

C2003 –

ENVIRONMENTAL CHEMISTRY

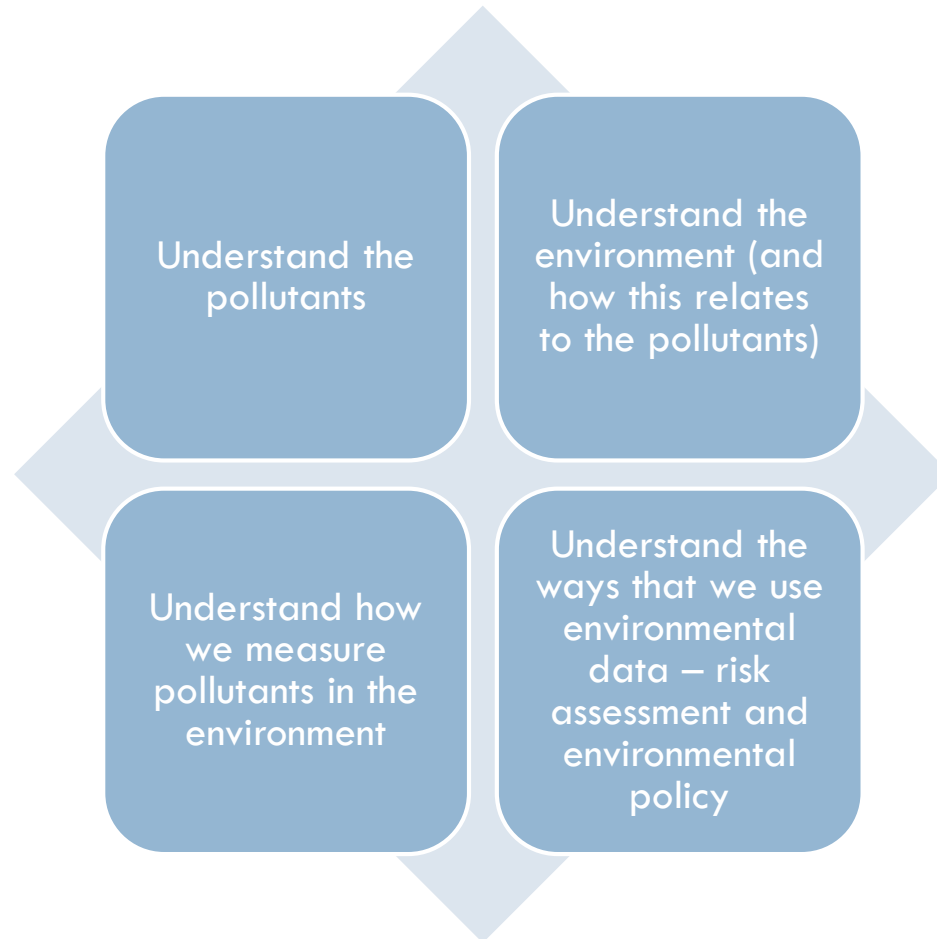


Course goals:

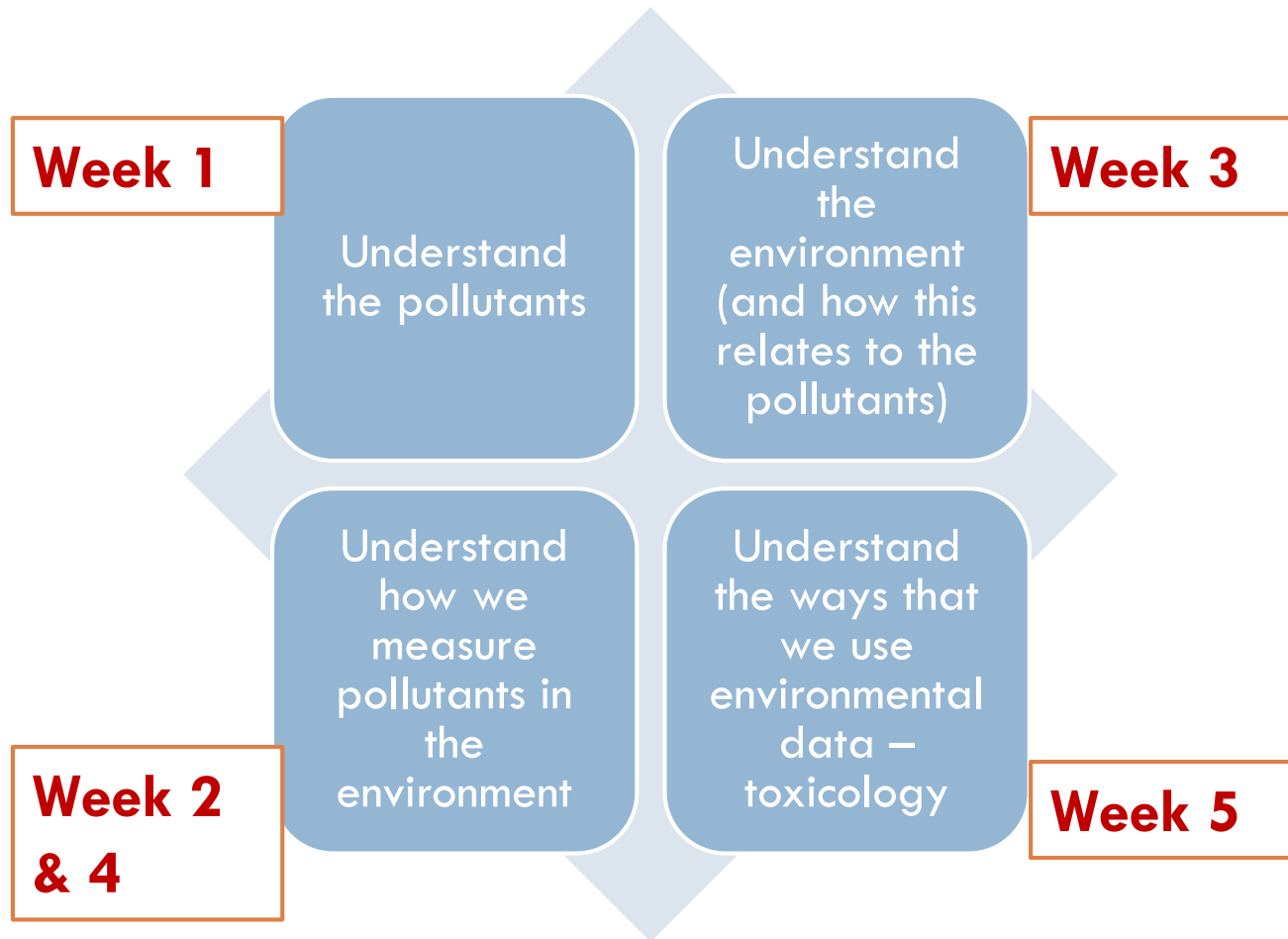
After this course, students should be able to:

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

This is pretty ambitious...so let's break it down a bit...

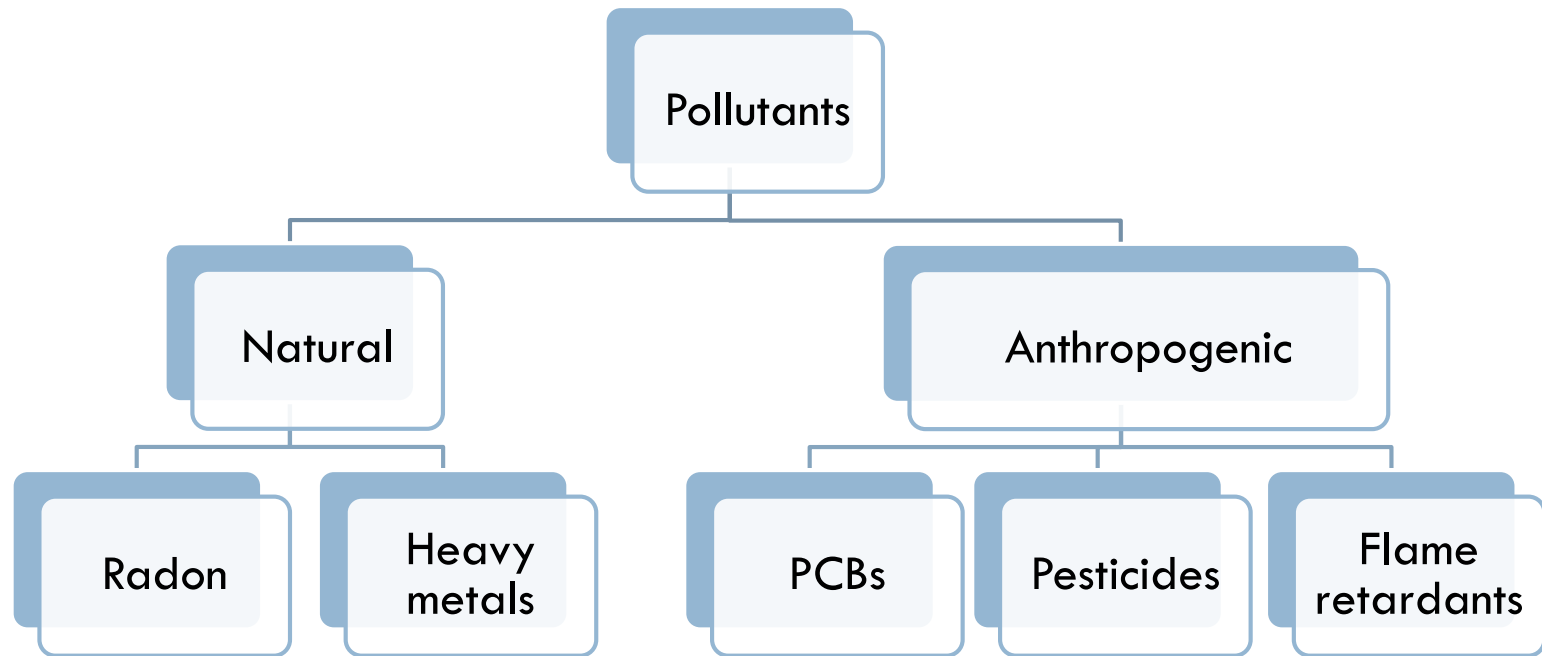


Course overview



What is pollution?

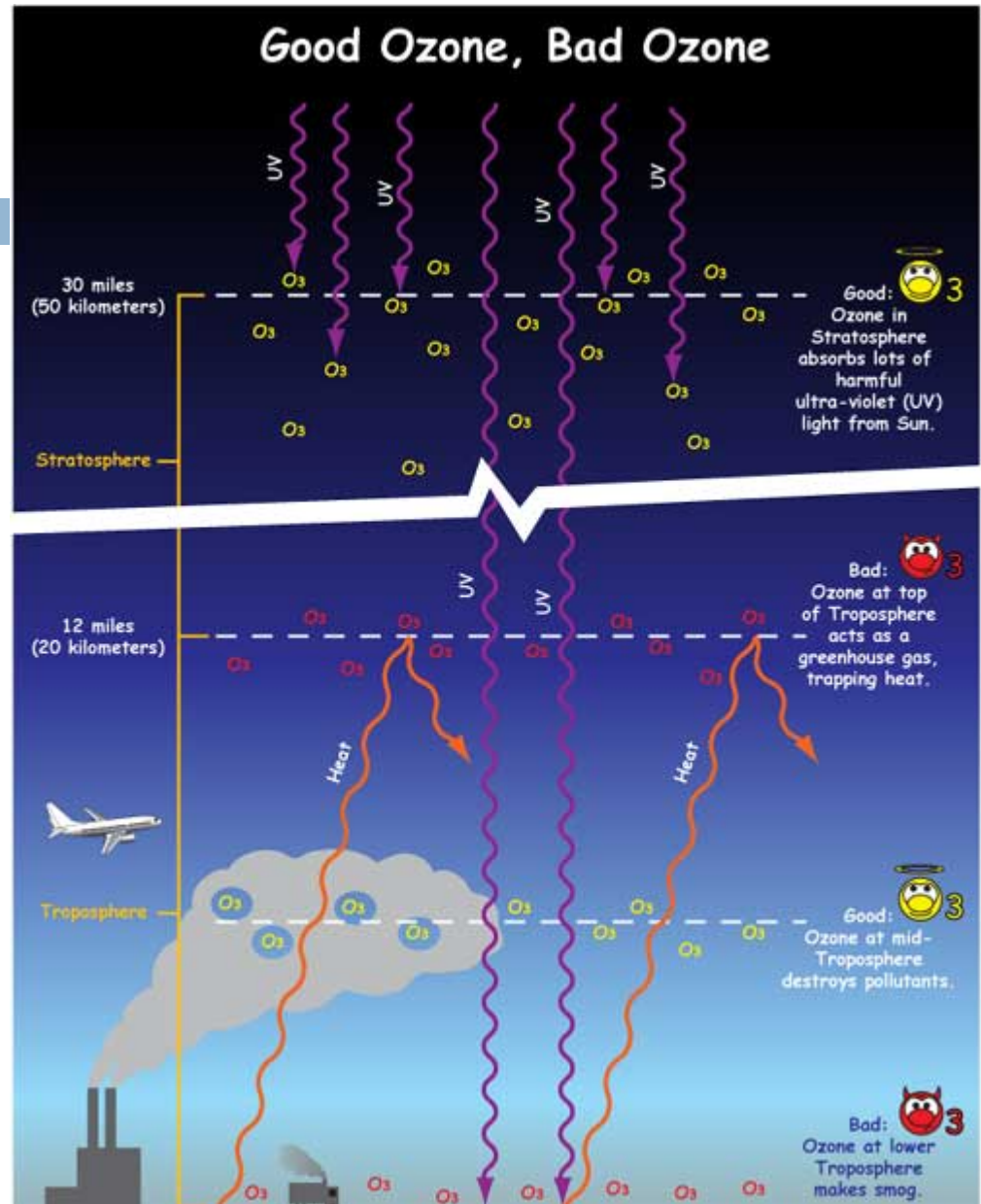
- Presence of a **substance in an environmental system** having a **harmful effect**
- The substance = *pollutant* or *contaminant*



Just a few examples...

Pollution depends on context...

