proportion of them children. And this has raised a controversy of Solomonic dimensions, pitting environmentalists against advocates of DDT use.



To spray or not to spray: Many African nations believe DDT is their only hope against malaria, but the powerful pesticide is not a magic bullet, the author argues. Many mosquito species have become resistant to the poison. Above, in 2001, an Ethiopian girl afflicted by the disease. (By Per-anders Pettersson -- Getty Images)

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Replacements for OCPs

- Current pesticide use is 2.5 million tonnes per year (Alavanja, 2009)
- OCPs are generally no longer used:
 - ~5000 tonnes DDT (produced in China, India and North Korea)¹ – 0.2% of global use
 - Only 6 countries reporting use of other OCPs (Ecuador, Honduras, Iran, Lesotho, Madagascar, Tajikistan, Ukraine) - ~2300 tonnes total in 2011²
- Replacement pesticides should have lower *persistence* and *bioaccumulative* potential

Currently used pesticides

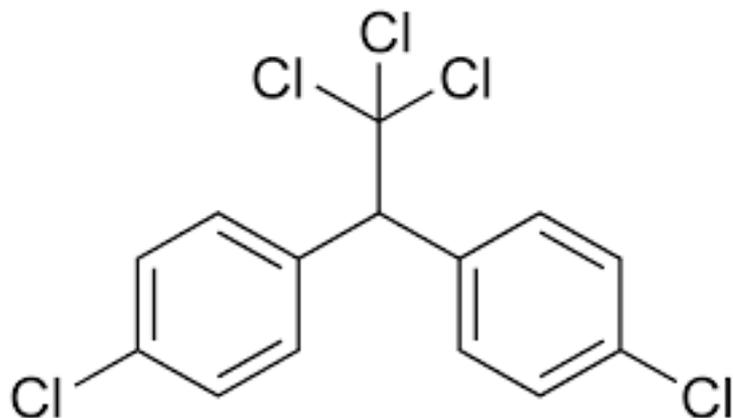
- Glyphosate (“Round-up”)
 - ▣ Herbicide
 - ▣ In use since 1970s
 - ▣ Most widely used chemical pesticide in world
 - ~650000 tonnes per year (>30% of world pesticide market)
- Atrazine
 - ▣ Herbicide
 - ▣ banned in EU but high use in many other countries
 - ▣ 70000 tonnes per year
- Chlorpyrifos
 - ▣ Most widely used insecticide
 - ▣ 170000 tonnes per year (~7% of world pesticide market)

Comparing 2 insecticides:

Chlorpyrifos vs. DDT

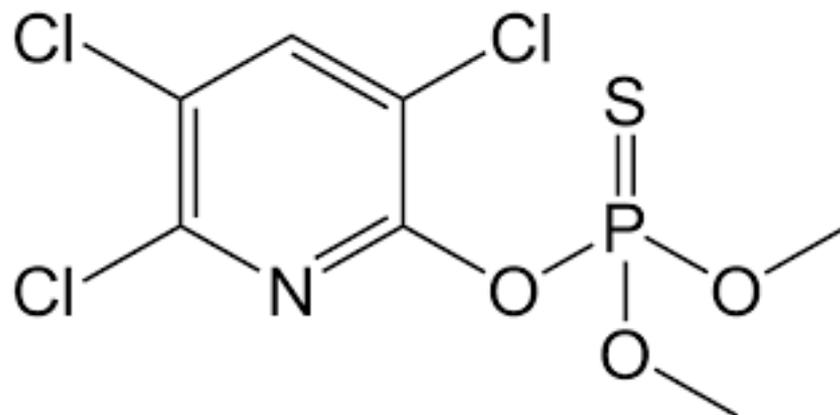
DDT

- Vapour pressure: 0.0003 Pa
- Solubility: 0.025 mg/L
- Half-life in soil: 2-15 yrs
- Overall environmental half-life: 1-5 yrs
- Characteristic travel distance: 255 km



Chlorpyrifos

- Vapour pressure: 0.001 Pa
- Solubility: 2 mg/L
- Half-life in soil: 60-120 days
- Overall environmental half-life: 30 days
- Characteristic travel distance: 62 km



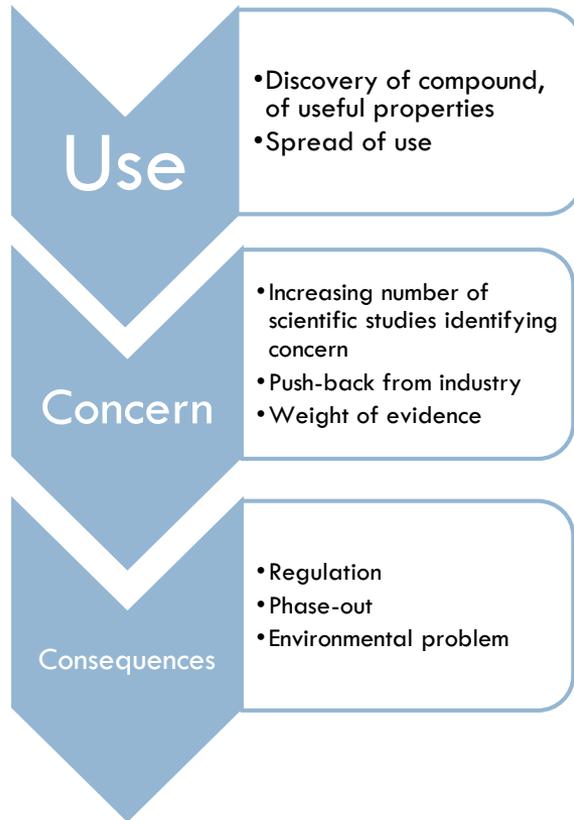


Any questions about pesticides?

Examples of SVOCs

- Pesticides
- **Industrial chemicals**
- By-products
- Additives in consumer products

Polychlorinated biphenyls - PCBs



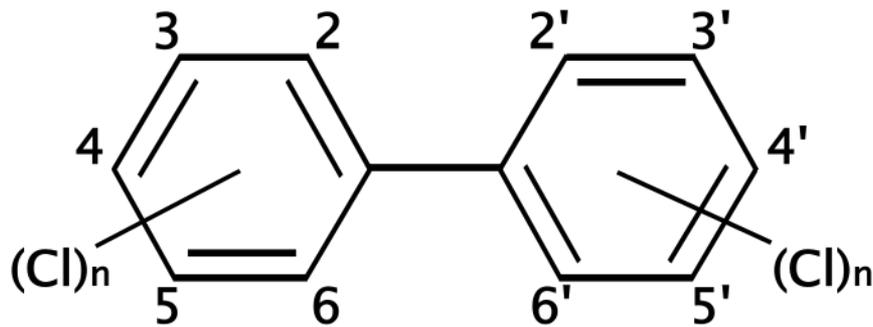
-High chemical and physical stability, even at high temperatures

→Desirable property!

- Industrially produced in 10 countries for a range of uses
- Can also occur as a by-product of some industrial processes, esp. cement production and pulp and paper industries
- First detected in environment in Swedish fish in 1966, many more reports followed
- Concerns about environmental persistence and bioaccumulation
- Production and new use banned by many countries in 1970s, 1980s
- Banned under Stockholm Convention

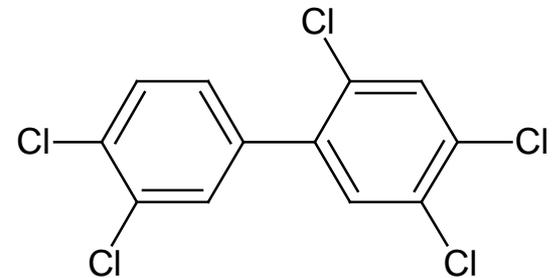
But...PCBs remain in use in old building equipment, electrical equipment, etc.

PCBs – chemical structure

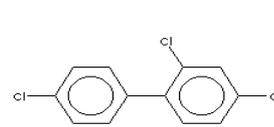


- 209 possible congeners
- 1 to 10 chlorines
- only 130 were used commercially
- Classified based on degree of chlorination

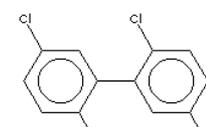
Indicator PCBs – 7 congeners:



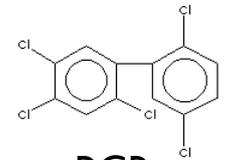
2,3,4,4',5-Pentachlorobiphenyl
PCB 118



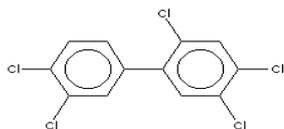
PCB
28



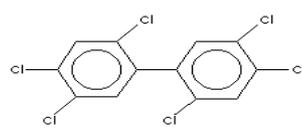
PCB
52



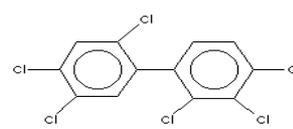
PCB
101



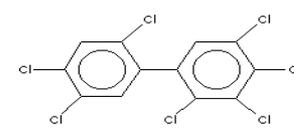
PCB
118



PCB
153



PCB
138



PCB
180

PCBs – health effects

- Acute vs. chronic effects
- Associated with cancer, liver function, skin effects at occupational exposure levels
- Prenatal exposure slows development in children
- Some evidence of link with breast cancer
- Dioxin-like PCBs

What were PCBs used for?

□ Transformers and capacitors

- Other electrical equipment including voltage regulators, switches, reclosers, bushings, and electromagnets
- Oil used in motors and hydraulic systems
- Old electrical devices or appliances containing PCB capacitors
- Fluorescent light ballasts
- Cable insulation
- Thermal insulation material including fiberglass, felt, foam, and cork
- Adhesives and tapes
- Oil-based paint

□ Caulking

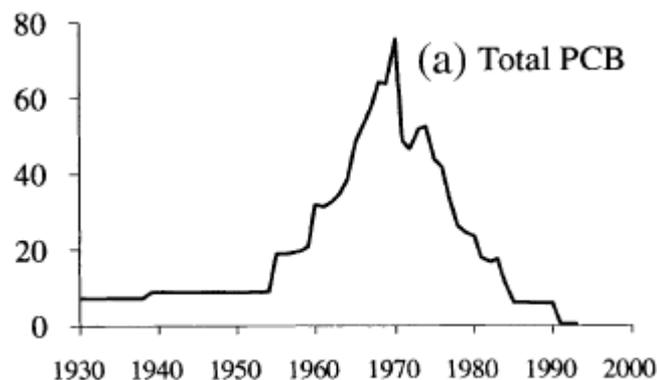
- Plastics
- Carbonless copy paper
- Floor finish



PCB production

Table 1
Total PCB production in t as reported in the literature

Producer	Country	Start	Stop	Amount	Reference
Monsanto	USA	1930	1977	641 246	de Voogt and Brinkman (1989)
Geneva Ind.	USA	1971	1973	454	de Voogt and Brinkman (1989)
Kanegafuchi	Japan	1954	1972	56 326	Tatsukawa (1976)
Mitsubishi	Japan	1969	1972	2461	Tatsukawa (1976)
Bayer AG	West Germany	1930	1983	159 062	de Voogt and Brinkman (1989)
Prodelec	France	1930	1984	134 654	de Voogt and Brinkman (1989)
S.A. Cros	Spain	1955	1984	29 012	de Voogt and Brinkman (1989)
Monsanto	U.K.	1954	1977	66 542	de Voogt and Brinkman (1989)
Caffaro	Italy	1958	1983	31 092	de Voogt and Brinkman (1989)
Chemko	Czechoslovakia	1959	1984	21 482	Schlösserová (1994)
		1939	1990	141 800	AMAP (2000)
		1972	1993	32 000	AMAP (2000)
		1960	1979	8000	Jiang et al. (1997)
		1930	1993	1 324 131	



over 1 million tonnes globally

Why are PCBs still in use?

- Because they are so useful for their purpose!
- Where they were used was not well-documented
- Challenges with removing all PCBs from use – current legislation only requires PCBs to be removed at >50 ppm

CN Tower, Toronto, Canada





Transformer is located in viewing area, 342 m high



Had to be cut apart by hand



Too big to be taken down elevator



Packed piece-by-piece into steel drums, removed by elevator



Any questions about PCBs?

Examples of SVOCs

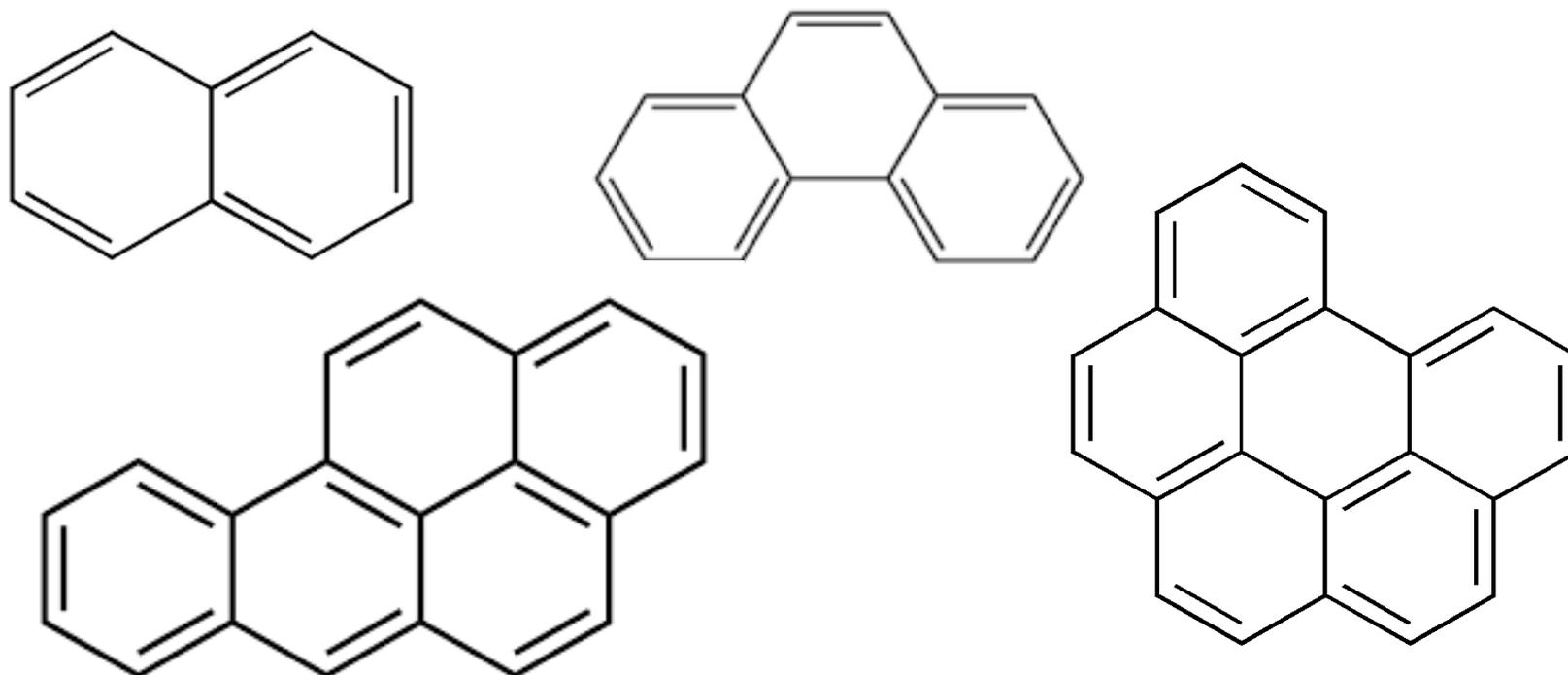
- Pesticides
- Industrial chemicals
- **By-products**
- Additives in consumer products

By-products

- By-products of industrial processes, combustion
- **Unintentionally produced** during industrial processes, fossil fuel combustion for heating, transportation, etc.
- Examples:
 - ▣ Polycyclic aromatic hydrocarbons
 - ▣ Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans

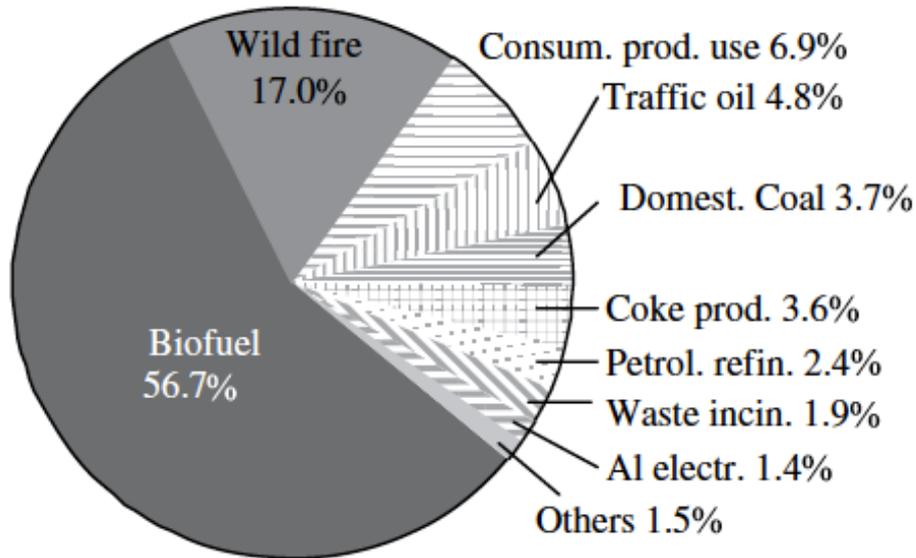
Polycyclic Aromatic Hydrocarbons (PAHs)

- By-products of combustion or fossil fuel processing
- Composed of two or more aromatic rings
- Many possible structures, but typically 3 to 6 rings