- Many are 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

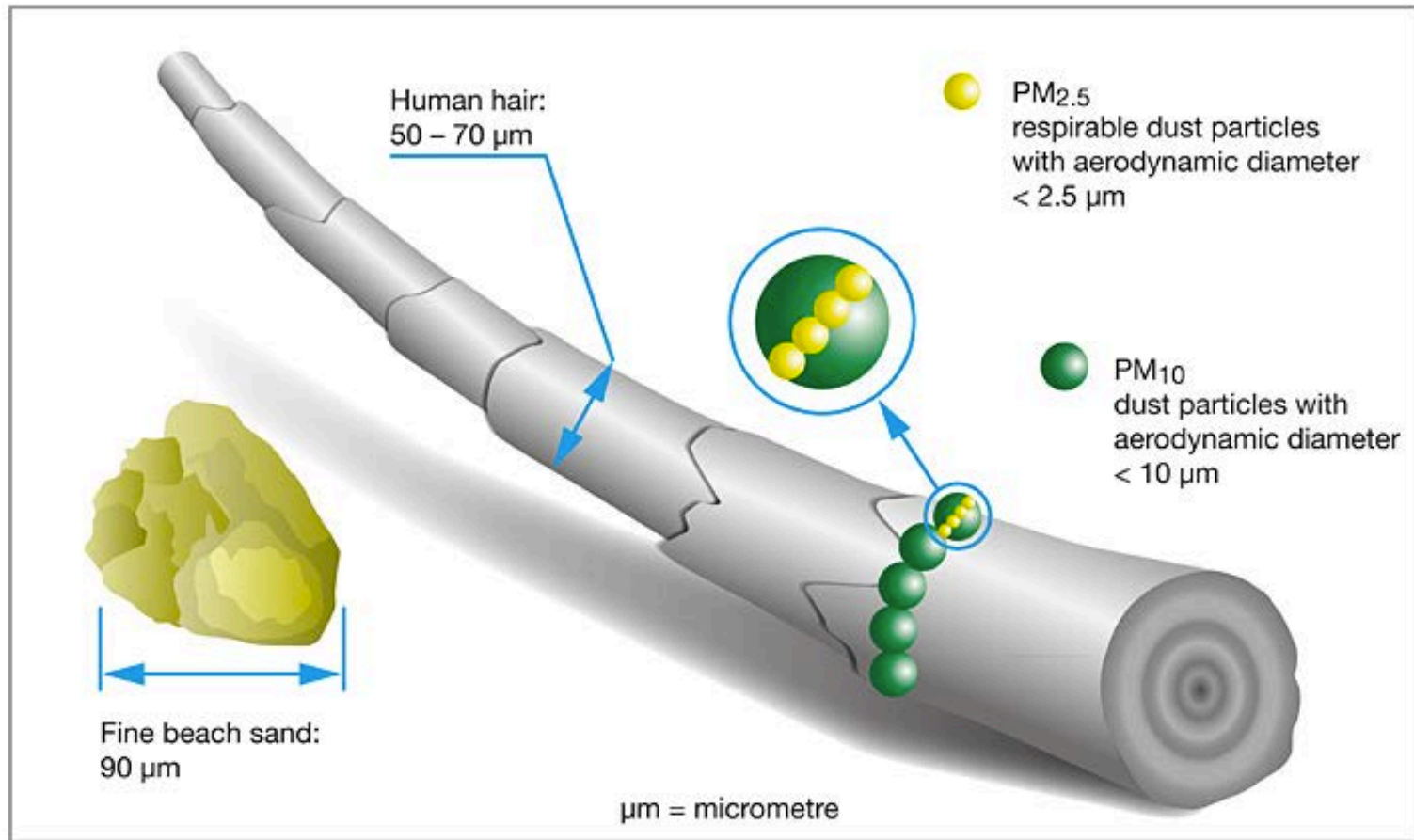
Types of pollutants

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

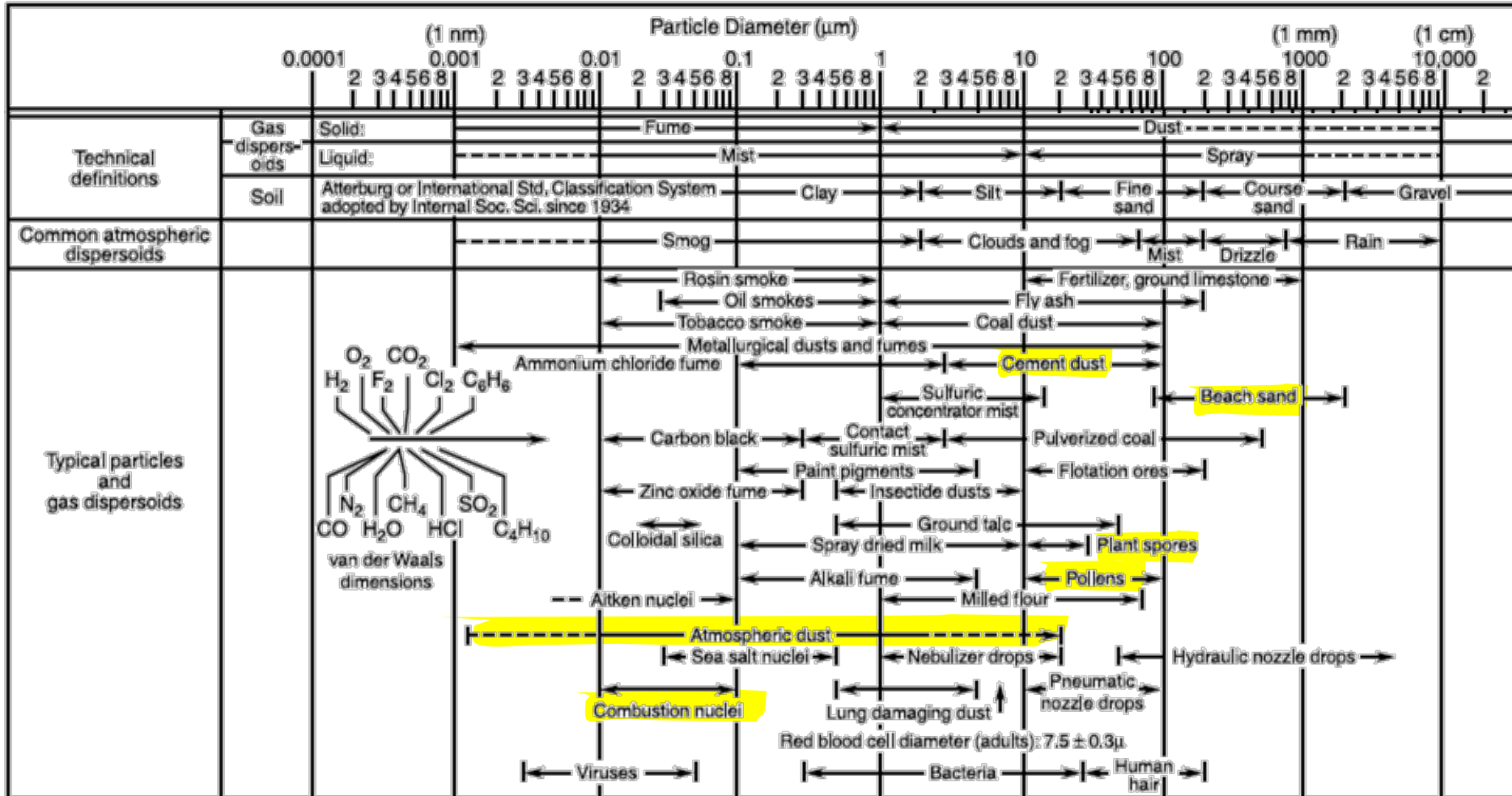
Particulate matter (PM)

- 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

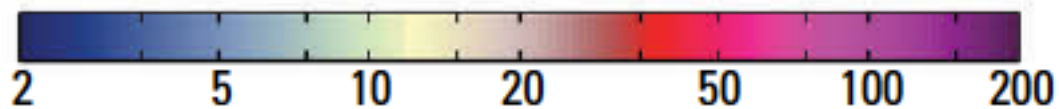
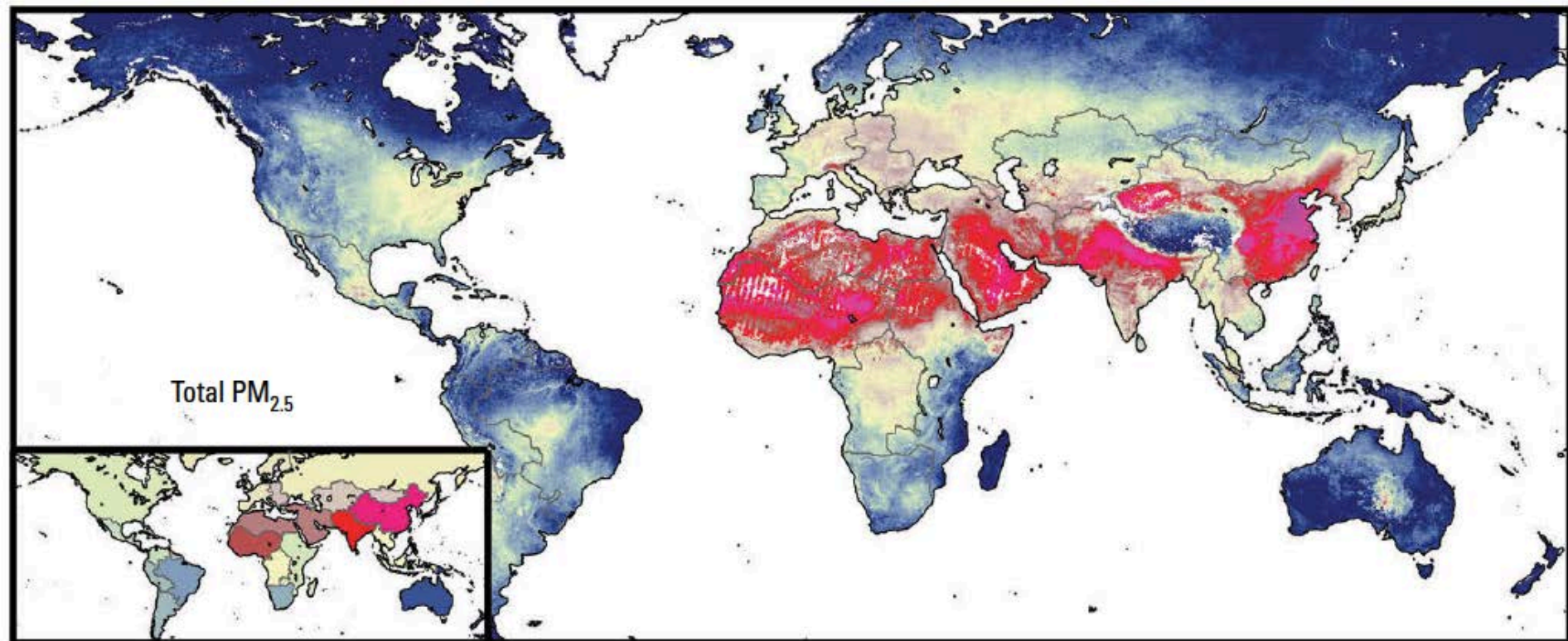


PM sizes and examples



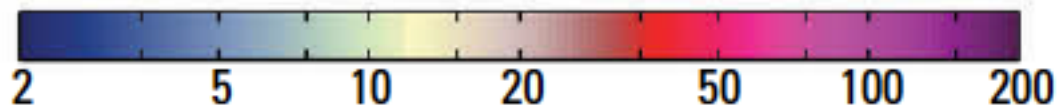
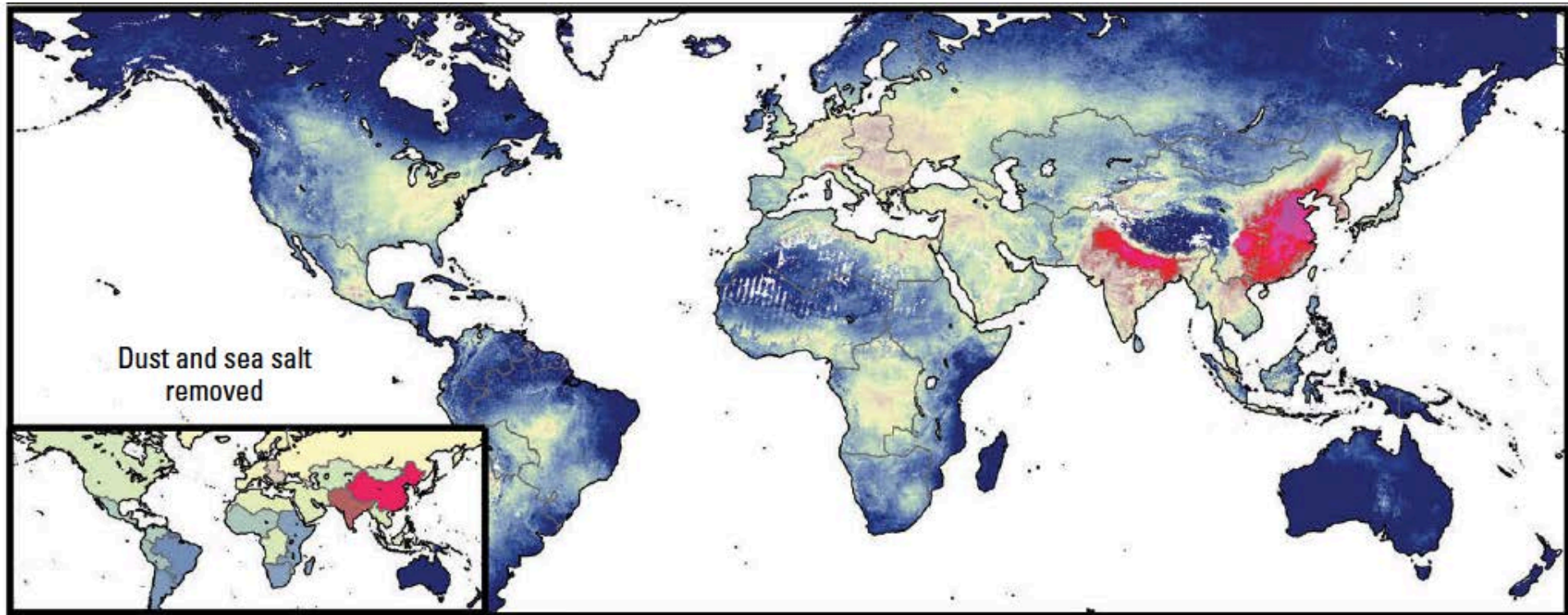
From Finlayson-Pitts and Pitts, 2000, *Chemistry of the Upper and Lower Atmosphere*

Particulate matter



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

Particulate matter – excluding dust and sea spray

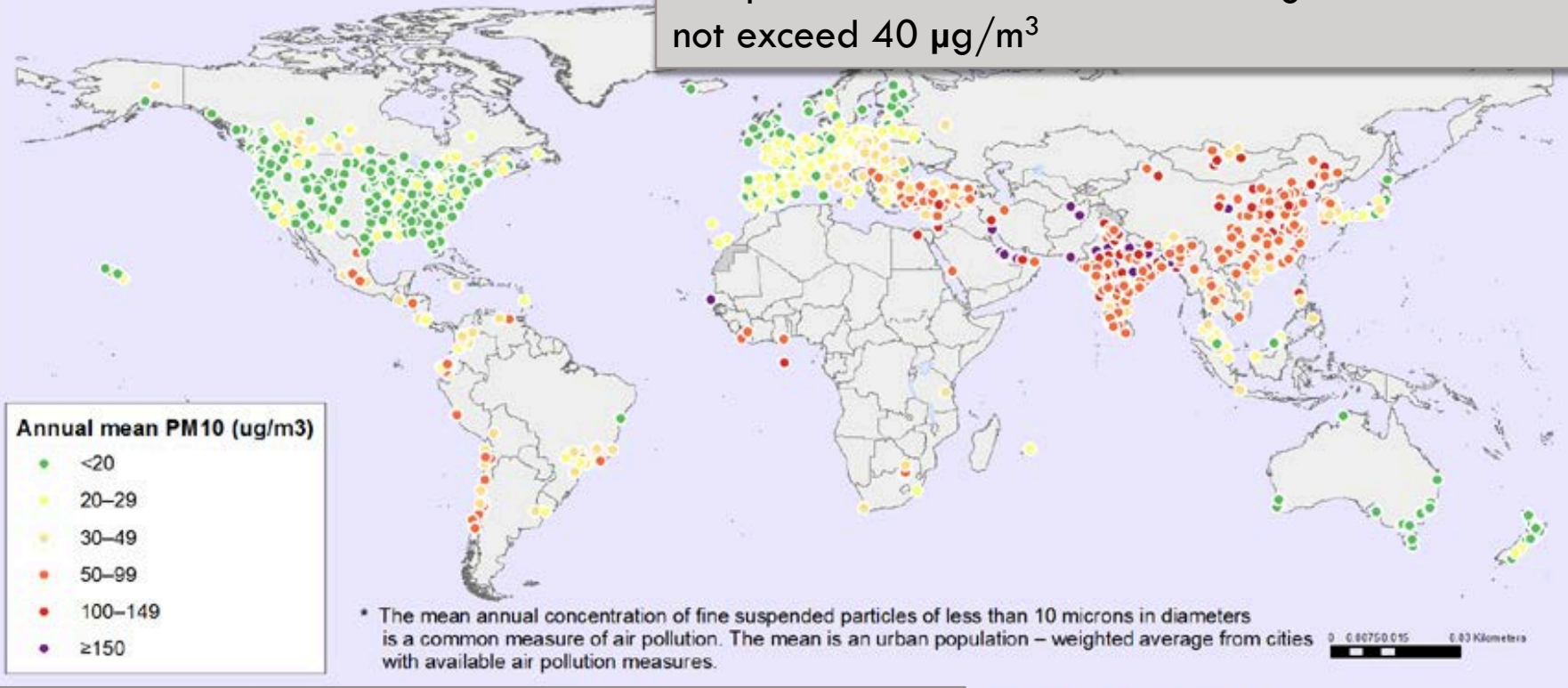


PM_{2.5} (µg/m³)