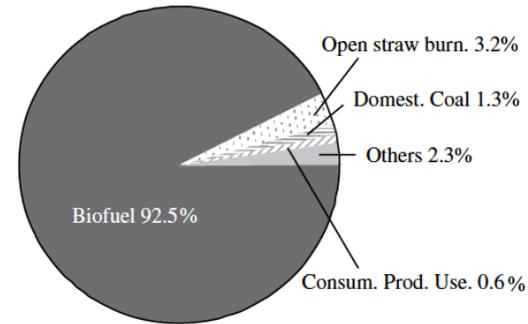


PAH Sources

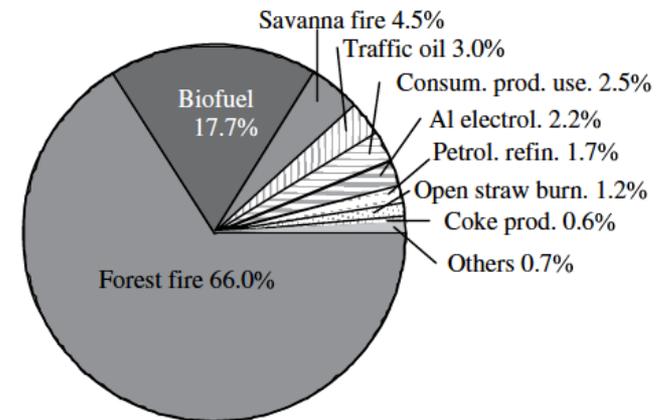
PAH16:



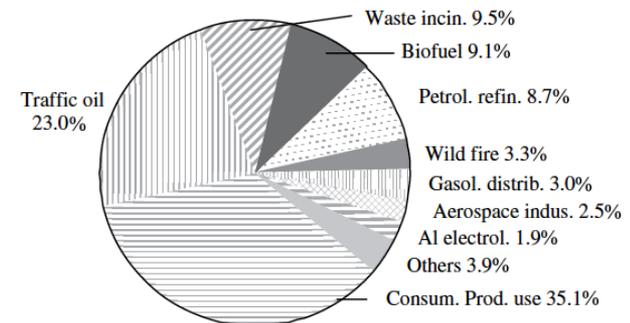
Global (530 Gg/y)



India (90 Gg/y)

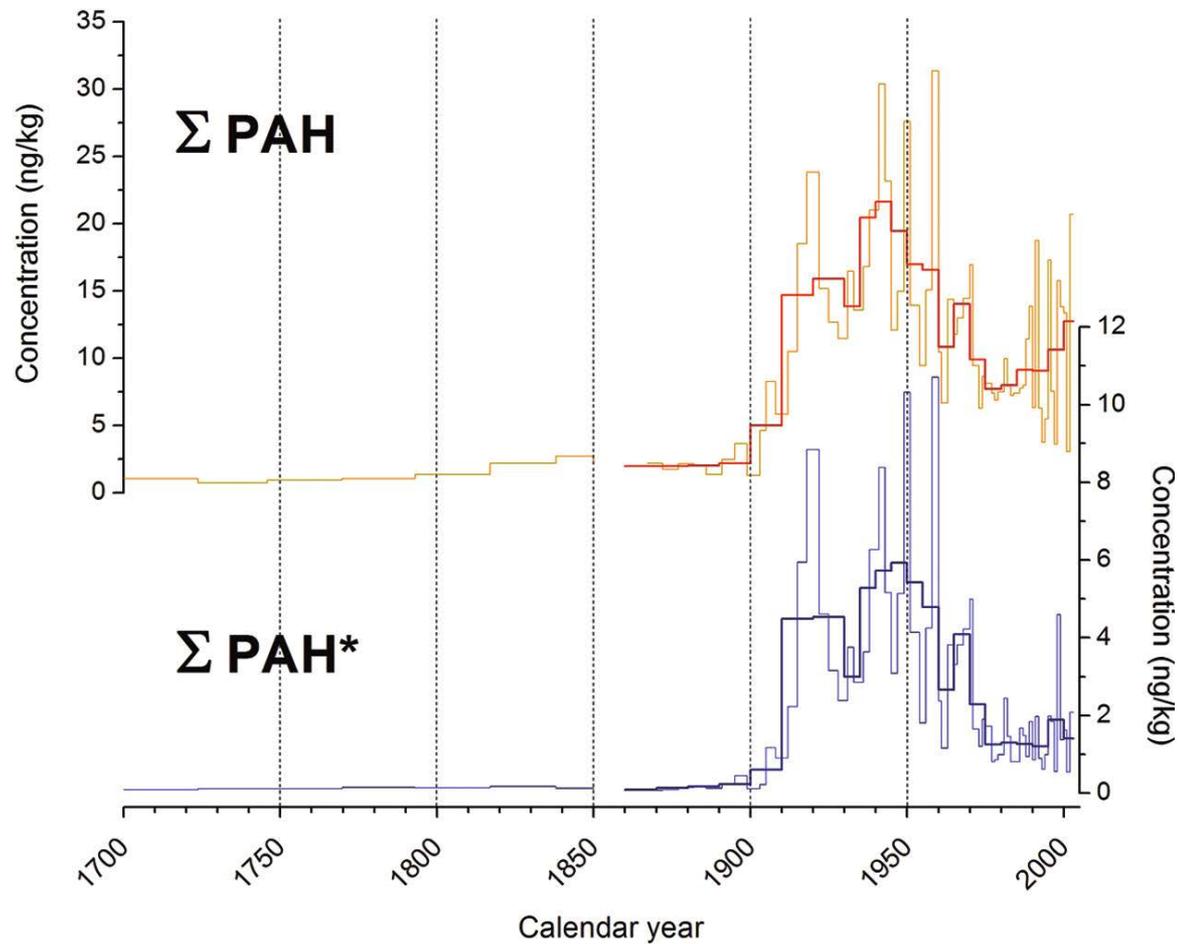


Brazil (19 Gg/y)



USA (32 Gg/y)

PAHs over the past 300 years





Any questions about PAHs?

Examples of SVOCs

- Pesticides
- Industrial chemicals
- By-products
- **Additives in consumer products**

Additives to consumer products

- Flame retardants
- Plasticizers

Flame retardants – organic or inorganic chemicals added to consumer products (furniture, electrical appliances, electronics) to suppress/delay/prevent the spread of fire

Plasticizers – additive chemicals that increase the flexibility, softness, fluidity of a material. Largely used in plastics.

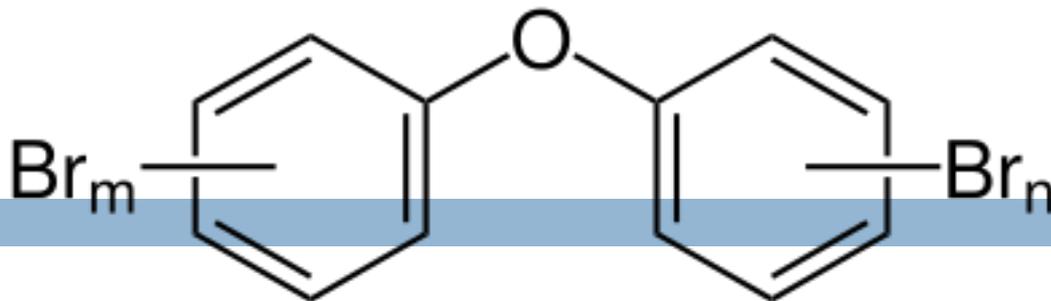
Flame retardants



<http://www.jptarpaulins.com/>

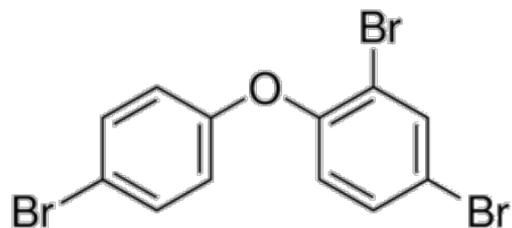
- To slow the spread of flames
- Organic or inorganic
- Wide range of applications (furniture, electronics, industrial/workplace textiles and protective equipment, vehicles)
- Required by fire safety regulations

PBDEs



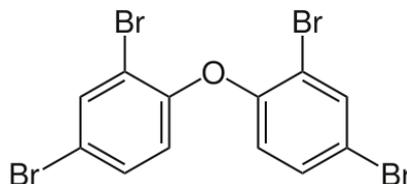
- Polybrominated diphenyl ethers
- Flame retardants
- Classified by either technical mixture or congener group
 - Confusing!! E.g., penta-BDE can refer to either the technical mixture called “Penta” or could refer to a PBDE with 5 bromines
 - Commercial mixtures sometimes distinguished as “c-penta”

PBDE naming - congeners



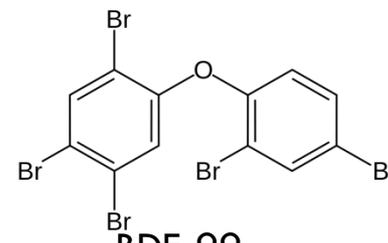
BDE-28

Tribromodiphenyl ether



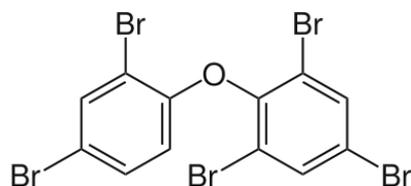
BDE-47

Tetrabromodiphenyl ether



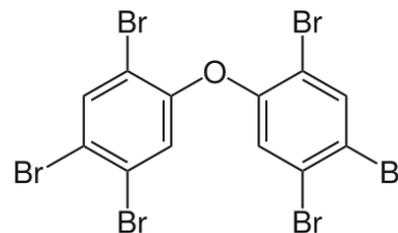
BDE-99

Pentabromodiphenyl ether



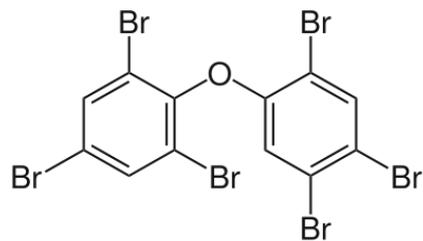
BDE-100

Pentabromodiphenyl ether



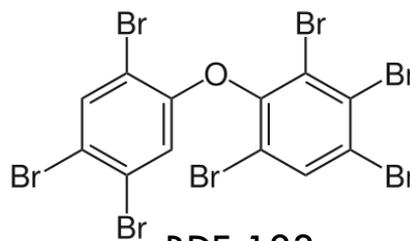
BDE-153

Hexabromodiphenyl ether



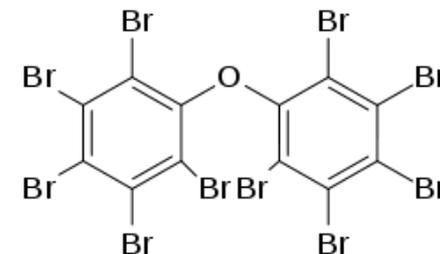
BDE-154

Hexabromodiphenyl ether



BDE-183

Heptabromodiphenyl ether



BDE-209

Decabromodiphenyl ether

Polybrominated Diphenyl Ethers: Uses

Penta

- ✦ Textiles, PUF, paint, household plastic products, automotive parts
- ✦ banned under Stockholm Convention

Octa

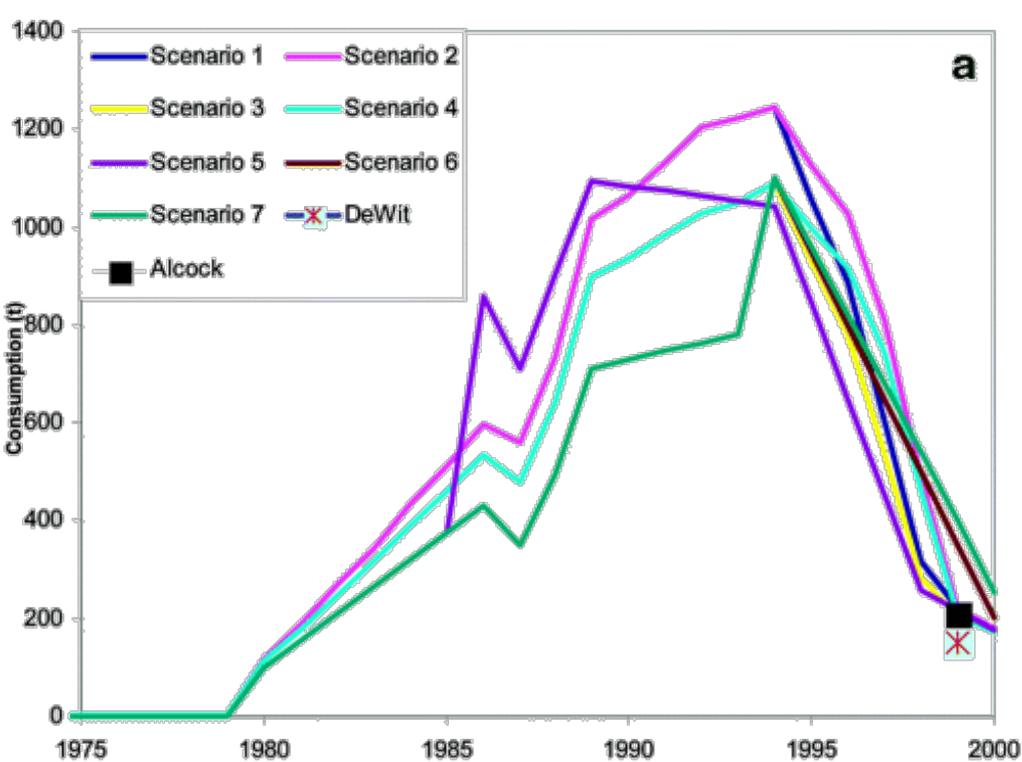
- ✦ ABS plastic for computers, casings, circuit boards, small appliances
- ✦ banned under Stockholm Convention

Deca

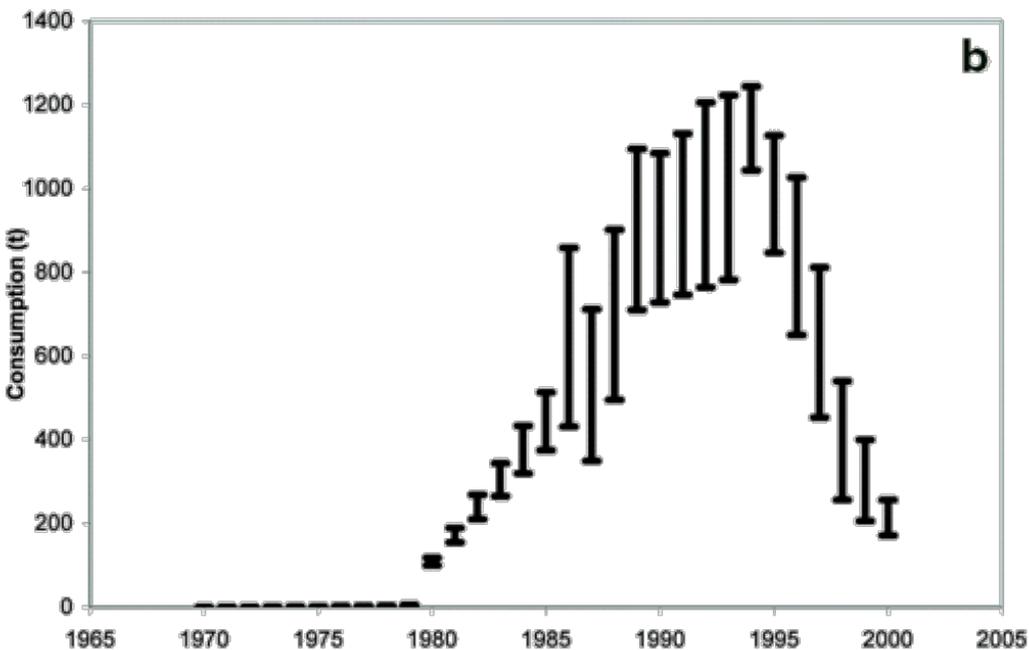
- ✦ Electrical & electronic equipment, casings for TVs, computers, textile backings (e.g., carpets)
- ✦ Still in use in some areas, phased out in Europe, North America

Human health concerns for PBDEs

- Thyroid active agents
 - ▣ Neurological impairments
- Maturation
 - ▣ Delay in puberty
- Developmental neurotoxicity
 - ▣ Impaired spontaneous motor behaviour, nonhabituation behaviour
- Learning & memory
 - ▣ Worsen with age



Estimated Historical Consumption Of Penta BDE in Europe



Prevedouros et al. 2004
 Environ Sci Technol
 38:3224-3231

Estimated Consumption Of BDEs in North America

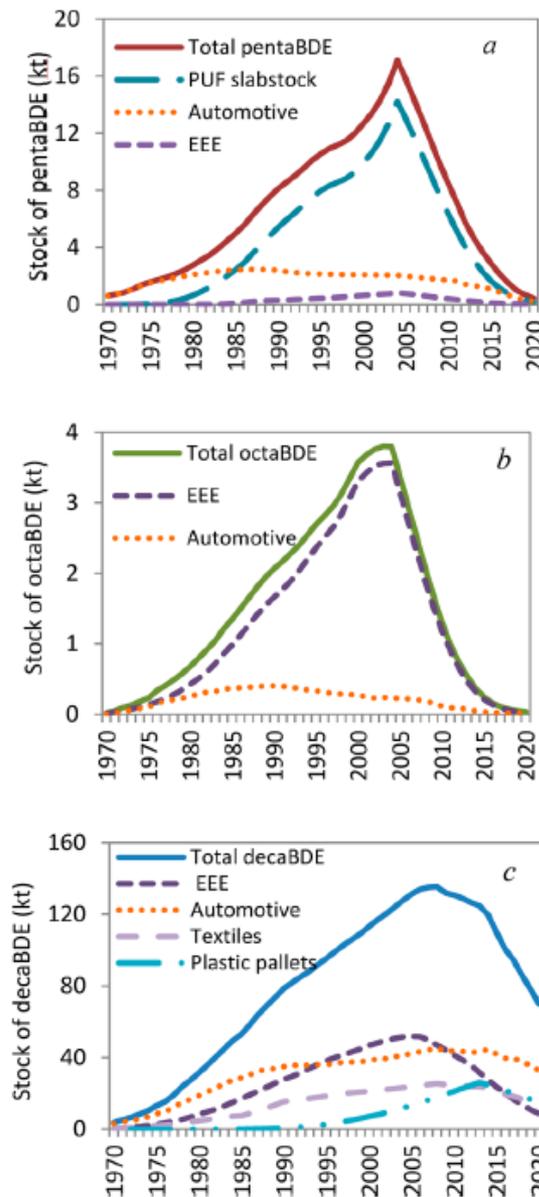


Figure 2. Stock of each PBDE commercial mixture in in-use products in the U.S. and Canada from 1970 to 2020, (a) pentaBDE in EEE, automotive vehicles, and PUF slabstock used in furniture, (b) octaBDE in automotive vehicles and EEE, and (c) decaBDE in plastic pallets, textiles, EEE, and automotive vehicles.