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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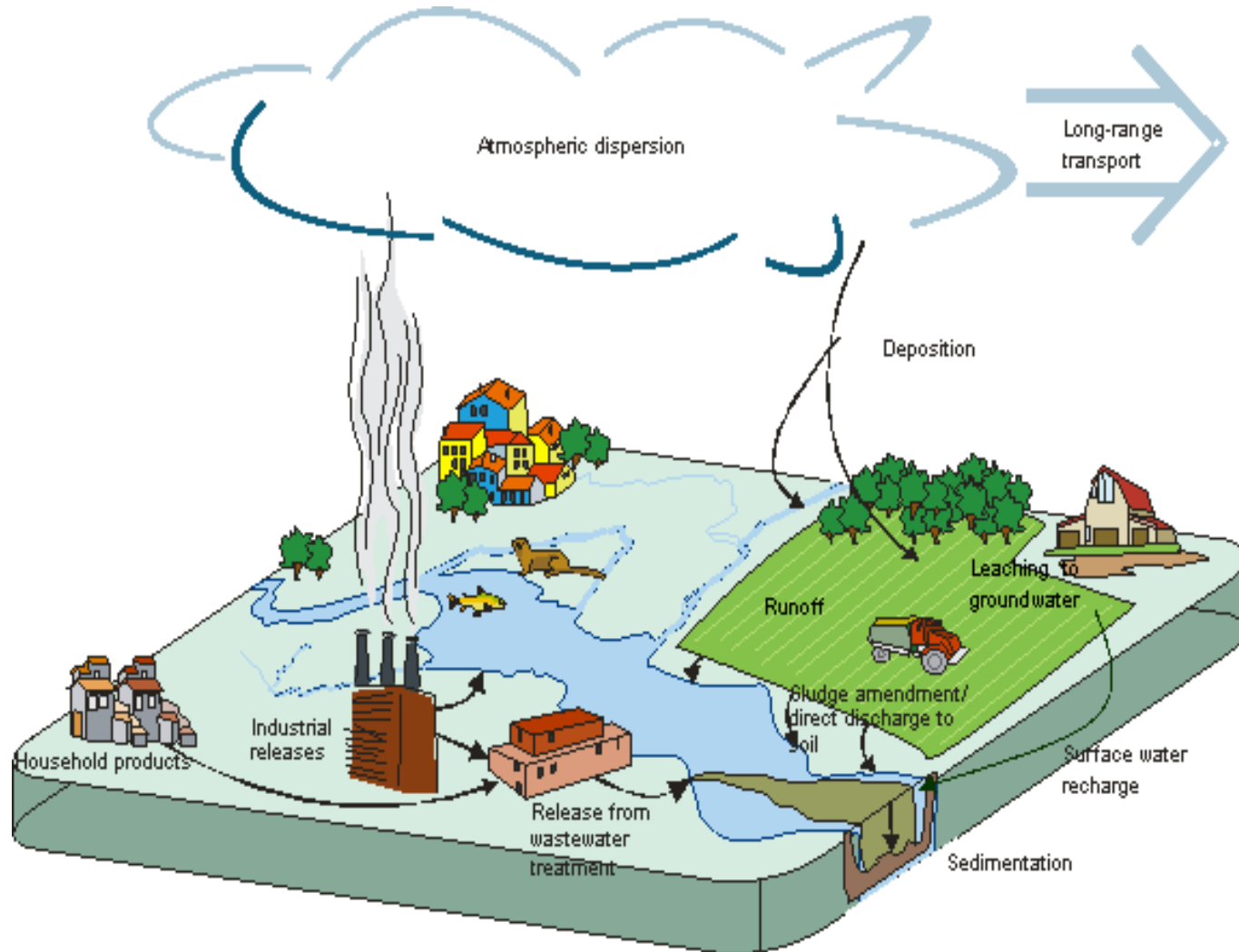
Semivolatile organic compounds (SVOCs)

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

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.

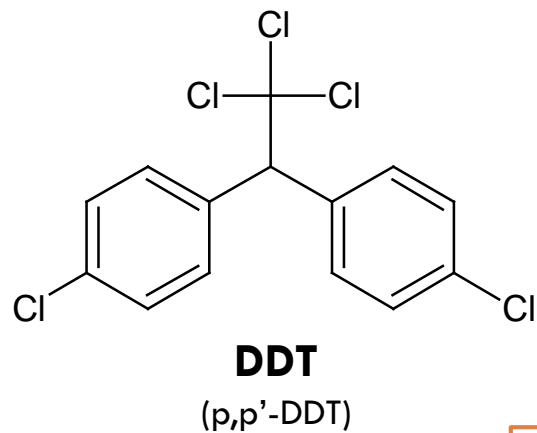
SVOCs in the environment



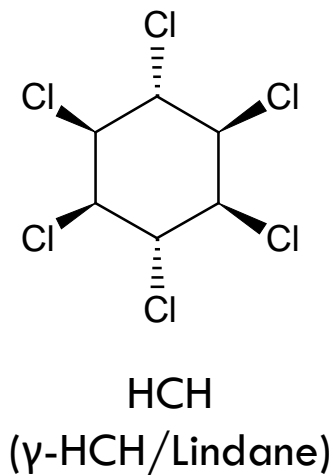
Examples of SVOCs

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

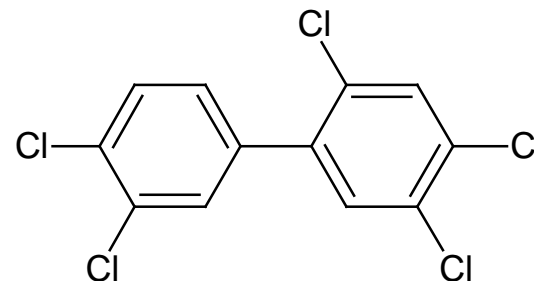
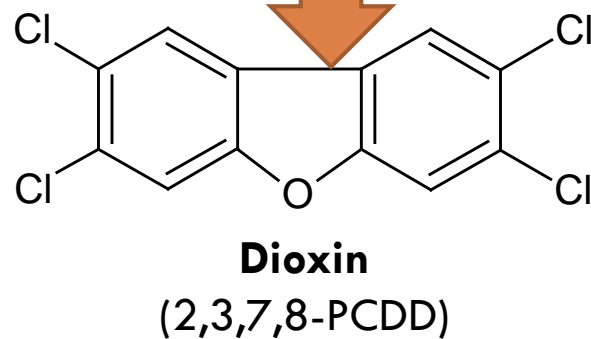
Well-known SVOCs



Pesticides



Industrial
chemical



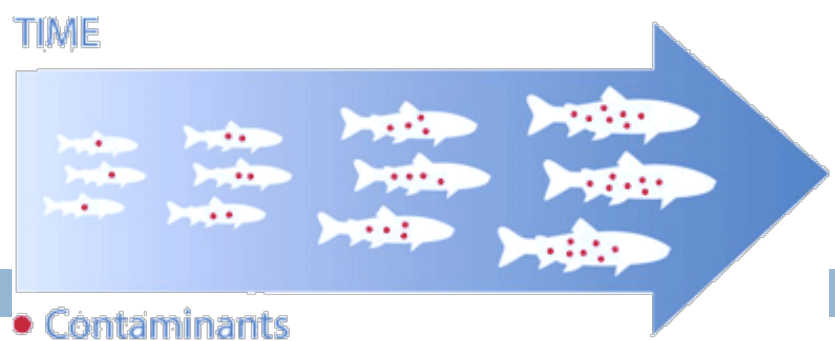
POPs / PBT

- 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”

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

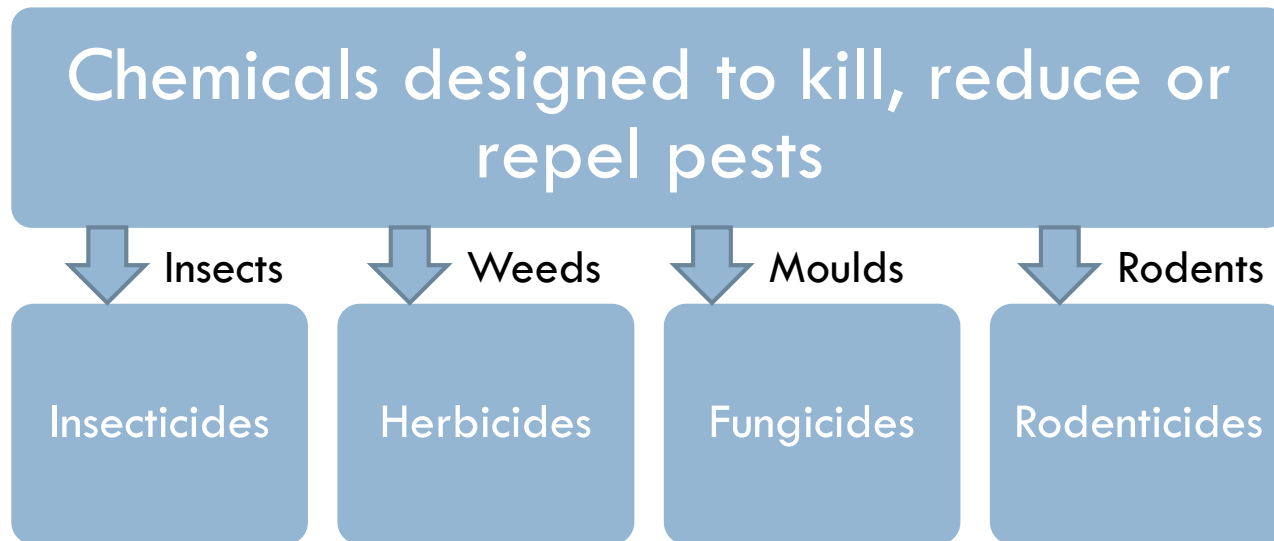
Toxicity

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

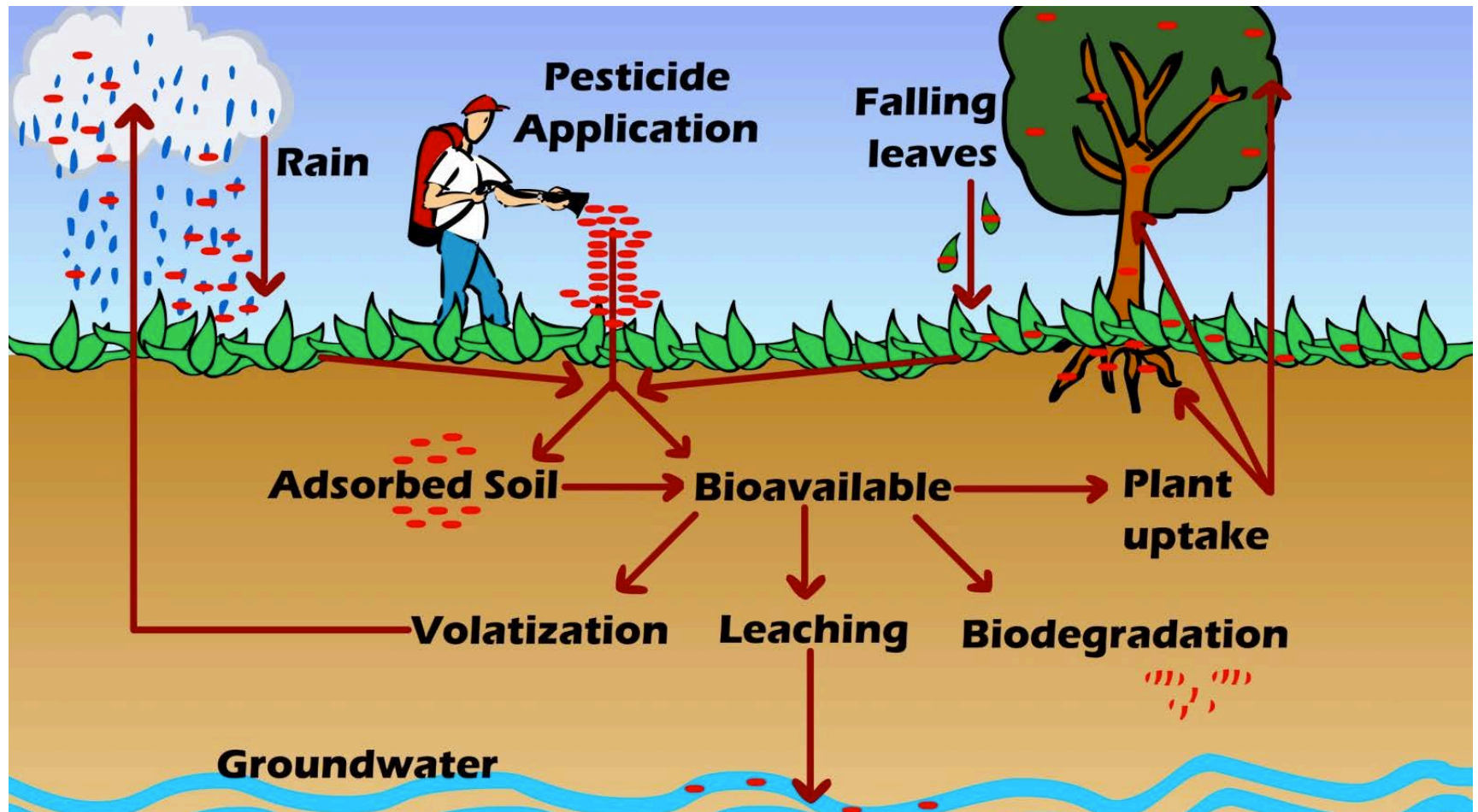
Examples of SVOCs

- **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)



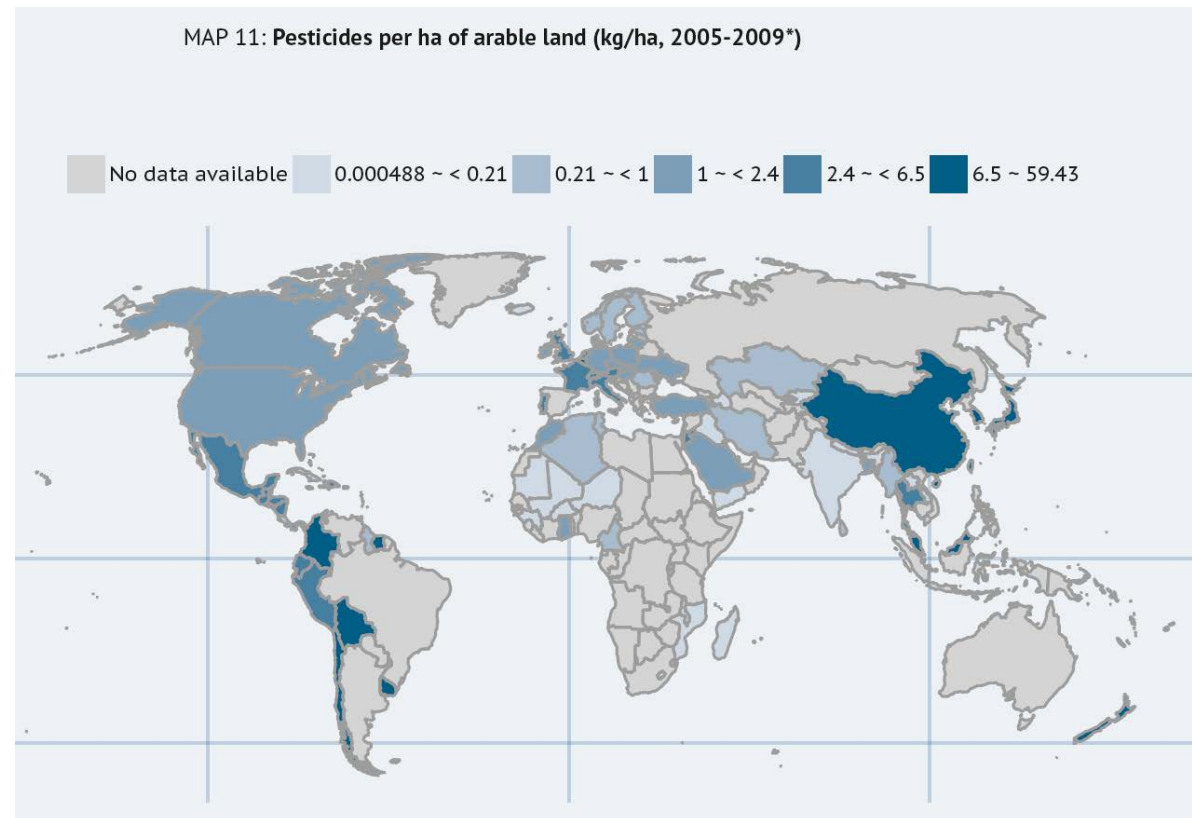
Insecticide



Herbicide



Fungicide

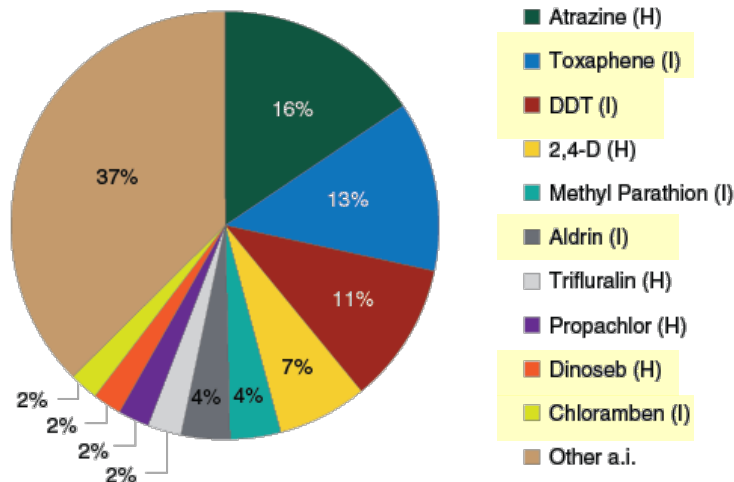


From FAO Statistical Yearbook, UN 2013

Most common pesticides

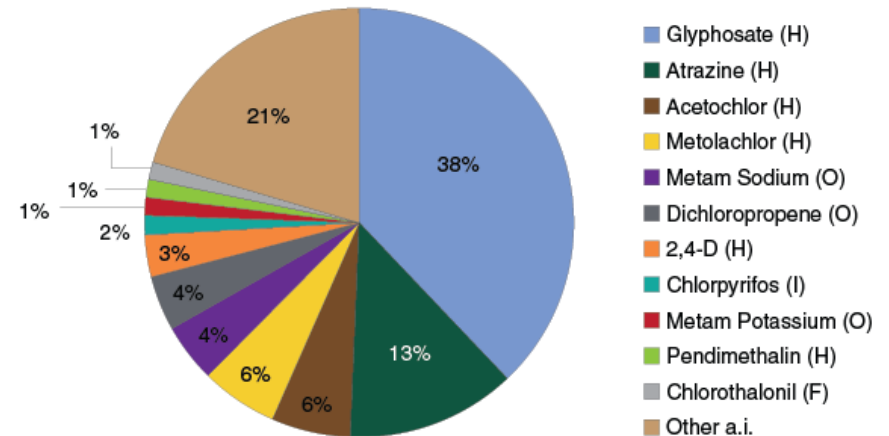
□ In 1960s...