How to PBDEs get from furniture into the environment?

- Volatilization
- Abrasion, physical breakdown of the furniture
- Direct partitioning to dust

Global distributions of PCBs and PBDEs

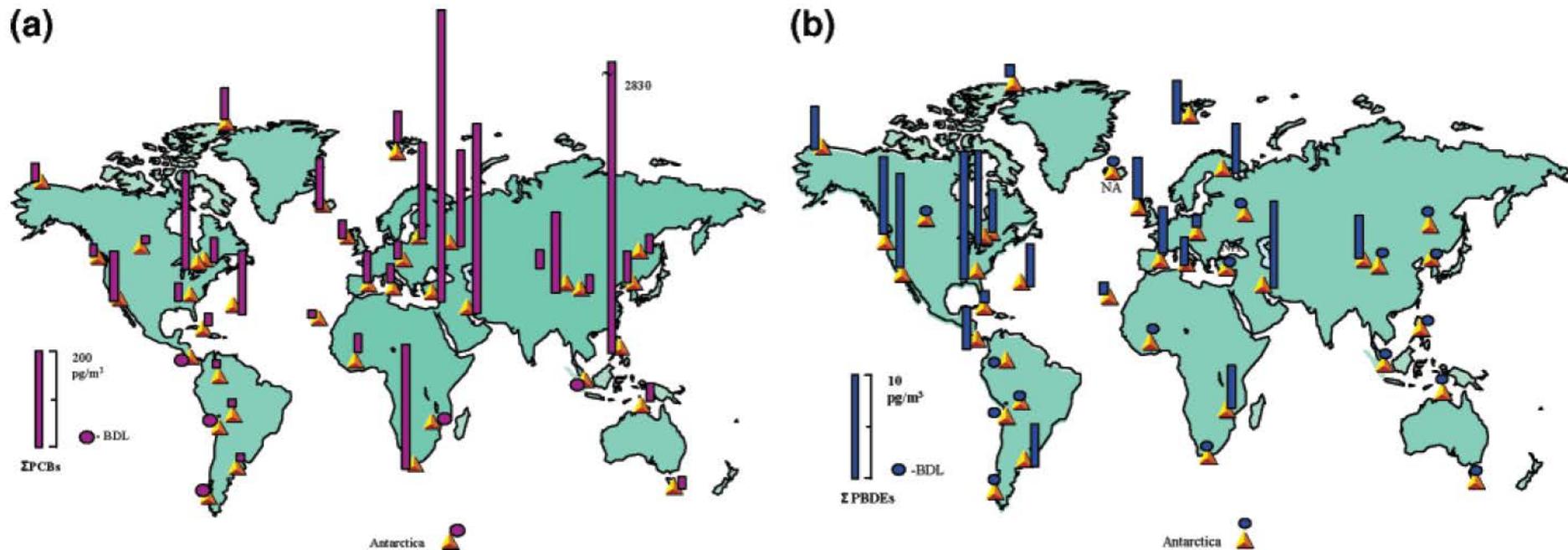


FIGURE 4. Air concentrations (pg/m³) of (a) PCBs and (b) PBDEs between December 2004 and March 2005 at GAPS sites. See Table S1 for BDL values.

From Pozo et al. 2006

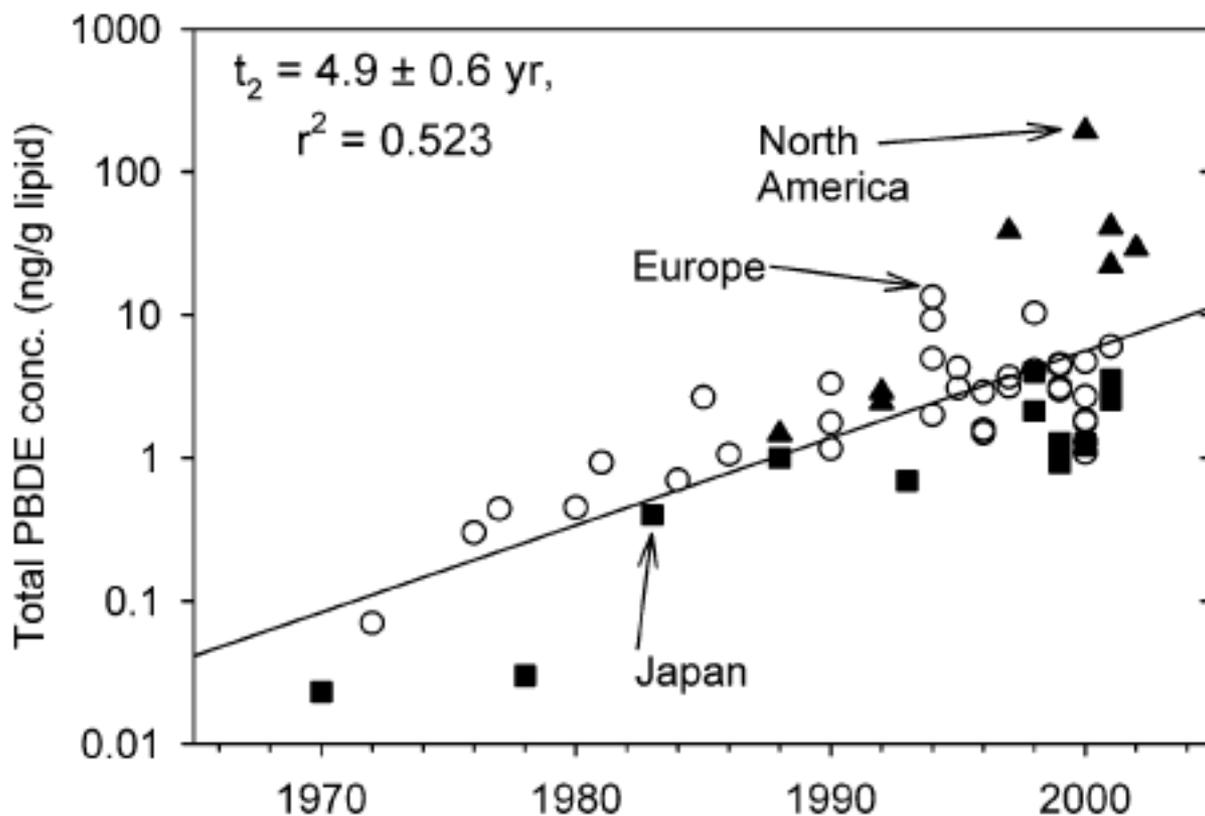
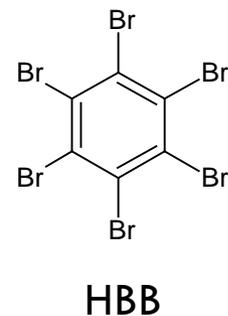
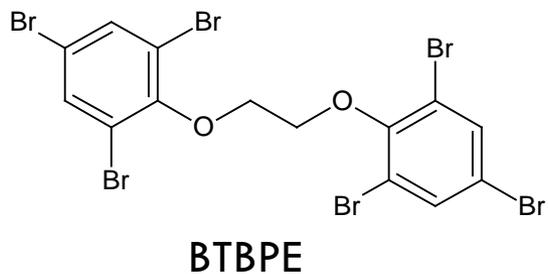
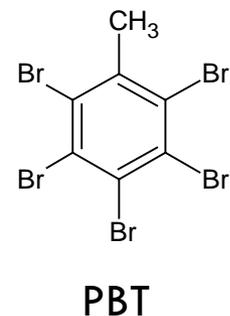
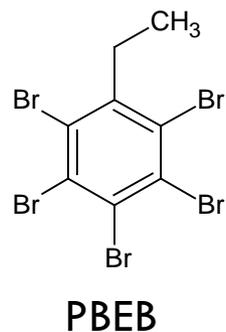
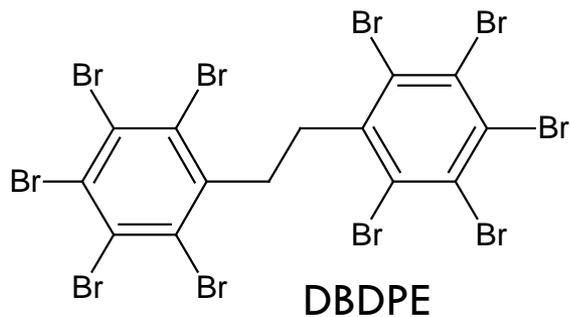
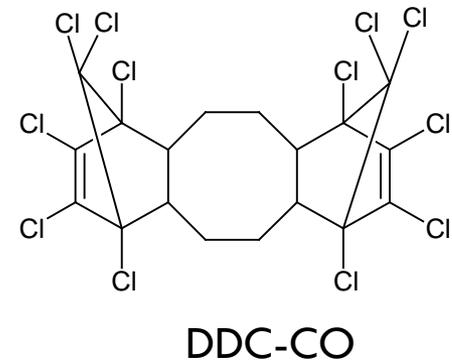
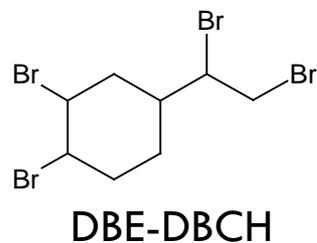
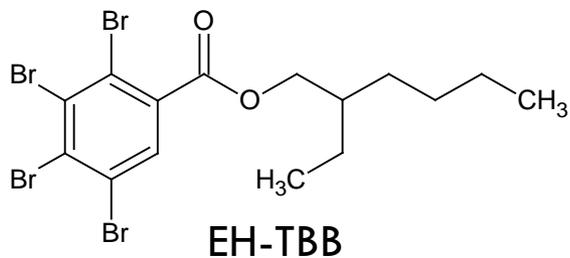