The 10 most heavily used pesticide active ingredients in 1968 included 5 insecticides and 5 herbicides (percent total pounds active ingredient applied on 21 selected crops)



□ Today...

The four most heavily used pesticide active ingredients in 2008 were herbicides (percent total pounds active ingredient applied on 21 selected crops)



Note: H = herbicide, I = insecticide.

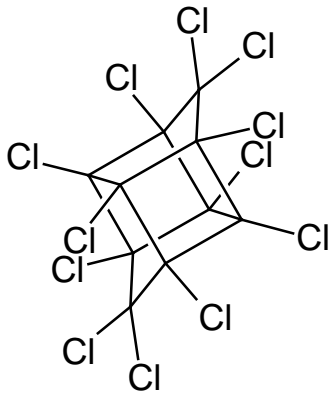
Source: USDA, Economic Research Service using USDA, National Agricultural Statistics Service and proprietary data.

Note: H = herbicide, I = insecticide, F = fungicide, and O = other.

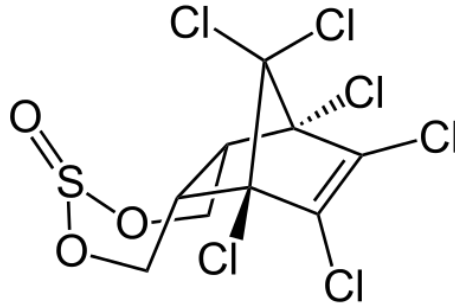
Source: USDA, Economic Research Service using USDA, National Agricultural Statistics Service and proprietary data.

Organochlorine pesticides

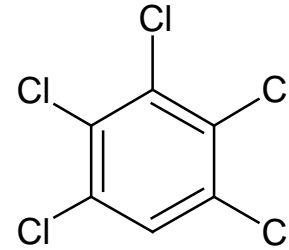
- OCPs = organochlorine pesticides
- What are the OCPs?
 - DDT
 - Hexachlorobenzene (HCB)
 - Pentachlorobenzene (PeCB)
 - Hexachlorocyclohexanes (multiple isomers)
 - Heptachlor/heptachlor epoxide
 - Aldrin/dieldrin/endrin
 - Chlordane (multiple isomers)
 - Endosulfan
 - Mirex
 - ...



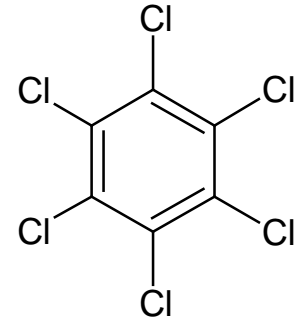
Mirex



Endosulfan

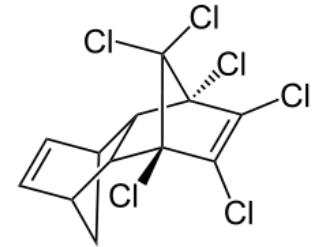


PeCB

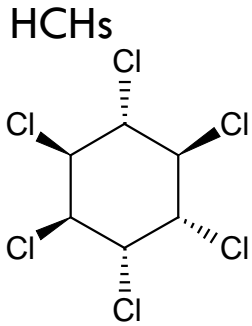


HCB

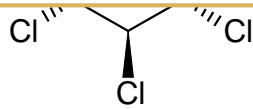
Chlorinated molecules – highly stable – therefore environmentally persistent



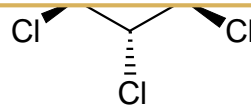
Aldrin



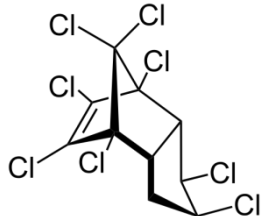
α



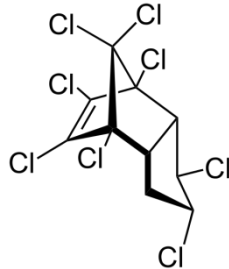
β



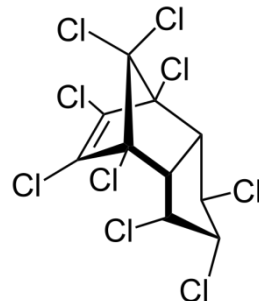
γ



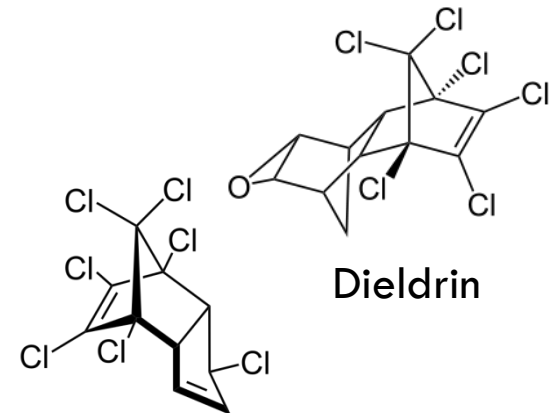
cis-chlordane



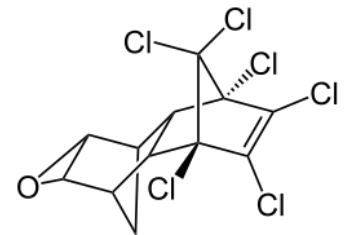
trans-chlordane



trans-nonachlor

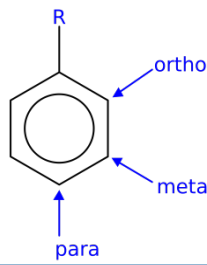


heptachlor

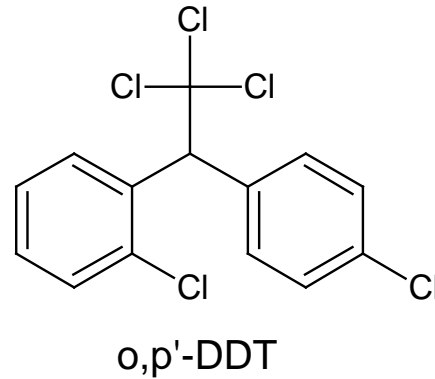
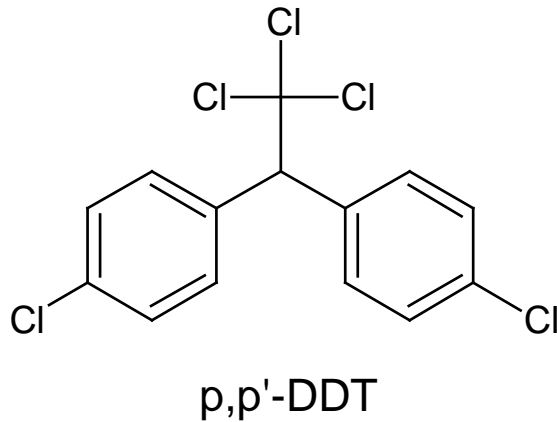


Dieldrin

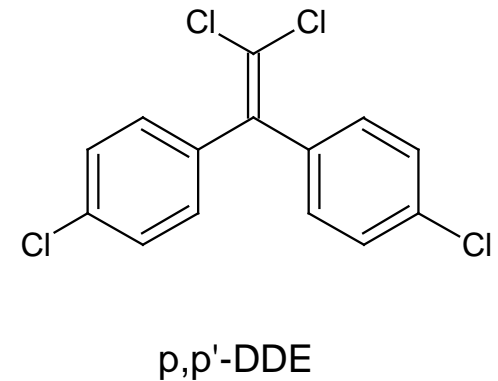
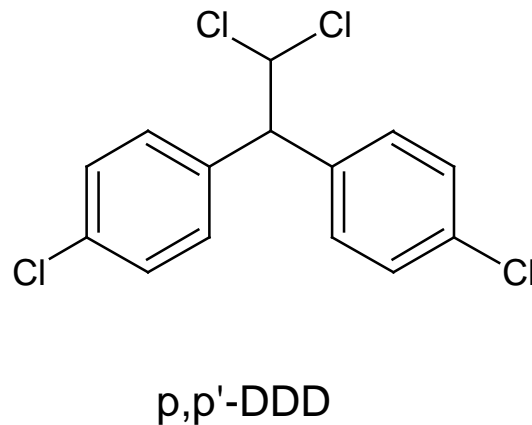
Case study 2: DDT



□ DDT – dichlorodiphenyl trichloroethane

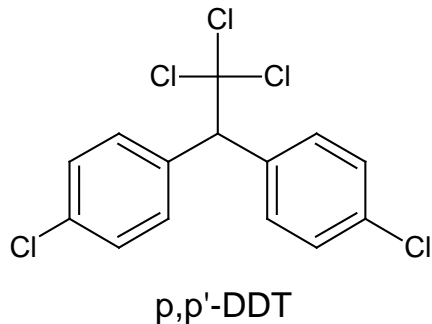


Degradation products/metabolites are often also considered:



Chemical DDT vs. Technical DDT

- Chemical DDT – dichlorodiphenyltrichloroethane, generally ***p,p'*-DDT** – the isomer with insecticidal properties
- Technical DDT – mixture of *p,p'*-DDT, *o,p'*-DDT, DDE and DDD
- DDE and DDD are impurities in technical mixture and breakdown products of DDT

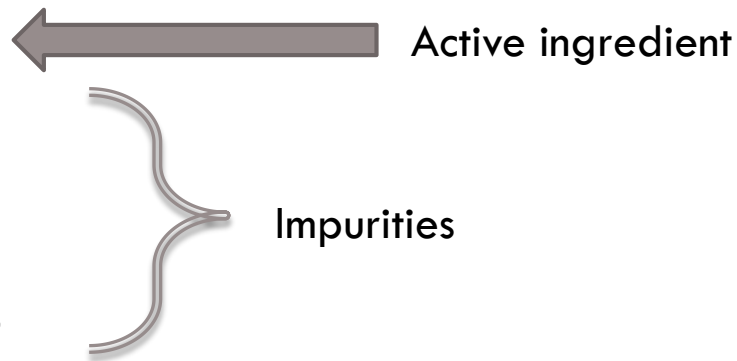


p,p'-DDT: 63-79%

o,p'-DDT: 8-21%

p,p'-DDD: 0-4%

o,p'-DDD: 0-0.05%



DDT – a brief history

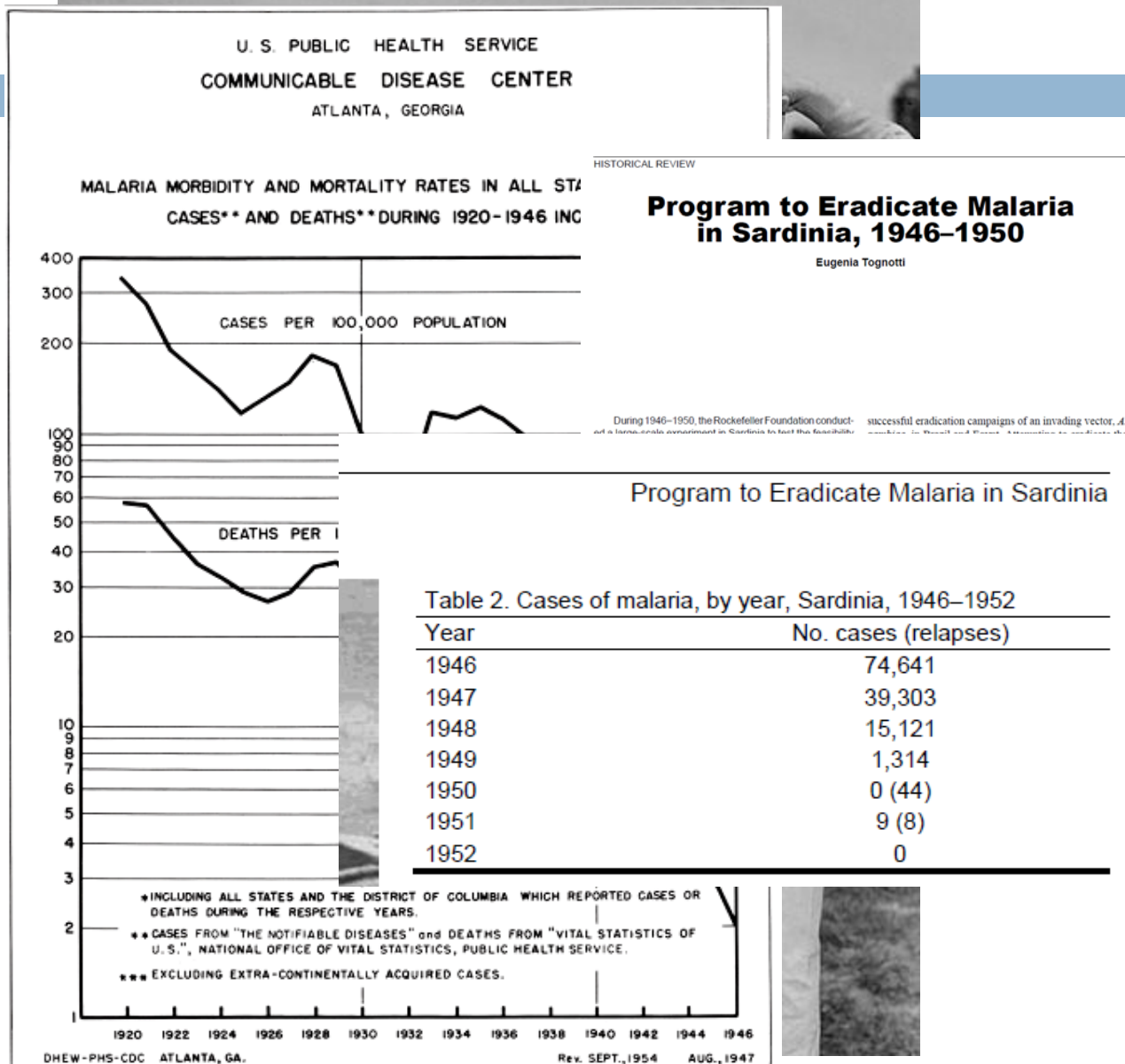
1872 – DDT was first synthesized by Austrian chemistry student

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

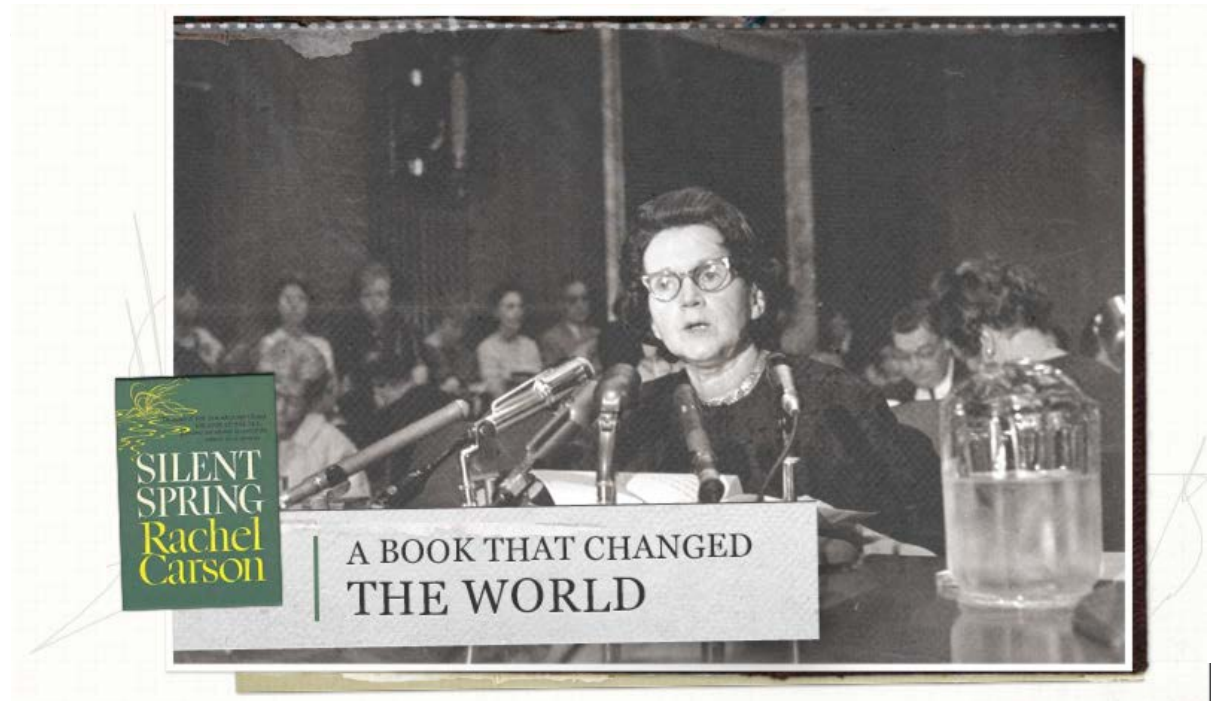
1962 - Rachel Carson's book *Silent Spring* blamed environmental destruction on DDT.