FIGURE 1. Total PBDE concentrations (Σ PBDE) in human blood, milk, and tissue (in ng/g lipid) shown as a function of the year in which the samples were taken; see Table 2. The three symbol types indicate the location from which the samples were collected. The overall regression is shown.

“Novel” flame retardants - NFRs – replacements for PBDEs



Phosphate- based flame retardants in consumer products

TABLE 1. Characteristics of the Polyurethane Foam Samples Analyzed in This Study^a

sample ID	source	year purchased	flame retardant detected	% by weight of flame retardant
1	chair	2004	unidentified	
2	mattress pad	2009	N/D	
3	leather couch	2005	unidentified	
4	sofa bed	2008	TDCPP	1.3
5	chair	2008	N/D	
6	foam from footstool	2006	TCPP	2.2
7	headrest of chair	2008	TCPP	0.5
8	chair	2006	TDCPP	3.2
9	chair	2004	TDCPP	3.0
10	chair	2007	TCPP	1.5
11	futon	N/A	pentaBDE	0.5
12	ottoman	2007	TCPP	0.7
13	chair	2003	TDCPP	1.0
14	chair	2006	TDCPP	2.9
15	pillow	2006	TDCPP	2.8
16	chair	2007	TDCPP	3.8
17	chair	2005	TDCPP	3.2
18	mattress pad	2006	TDCPP	1.2
19	couch	2007	TDCPP	5.0
20	chair	2005	TDCPP	2.5
21	office chair	2005	N/D	
22	futon	2008	TDCPP	2.8
23	nursery glider/rocker	2009	TDCPP	2.9
24	foam insulation from sieve/shaker	2008	TDCPP	2.2
25	baby stroller	2009	TDCPP	NM
26	couch	2007	TBB, TBPH	4.2

^a N/A - Not available. N/D - Not detected. NM - not measured due to low mass of foam available. TDCPP - Tris-(1,3-dichloro-2-propyl)phosphate. TCPP - Tris(1-chloro-2-propyl)phosphate. PentaBDE - Pentabromodiphenyl ether commercial mixture. TBB - ethylhexyl 2,3,4,5-tetrabromobenzoate. TBPH - bis(2-ethylhexyl) tetrabromophthalate.



Any questions about flame retardants?

Stockholm Convention

- Stockholm Convention on Persistent Organic Pollutants is an **international environmental treaty**, signed in **2001** and effective from **May 2004**, that aims to eliminate or restrict the production and use of persistent organic pollutants (POPs).
- Now with 21 compounds/compound groups in 3 categories
 - ▣ Annex A – countries must eliminate production and use
 - ▣ Annex B – countries must restrict production and use
 - ▣ Annex C – countries must reduce unintentional releases

Stockholm Convention Compounds

- Pesticides: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, pentachlorobenzene, hexachlorobenzene, mirex, toxaphene, hexachlorocyclohexane, chlordecone, pentachlorophenol and its salts/esters, endosulfan
- Industrial and household chemicals: hexachlorobenzene, hexabromobenzene, polychlorinated biphenyls (PCBs), hexabromocyclododecane, tetraBDE and penta BDE (c-pentaBDE), hexaBDE and heptaBDE (c-octaBDE), perfluorooctane sulfonic acid and its salts, polychlorinated naphthalenes
- By-products: pentachlorobenzene, hexachlorobenzene, hexachlorobutadiene, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), and PCBs

Stockholm Convention compounds

Annex	
A <u>eliminate</u>	Aldrin, Chlordane, Chlordecone, Dieldrin, Endrin, Heptachlor, Hexabromobiphenyl, Hexabromocyclododecane, Tetra & PentaBDEs, Hexa & HeptaBDEs, Hexachlorobenzene, Hexachlorobutadiene, Hexachlorocyclohexanes, Mirex, Pentachlorobenzene, Pentachlorophenol and its salts and esters, PCBs, Polychlorinated naphthalenes, technical Endosulfan and isomers, Toxaphene
B <u>restrict</u>	DDT Perfluorooctane sulfonic acid and its salts Perfluorooctane sulfonyl fluoride
C (Unintentional production) <u>reduce</u>	Pentachlorobenzene Hexachlorobenzene PCDD PCDF PCBs Polychlorinated naphthalenes

Chemicals to know

- Particulate matter
- DDT
- PCBs
- PAHs
- PBDEs

What to know...

ABOUT EACH COMPOUND:

- What is the source/use of the compound
 - ▣ Industrial? Emission by-product?
- General information about the structure (is it chlorinated or brominated, is it just one compound or is it a group of compounds...?)
- Status
 - ▣ Is the chemical still in use? Where is it legal/illegal?
- Where do we find the chemical?
 - ▣ In the environment? In humans? How and where are humans exposed?

Class project

- Pick one of the chemicals from the Stockholm Convention that we have not yet discussed
- Prepare a short presentation that answers questions about the compound.
- For details, see handout.

Extra compound info

Dioxins and furans

Phthalates

(not exam material – just for interest)

Dioxins and furans

Dioxins in the news...

BBC News Sport Weather Earth Future Shop

NEWS EUROPE

Home UK Africa Asia Australia Europe Latin America Mid-East US & Canada Business Health

7 January 2011 Last updated at 08:22 GMT



Dioxin animal feed scare shuts German farms

More than 4,700 German farms have been closed after dioxin was found in animal feed.

Officials insist the risk to human health is low, but a precautionary ban on the use of animal feed containing dioxin has been imposed.

Ultimatum for Italy in cheese dioxin scare

Most of the affected farms are in southern Italy.

Meanwhile, the European Commission has said that the dioxin levels in the cheese are not a health risk.

Brussels yesterday increased pressure on Italy to provide details about the scale of a potential crisis over links between cheese and cancer, warning that buffalo mozzarella could be banned across the EU.

The European commission demanded more information from the Italian authorities on carcinogenic dioxins found in buffalo mozzarella made in the Naples area, and set the Italian government a deadline for compliance.

A commission health spokeswoman said buffalo mozzarella could be removed from supermarket shelves across the EU and that Italy faced a European export ban unless Brussels' conditions were met.

Japan and South Korea have already banned imports of the fine cheese made from buffalo herds in the Campania region of southern Italy.

Italy disclosed last week that high levels of dioxins - mostly poisonous chemical byproducts of the manufacture of herbicides and bactericides - were found in the milk of 66 herds of buffalo around Naples. However, none of the tainted cheese had been exported, Italian officials said.

Paolo De Castro, Italy's farming minister, blamed the media for a food scare that has seen Italian sales of mozzarella slump by 30%. In between mouthfuls of the cheese, he said: "The produce has been seized, so there is no health risk." But he

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- Here are your CliffsNotes for the Netanyahu speech
- The case against Netanyahu's speech to Congress
- Sweden blocks plan to honor woman who hit a neo-Nazi with a purse

Posted at 01:47 PM ET, 08/09/2012

Agent Orange's health effects continued long after the Vietnam War's end

By Olga Khazan

The United States and Vietnam on Thursday began a clean-up of the remnants of Agent Orange, a defoliant that American planes sprayed on the South Vietnamese jungle in order to deprive Viet Cong of tree cover during the Vietnam War.

Agent Orange, which contains a compound called dioxin, has been linked to cancer and severe birth defects. Up to three million Vietnamese people were exposed to the chemical and at least 150,000

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Deadly dioxin used on Yushchenko

Tests have revealed that the chemical used to poison Ukrainian opposition leader Viktor Yushchenko was pure TCDD, the most harmful known dioxin.



Yushchenko's disfigurement could take two years to heal

TCDD is a contaminant found in Agent Orange - a herbicide used by US troops in the Vietnam war and blamed for serious health problems.

Mr Yushchenko, who faces PM Viktor Yanukovich in a repeat poll on 26 December, fell ill in September.

Scientists say the poison could not have occurred naturally in his blood.

Blood samples taken in Vienna, where Mr Yushchenko was treated, were sent to the Dutch capital, Amsterdam, for further analysis.

BBC NEWS: VIDEO AND AUDIO
Yushchenko says who is to blame for his illness



THE 'ORANGE REVOLUTION'

KEY STORIES

- Yushchenko poison confirmed
- Ukraine 'stealing Europe's gas'
- Kiev remembers revolution

ANALYSIS AND FEATURES

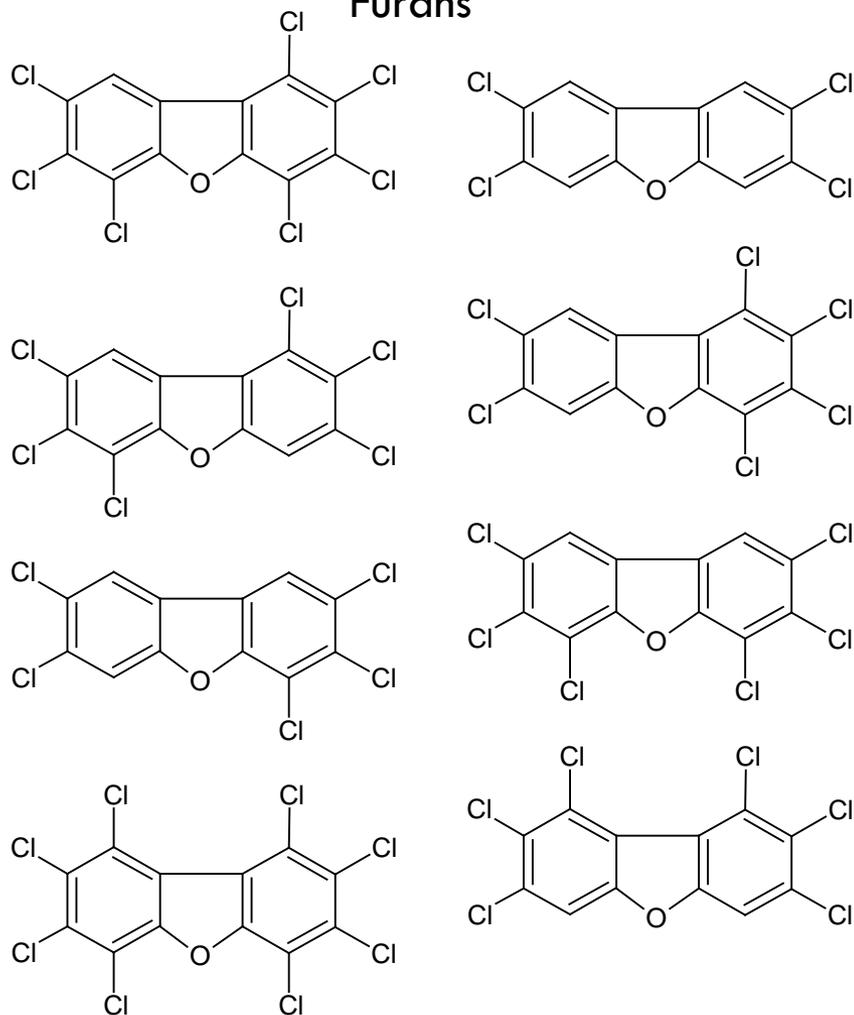


Orange pop
Ukrainians still cherish the sounds of revolution a year on

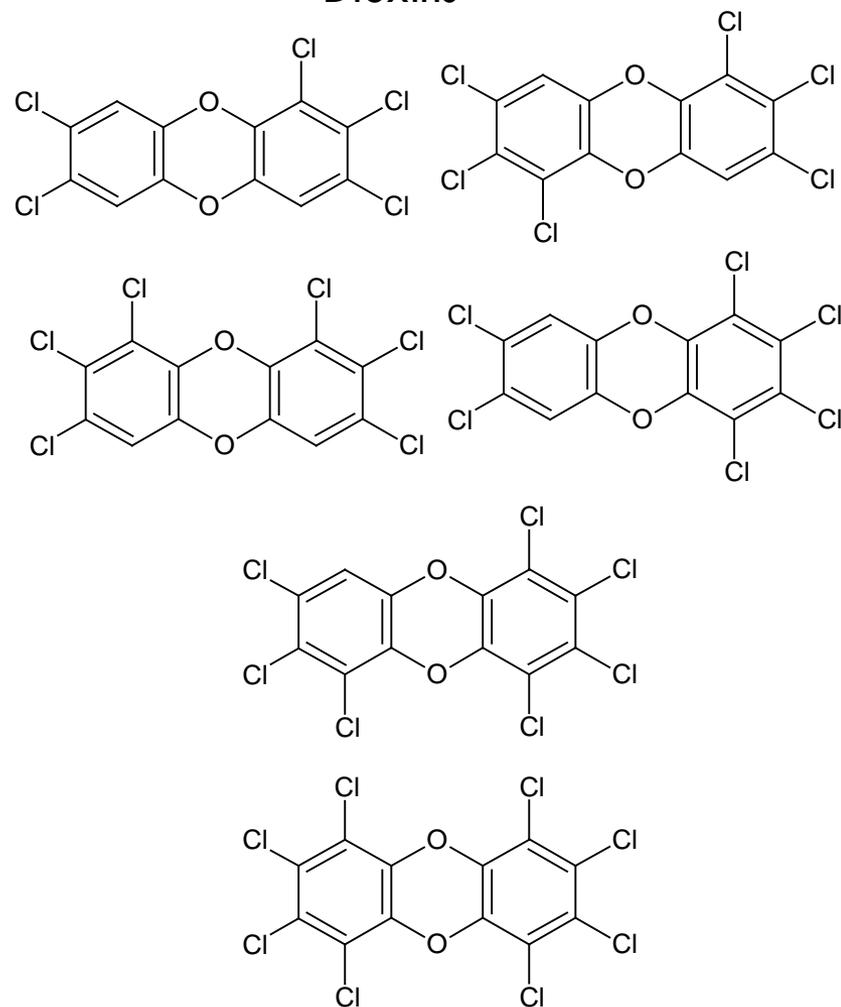
- Cynicism clouds dreams
- Revolution supporters in distress
- Ukraine's heroes turn into foes
- Warm US welcome
- Mending fences with Russia

Dioxins and furans – chemical structures

Furans



Dioxins



Sources of PCDD/Fs

- Unintentionally produced
- During inefficient/incomplete combustion, especially waste burning
- By-product from chemicals manufacturing
- Major sources are: waste incineration, automobile emissions, metal industries, burning of peat, coal, wood

PCDD/F Source Inventory

Table 6
PCDD/PCDF release inventories for Asian countries (1) (DEH, 2004; UNEP, 2004). Releases in g TEQ/a

Cat.	Source categories	Australia – 2002					Cambodia – 2004					Sri Lanka – 2002				
		Air	Water	Land	Product	Residue	Air	Water	Land	Product	Residue	Air	Water	Land	Product	Residue
1	Waste incineration	6.5	0.36	21.9	ND	ND	40.7	0	0	0	0.78	20.3	0.055	NA	NA	0.133
2	Ferrous and non-ferrous metal production	112	0.0	44.4	ND	ND	0.41	0	0	0	1	5.52	ND	NA	NA	49.8
3	Heat and power generation	35.0	0.0	31.8	ND	ND	10.3	0	0	0	1.69	19.3	ND	ND	NA	0.096
4	Production of mineral products	1.9	0.0	0.0	ND	ND	0.099	0	0	0	0	1.37	NA	ND	ND	0.002
5	Transportation	9.1	0.0	0.0	ND	ND	0.005	0	0	0	0	0.54	NA	NA	NA	ND
6	Open burning processes	330	0.0	1030	ND	ND	218	0	14.6	0	316	121	ND	ND	NA	29.4
7	Production and use of chemicals and consumer goods	0.43	0.43	110	ND	ND						ND	ND	ND	0.446	ND
8	Miscellaneous	0.31	0.0	0.15	ND	ND	3.64	0	0	0	0	3.46	ND	ND	ND	0.074
9	Landfills and waste dumps	0.0	2.61	40.3	ND	ND						ND	0.024	ND	6	0.022
1-9	Total	495	3.42	1300	ND	ND	273	0	14.6	0	319	171.5	0.08	0.0	6.45	79.5
	Grand total			1800					607					258		

Australia, Cambodia, Sri Lanka – Main source to air is open burning

Secondary sources are:

Australia – metal production

Cambodia and Sri Lanka – waste incineration and heat and power generation

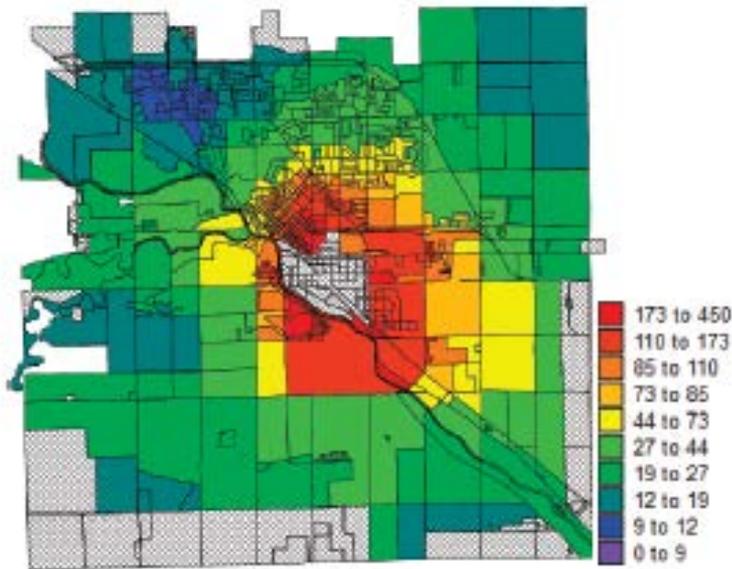
Spatial patterns of PCDD/Fs

- Higher concentrations closer to sources, in highly developed, industrialized areas
- Concentrations patterns in air, soil, sediment and biota mirror each other
- Trends on a large scale – globally – and small scale - locally

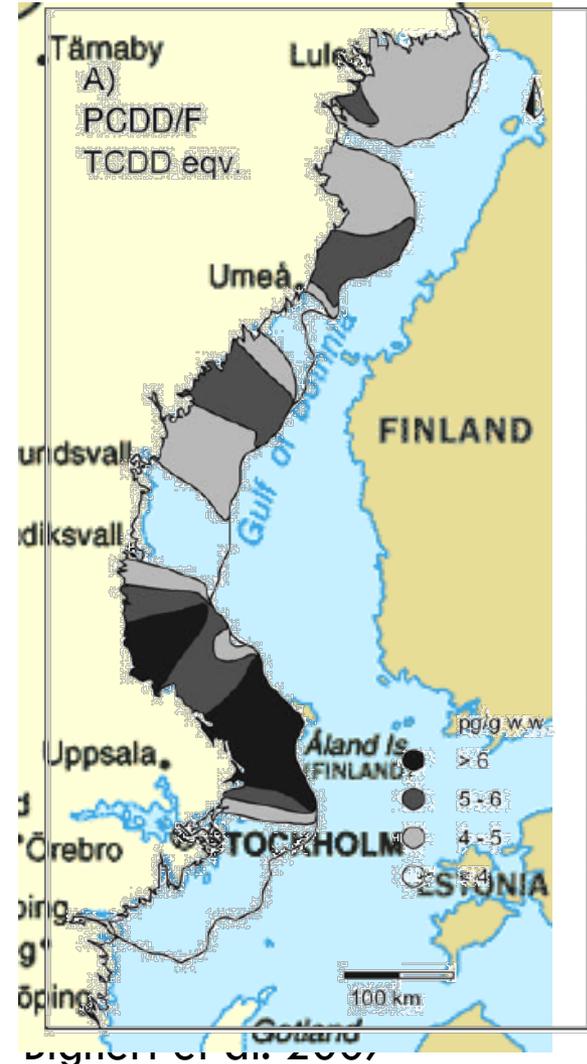
Local scale – PCDD/Fs in soil around an incinerator

Regional scale – PCDD/Fs in fish from the coast of Sweden

(c) Mean concentration



Goovaerts et al. 2008



Plasticizers - Phthalate esters

- One of the most broadly used classes of synthetic compounds
- 1-2 million tonnes per year
- Plasticizers – increase material flexibility and transparency
- Up to 60% by weight of material
- Wide range of uses: vinyl building and construction materials (e.g: flooring, wall coverings, piping), adhesives, sealants, printing inks, paints, and medical applications (eg: blood storage bags), wood finishes, detergents, adhesives, plastic plumbing pipes, lubricants, solvents, insecticides, cosmetics and personal care products, including perfume, hair spray, soap, shampoo, nail polish, and skin moisturizers

Phthalate exposure

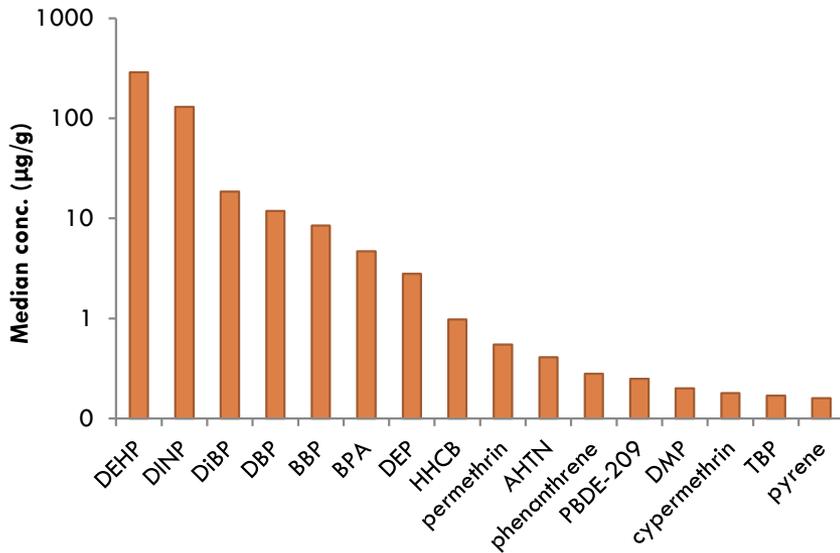
- Through eating, drinking foods that were in contact with phthalate-containing plastics
- Use of personal care products containing phthalates (dermal absorption)
- Inhaling air or ingesting dust containing phthalates

Phthalates

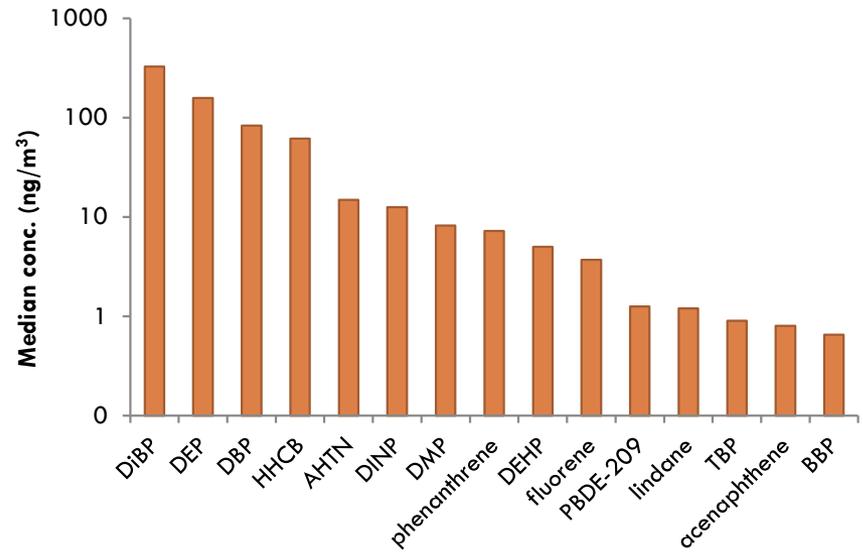
- Usually the highest concentration synthetic compound found in indoor dust and air
- Levels typically 10-100x higher than other SVOCs

Dust and air samples from 30 homes, Western France¹:

Median conc. in settled dust ($\mu\text{g/g}$)



Median conc. in indoor air (ng/m^3)



¹ Blanchard et al. 2014 *Environ Sci Tech*

Health risks of phthalates

- Reproductive effects, especially in men
- Associated with diabetes in women (James-Todd et al., *Environmental health perspectives*, 2012)
- Occurrence of asthma and allergies in children (Jaakkola and Knight, *Environmental health perspectives*, 2010)
- Autism spectrum disorders (Kalkbrenner et al. *Current Problems in Pediatric and Adolescent Health Care*, 2014)

Current regulatory status

IP/11/196

Brussels, 17 February 2011

Chemicals/REACH: six dangerous substances to be phased out by the EU

Six substances of very high concern will be banned within the next three to five years unless an authorisation has been granted to individual companies for their use. These substances are carcinogenic, toxic for reproduction or persist in the environment and accumulate in living organisms. Operators wishing to sell or use these substances will need to demonstrate that the required safety measures have been taken to adequately control the risks, or that the benefits for the economy and society outweigh the risks. Where feasible alternative substances or techniques exist, a timetable for substitution will also have to be submitted. Today's Commission decision follows the successful first phase of registration and notification of chemicals (see [IP/10/1632](#), [IP/11/2](#)). It is part of REACH, Europe's initiative to make the use of chemicals safer.

DEHP, DBP, BBP – should have been banned in EU this year (February 2015)...

But...

“This ban will only cover these substances when they are:

- Supplied on their own;
- Supplied in a mixture;
- Incorporated into an article with the European Union.

Imported articles containing any of these substances that were incorporated outside the EU are not covered by the Authorisation process.”

EU REACH Legislation

DHP – reproductive toxin

DEHP – serious effects on environment

DEHP, DBP, BBP, DIBP – serious effects on human health