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 TRIMZ CO., INC., Division of UNITED WALLPAPER

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

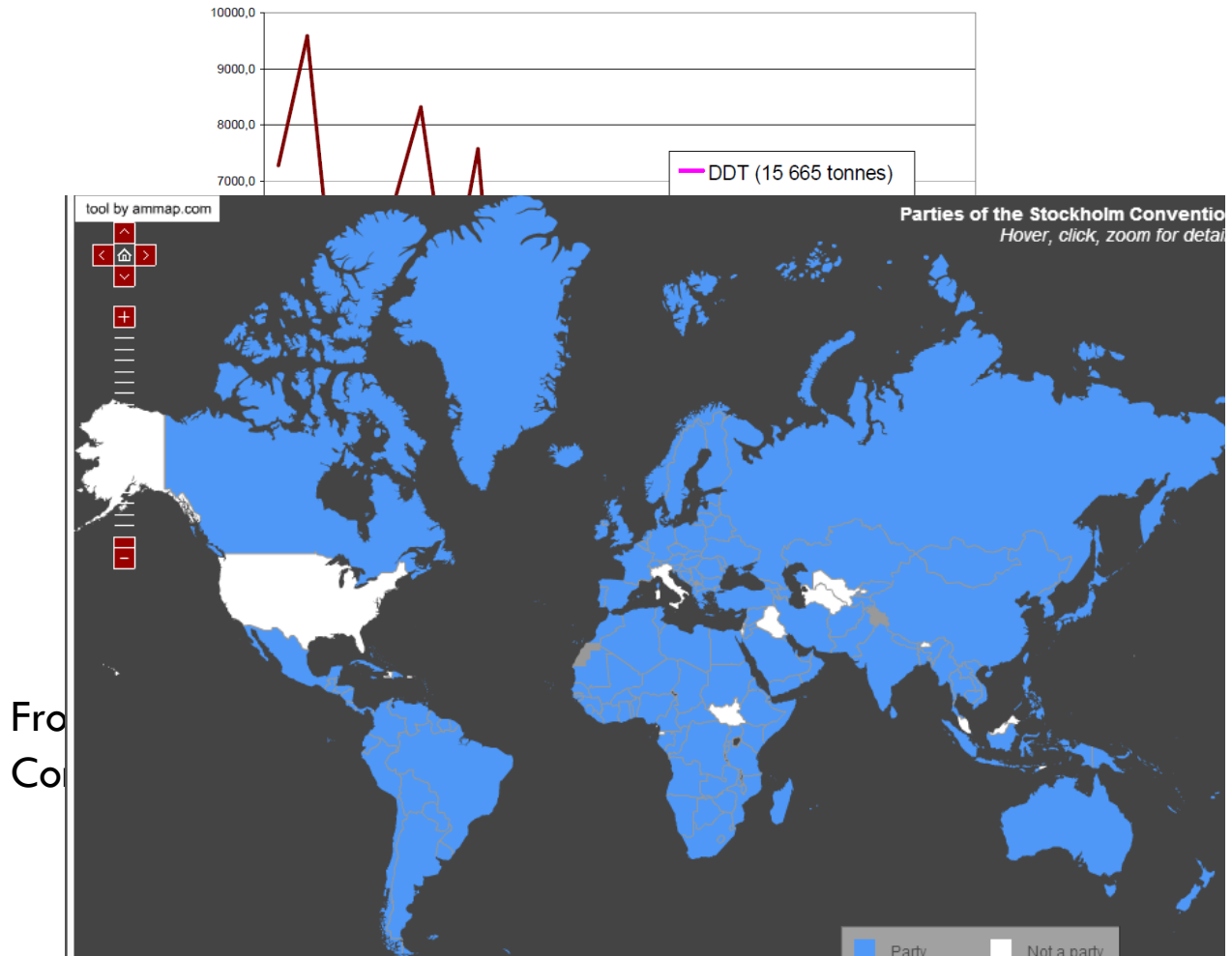
©1947, TRIMZ CO., INC.



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)



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?

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

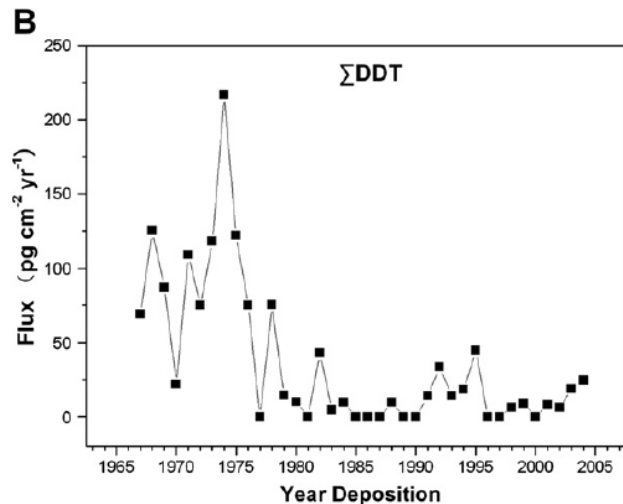
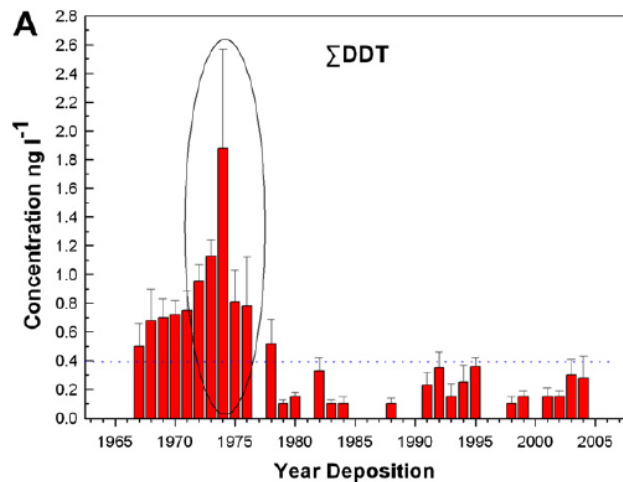


Fig. 4. Concentration (A) and deposition flux (B) of DDT in the ice core from East Rongbuk glacier (Mt. Everest, The Himalayas).

(Wang et al., Atmospheric Environment, 2008)

DDT compounds in precipitation from North America, 1995-2005

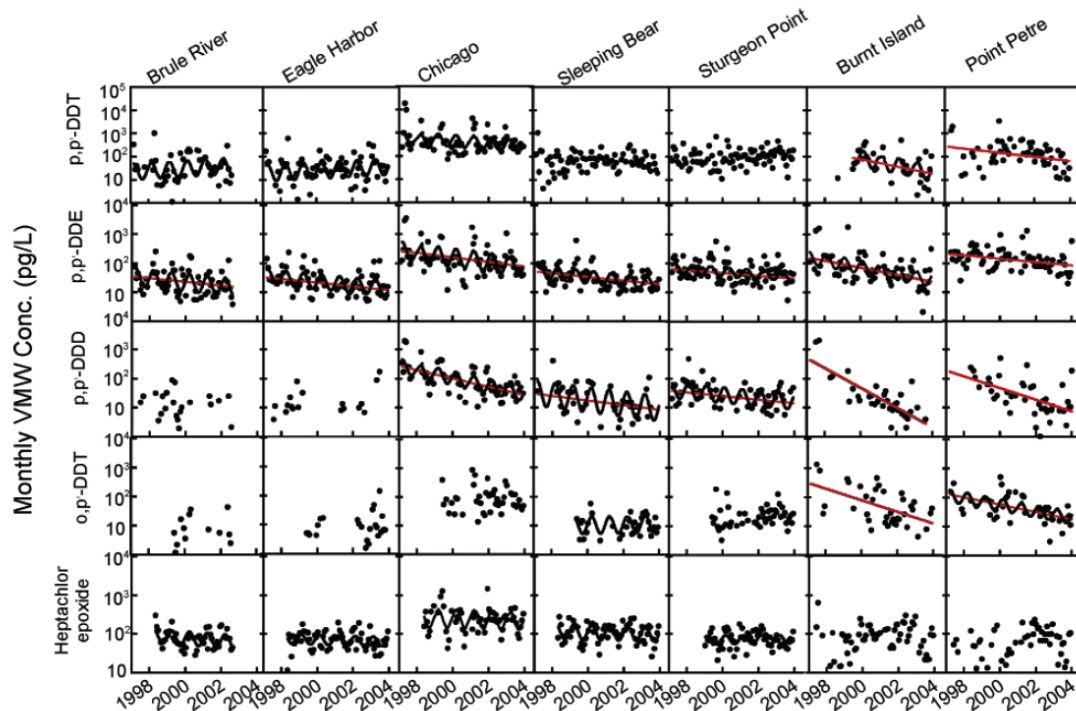


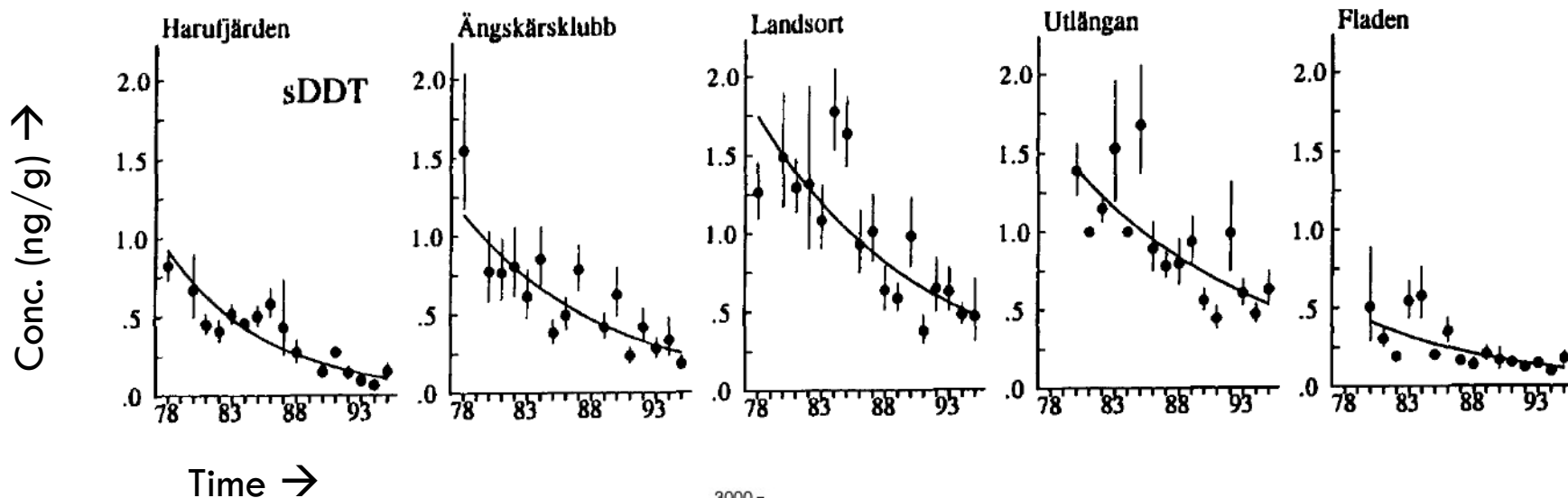
FIGURE 4. Organochlorine pesticide concentrations in precipitation collected at 7 IADN sites near the Great Lakes. The black curve is the fitted line of the sinusoidal model with the period length (a_2) set to one year. The red lines indicate long-term significant decreasing or increasing trends. Detailed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

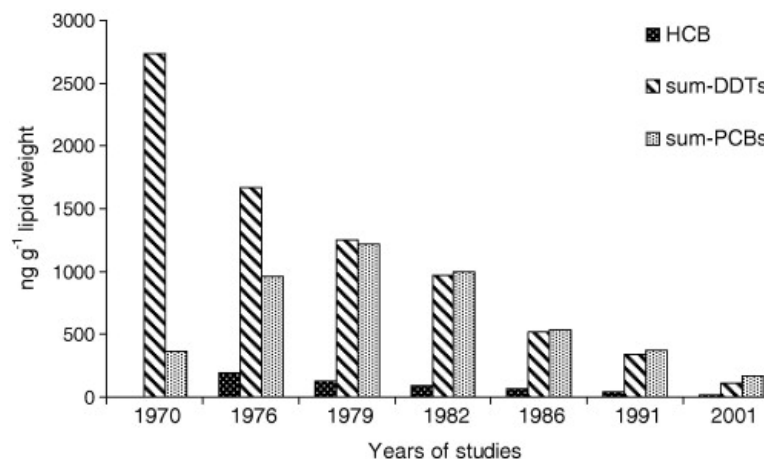
A. Bignert et al./Environmental Pollution 99 (1998) 177-198



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

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

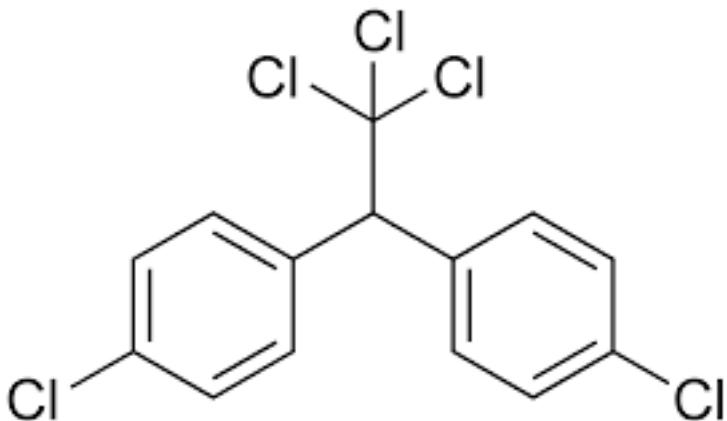
- Glyphosate (“Round-up”)
 - ▣ Herbicide
 - ▣ In use since 1970s
 - ▣ Most widely used chemical pesticide in world
 - ~650000 tonnes per year (>30% of world pesticide market)
- Atrazine
 - ▣ Herbicide
 - ▣ banned in EU but high use in many other countries
 - ▣ 70000 tonnes per year
- Chlorpyrifos
 -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

Comparing 2 insecticides:

Chlorpyrifos vs. DDT

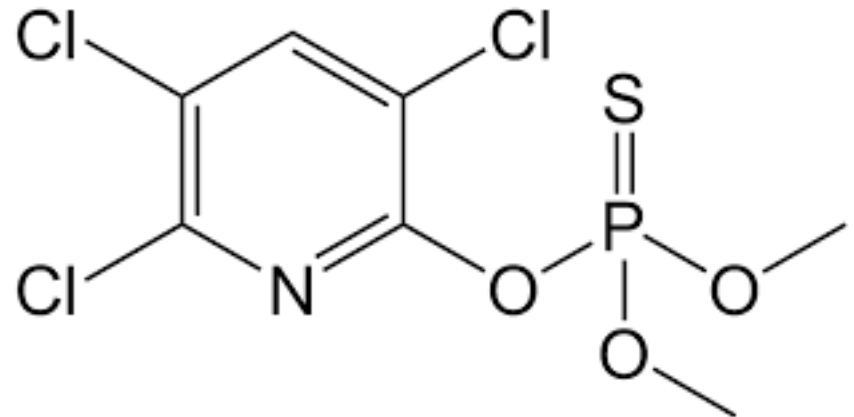
DDT

- 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



Comparing 2 insecticides:

Chlorpyrifos vs. DDT

DDT

- ASTDR oral reference dose: 0.0005 mg/kg/day
- LD50:
~100-1000 mg/kg
- Not acutely toxic to birds, but acutely toxic to aquatic organisms
- Evidence for reproductive, mutagenic and teratogenic effects in humans

Chlorpyrifos

- US EPA oral reference dose: 0.003 mg/kg/day
- LD50:
~80-300 mg/kg
- Toxic to birds (LD50 8-100 mg/kg)
- Not identified as reproductive toxic, or teratogenic, mutagenic

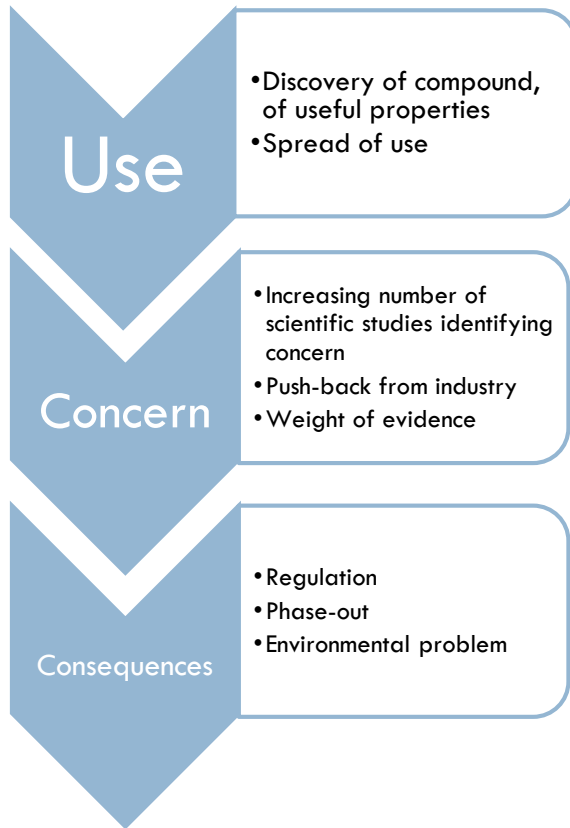


Any questions about pesticides?

Examples of SVOCs

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

Polychlorinated biphenyls - PCBs



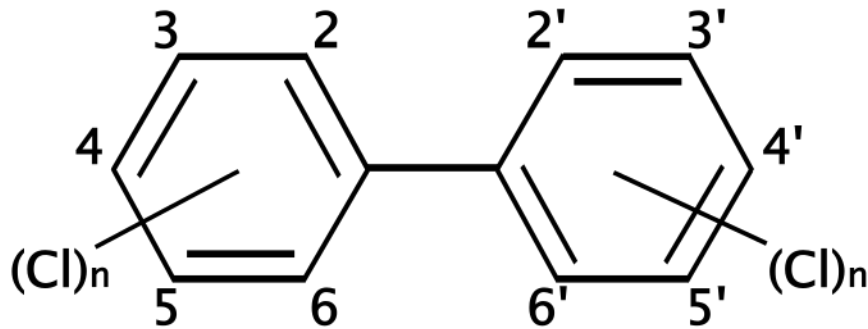
-High chemical and physical stability, even at high temperatures

→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

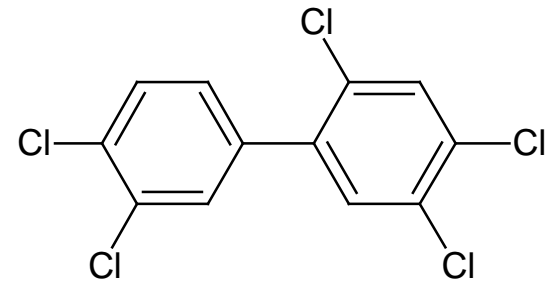
But...PCBs remain in use in old building equipment, electrical equipment, etc.

PCBs – chemical structure

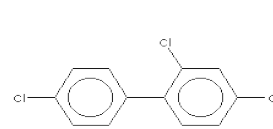


- 209 possible congeners
- 1 to 10 chlorines
- only 130 were used commercially
- Classified based on degree of chlorination

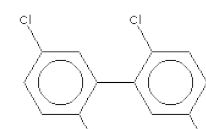
Indicator PCBs – 7 congeners:



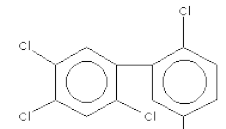
2,3,4,4',5-Pentachlorobiphenyl
PCB 118



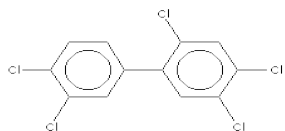
PCB
28



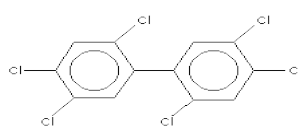
PCB
52



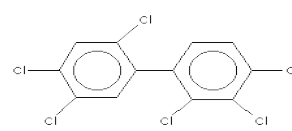
PCB
101



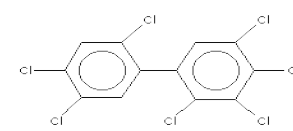
PCB
118



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



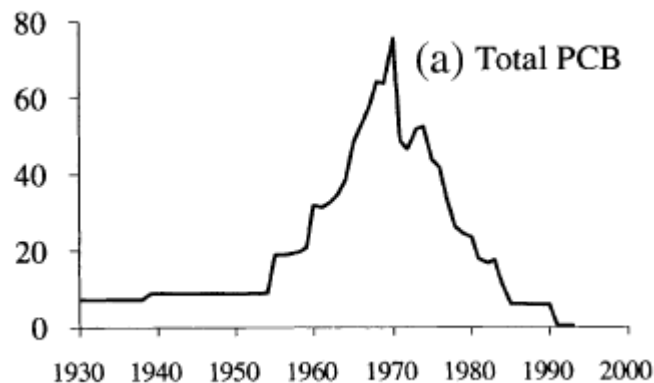
Sanexen Environmental Services



PCB production

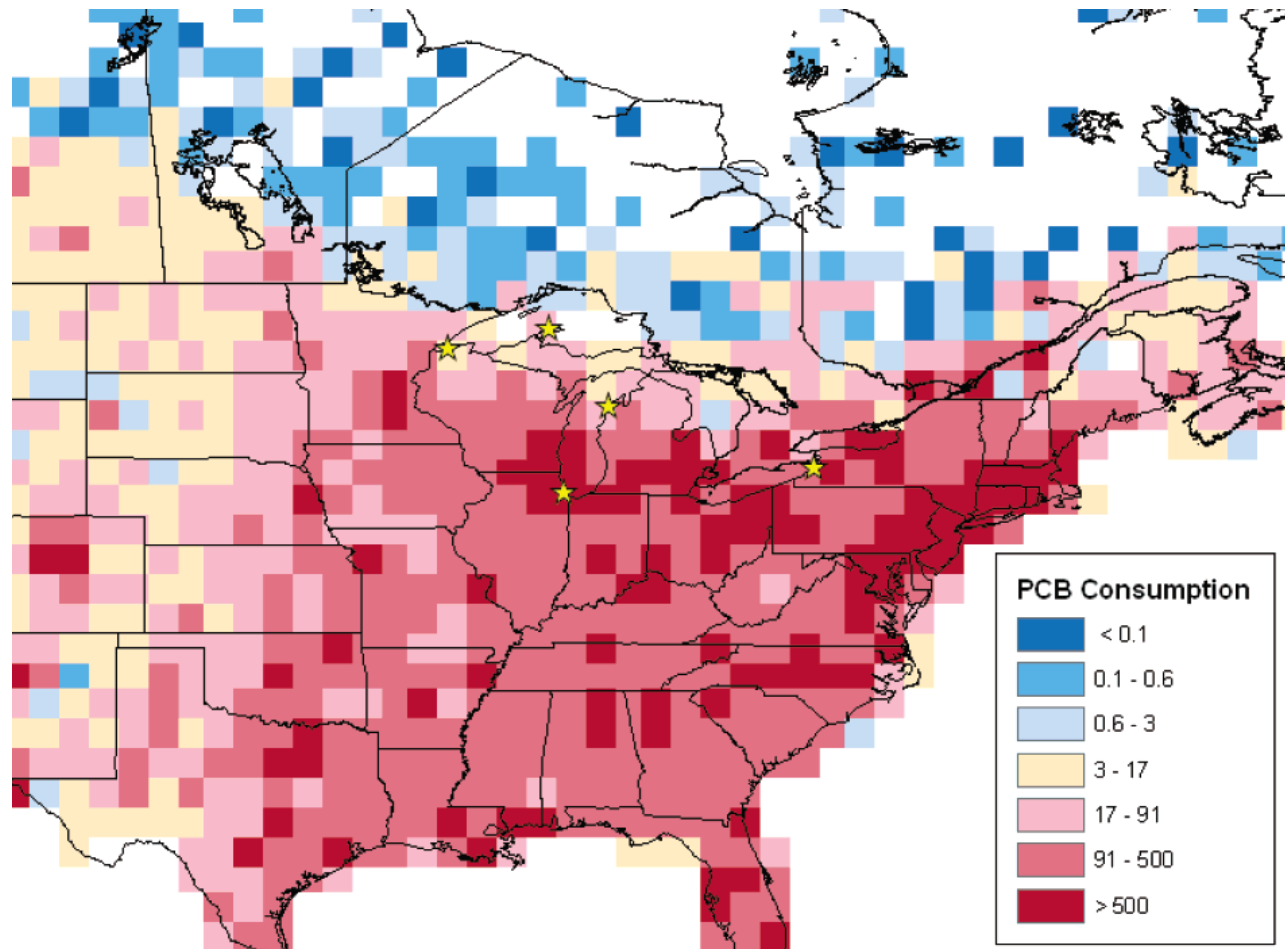
Table 1
Total PCB production in t as reported in the literature

| 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 | Schlosserová (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

PCB use in North America – in tonnes



Hafner and Hites, ES&T, 2003

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

Dioxins and furans

Dioxins in the news...

BBC News Sport Weather Earth Future Shop

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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

The Washington Post PostTV Politics Opinions Local Sports National World Business

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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.

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.



Yushchenko's disfigurement could take two years to heal

BBC NEWS: VIDEO AND AUDIO

Yushchenko says who is to blame for his illness

VIDEO

THE 'ORANGE REVOLUTION'

KEY STORIES

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

ANALYSIS AND FEATURES

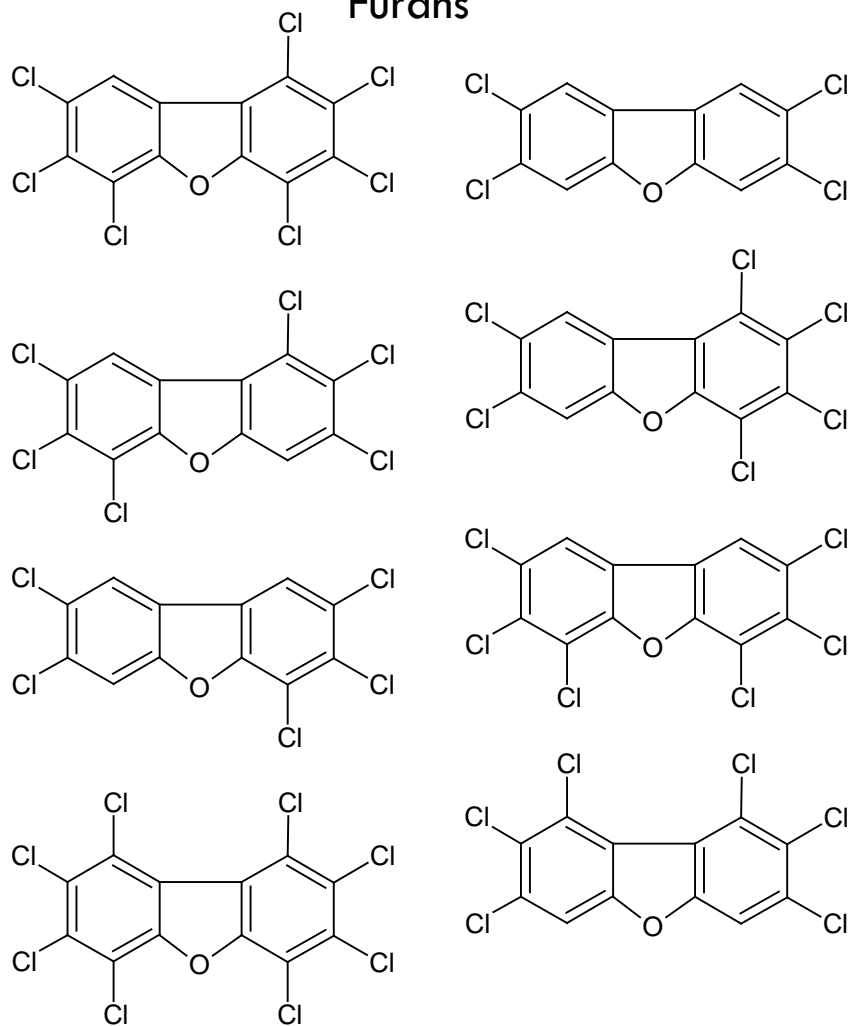
Orange pop

Ukrainians still cherish the sounds of revolution a year on

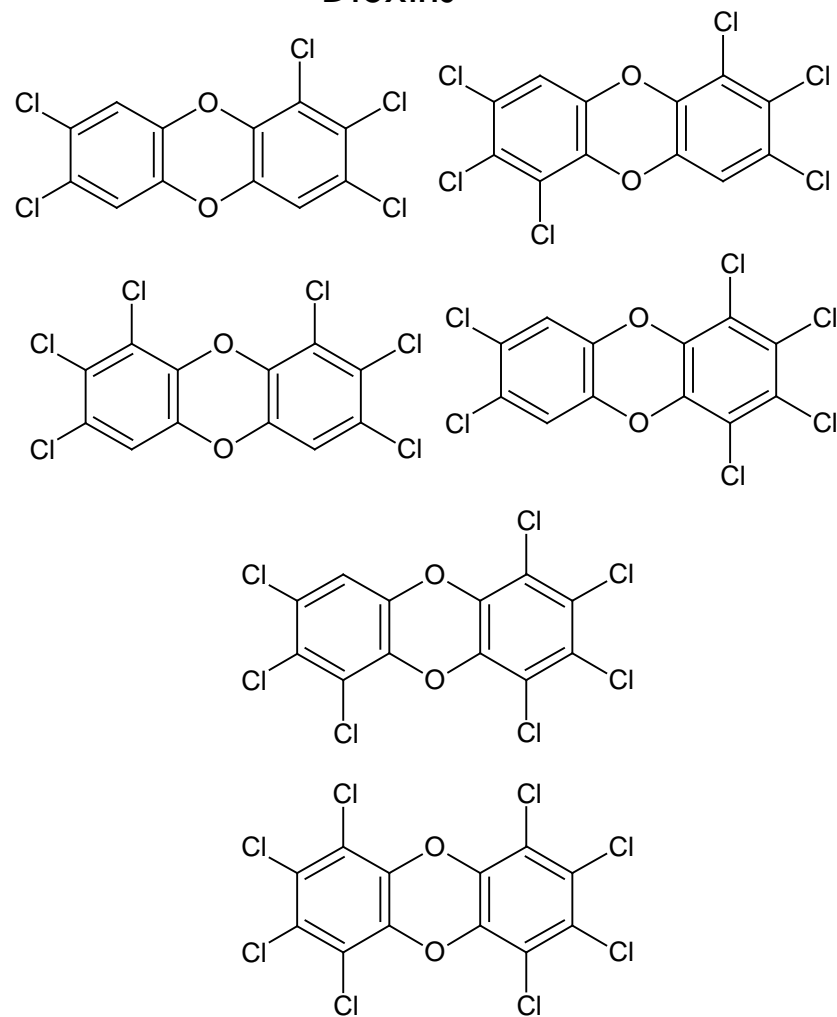
- Cynicism clouds dreams
- Revolution supporters in distress
- Ukraine's heroes turn into foes
- Warm US welcome
- Mending fences with Russia

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

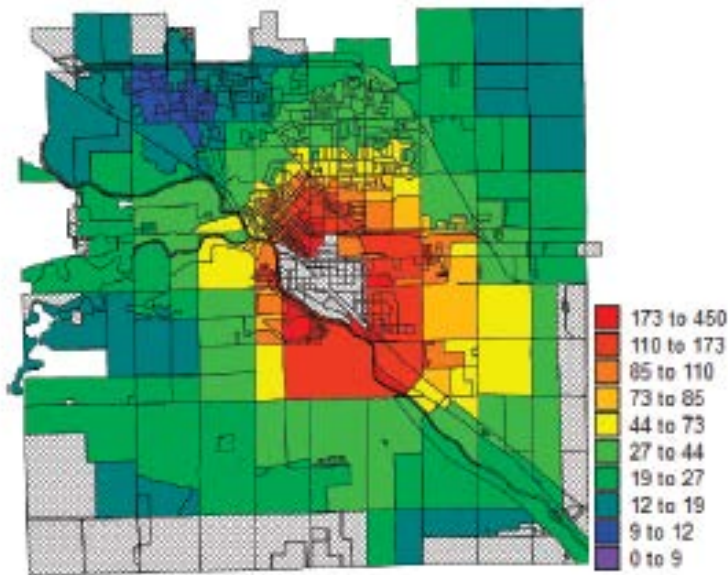
Spatial patterns of PCDD/Fs

- 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

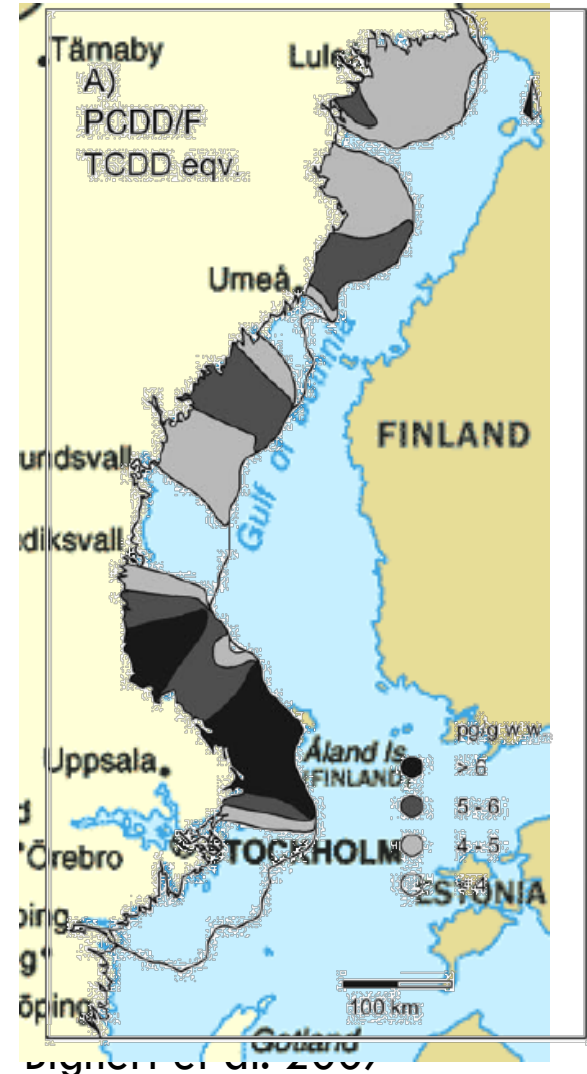
Local scale – PCDD/Fs in soil around an incinerator

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

(c) Mean concentration

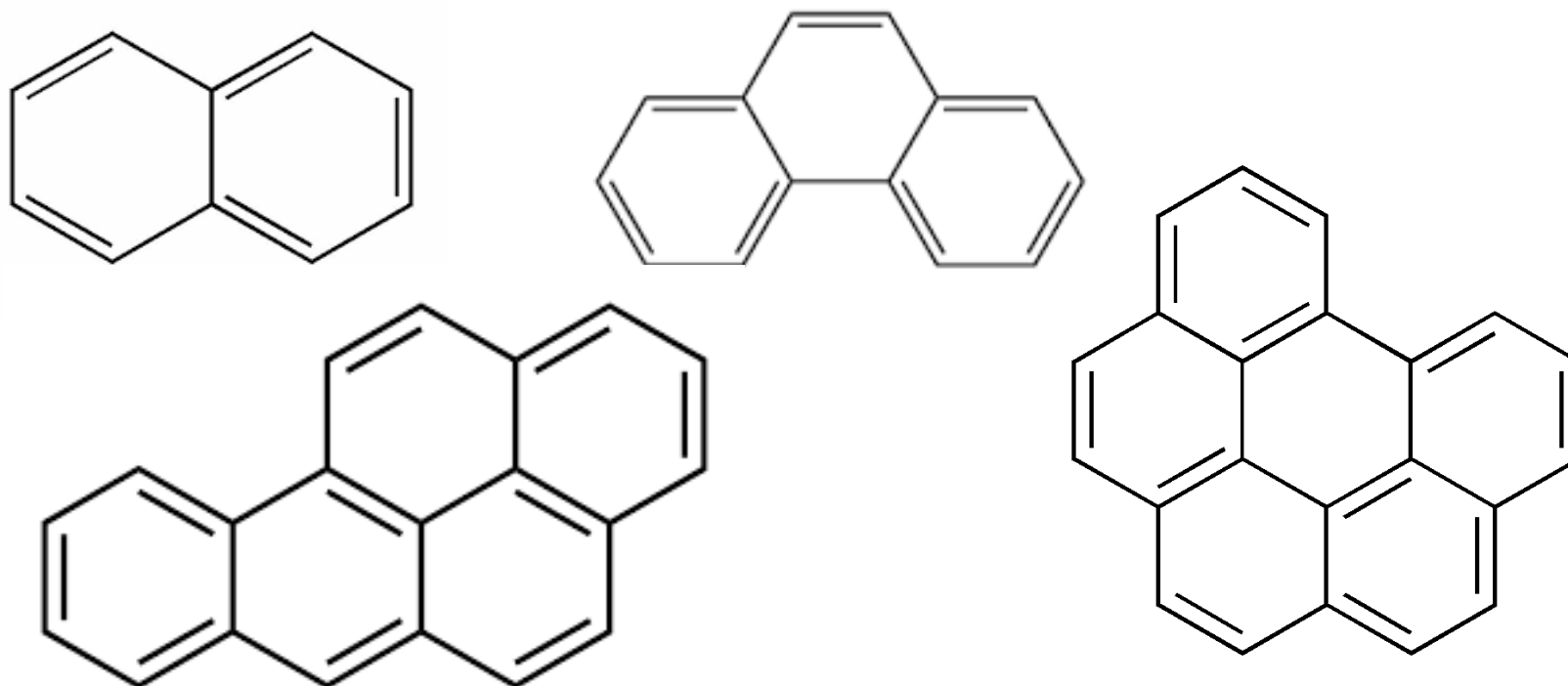


Goovaerts et al. 2008



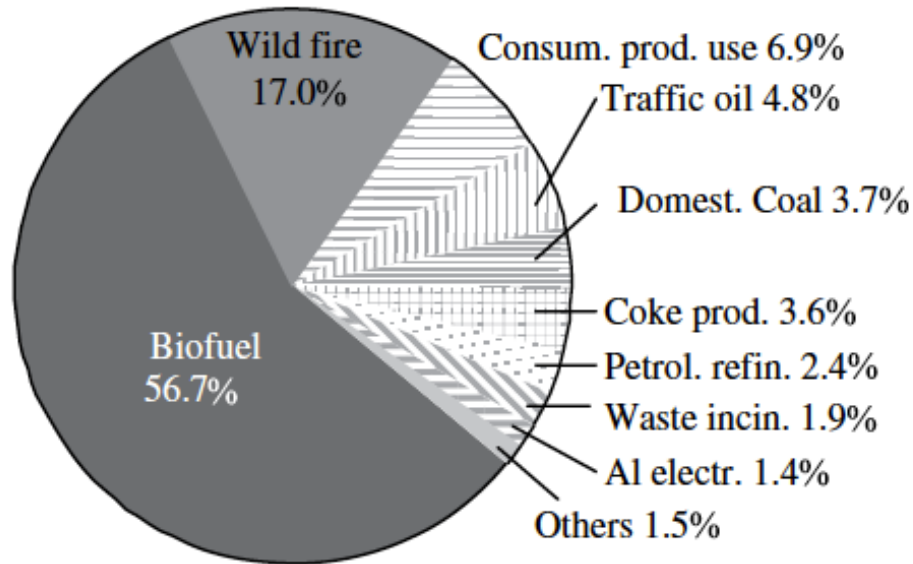
Polycyclic Aromatic Hydrocarbons (PAHs)

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

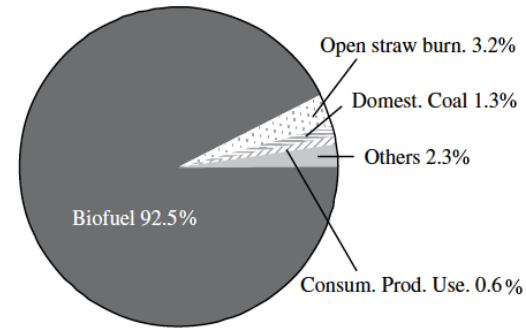


PAH Sources

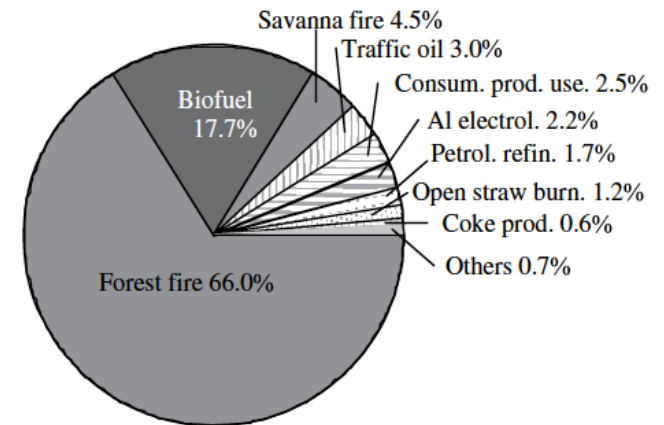
PAH16:



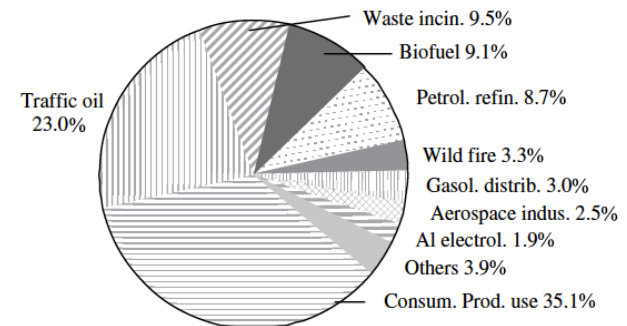
Global (530 Gg/y)



India (90 Gg/y)

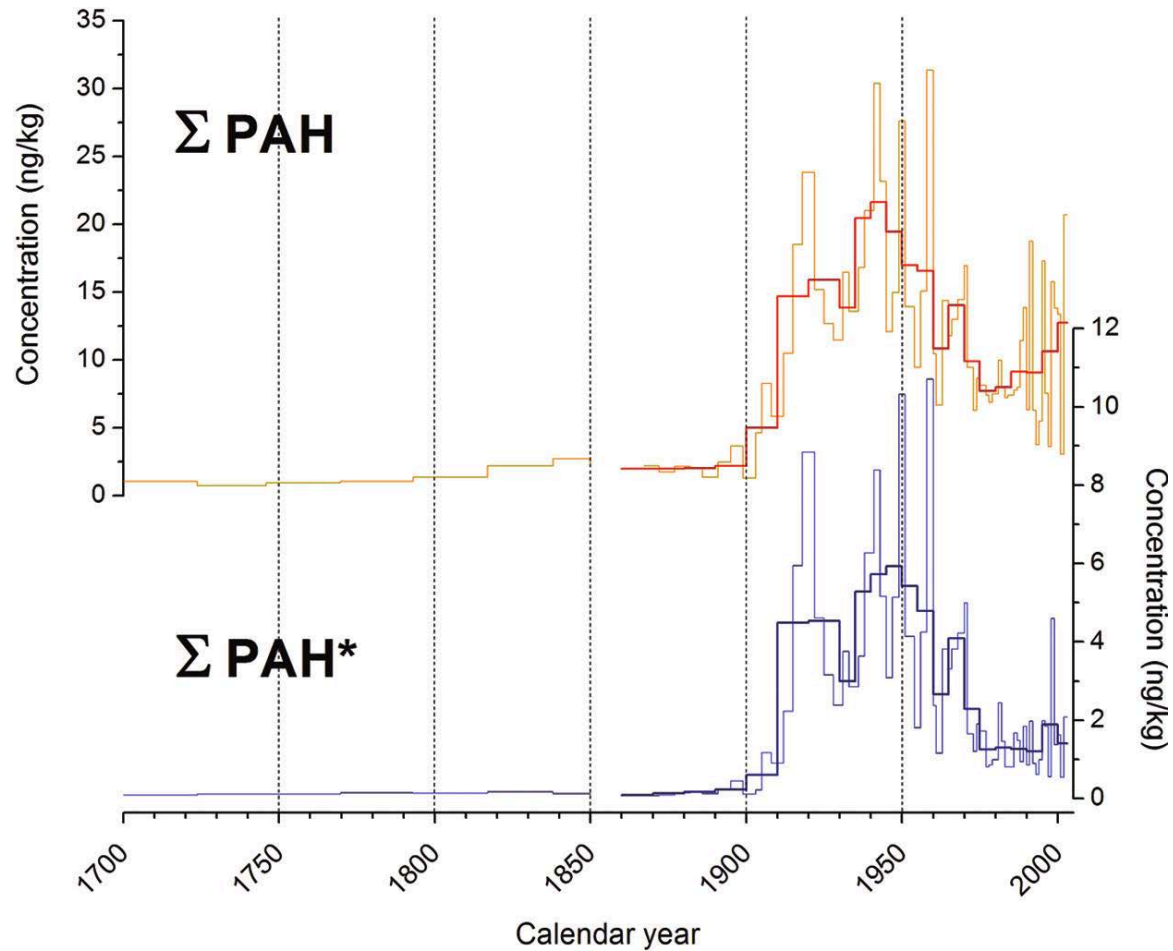


Brazil (19 Gg/y)



USA (32 Gg/y)

PAHs over the past 300 years





Any questions about PCDD/Fs or 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.

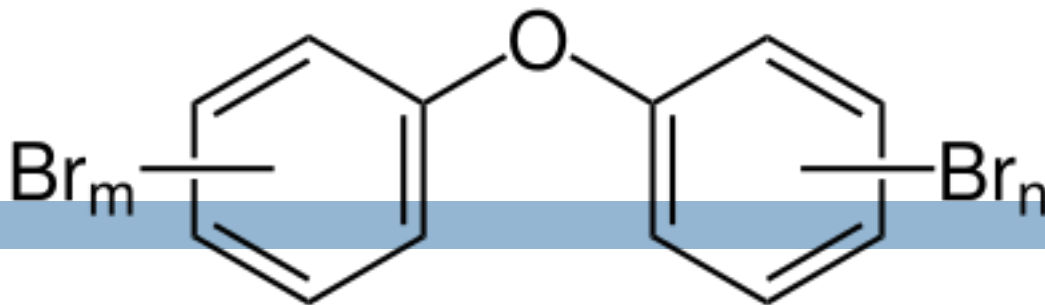
Flame retardants



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

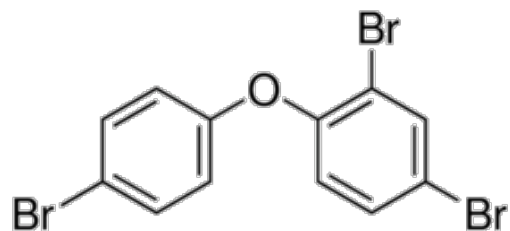
- To slow the spread of flames
- Organic or inorganic
- Wide range of applications (furniture, electronics, industrial/workplace textiles and protective equipment, vehicles)
- Required by fire safety regulations

PBDEs



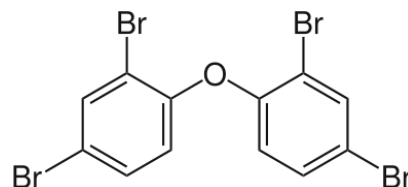
- Polybrominated diphenyl ethers
- Flame retardants
- Classified by either technical mixture or congener group
 - Confusing!! E.g., penta-BDE can refer to either the technical mixture called “Penta” or could refer to a PBDE with 5 bromines
 - Commercial mixtures sometimes distinguished as “c-penta”

PBDE naming - congeners



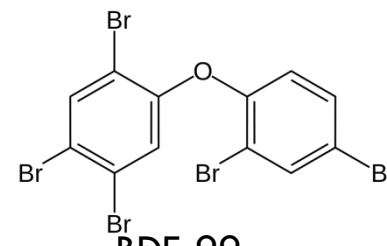
BDE-28

Tribromodiphenyl ether



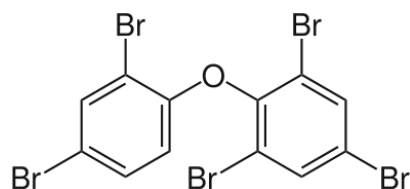
BDE-47

Tetrabromodiphenyl ether



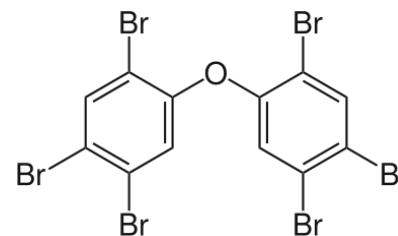
BDE-99

Pentabromodiphenyl ether



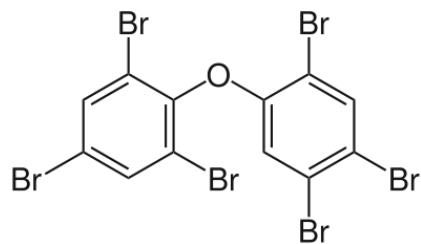
BDE-100

Pentabromodiphenyl ether



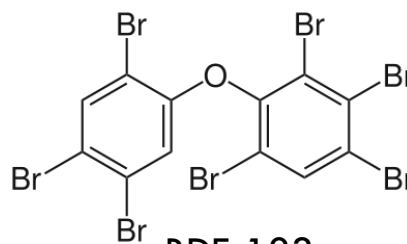
BDE-153

Hexabromodiphenyl ether



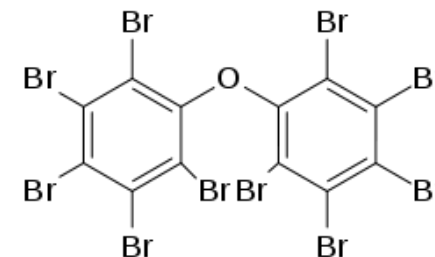
BDE-154

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

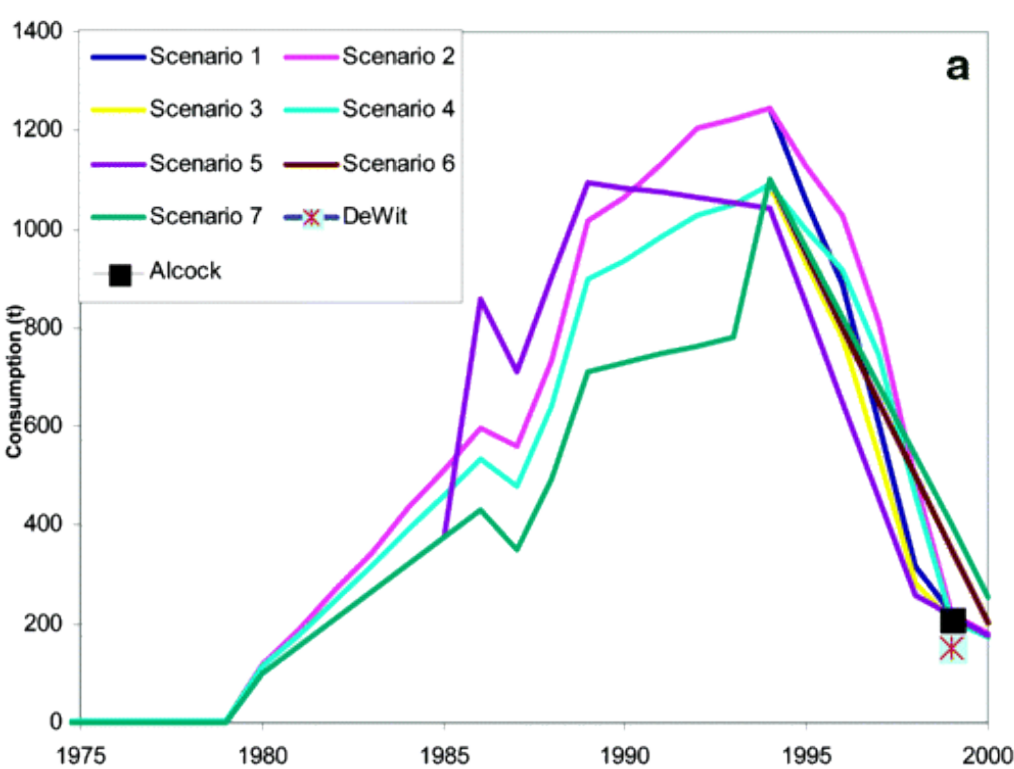
- ✦ ABS plastic for computers, casings, circuit boards, small appliances
- ✦ banned under Stockholm Convention

Deca

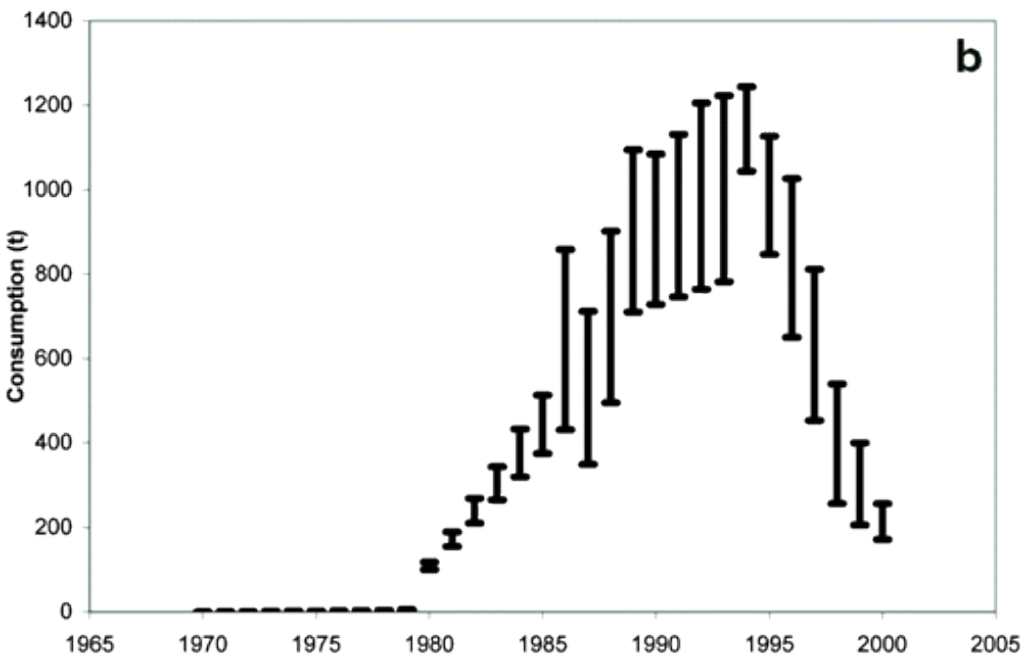
- ✦ Electrical & electronic equipment, casings for TVs, computers, textile backings (e.g., carpets)
- ✦ Still in use in some areas, phased out in Europe, North America

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

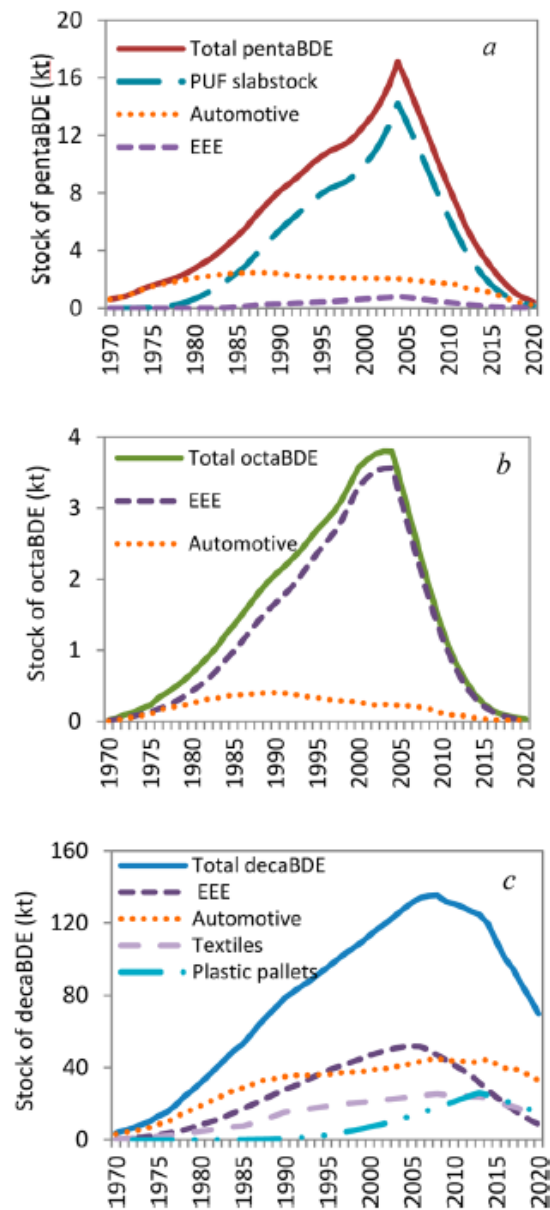


Figure 2. Stock of each PBDE commercial mixture in in-use products in the U.S. and Canada from 1970 to 2020, (a) pentaBDE in EEE, automotive vehicles, and PUF slabstock used in furniture, (b) octaBDE in automotive vehicles and EEE, and (c) decaBDE in plastic pallets, textiles, EEE, and automotive vehicles.

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

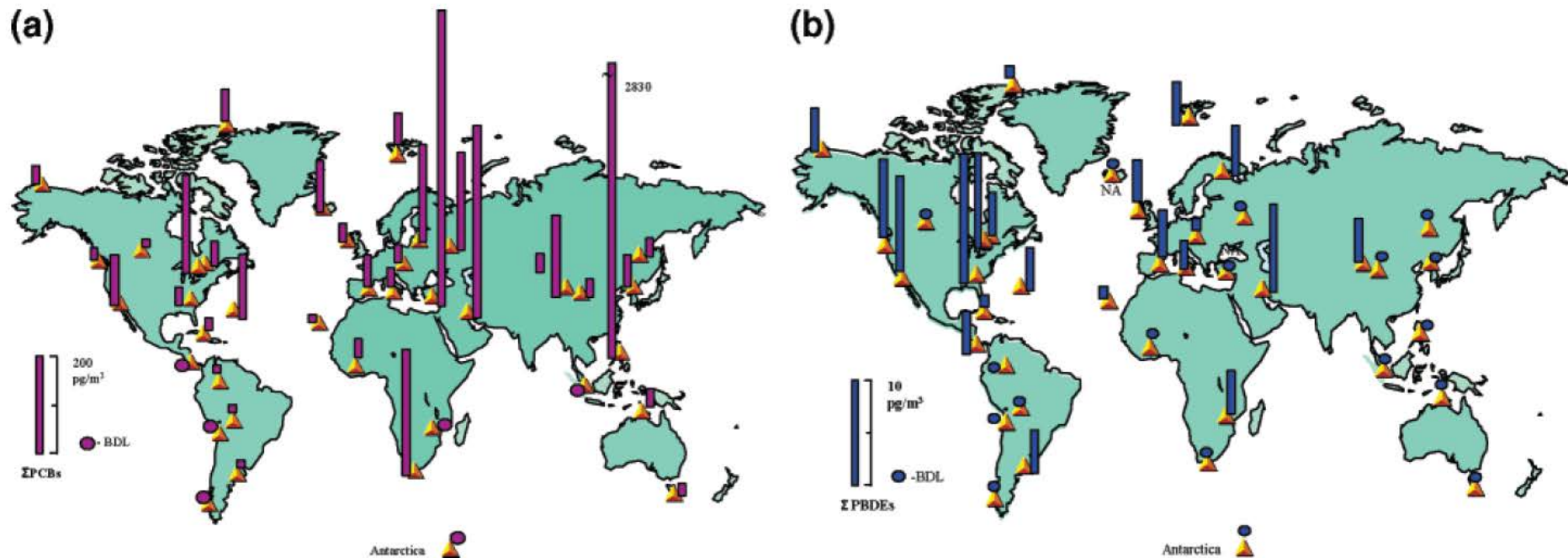


FIGURE 4. Air concentrations (pg/m^3) of (a) PCBs and (b) PBDEs between December 2004 and March 2005 at GAPS sites. See Table S1 for BDL values.

From Pozo et al. 2006

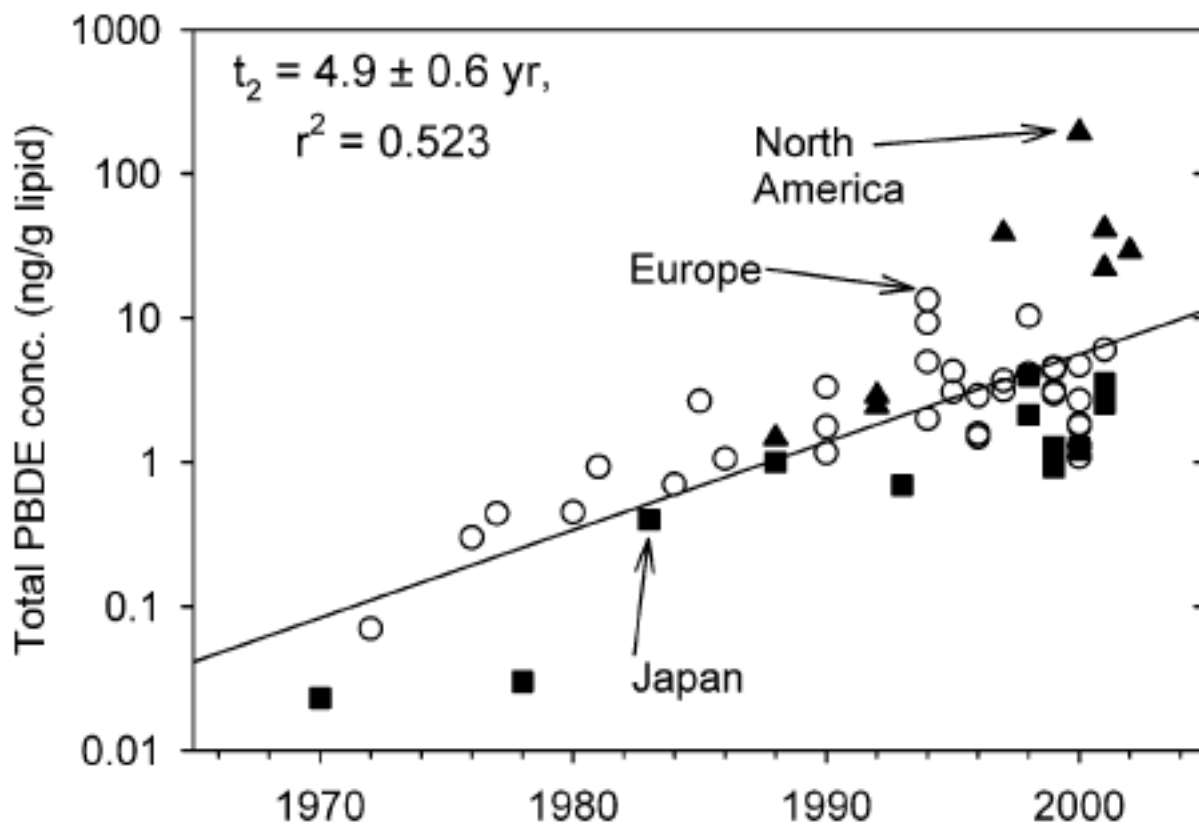
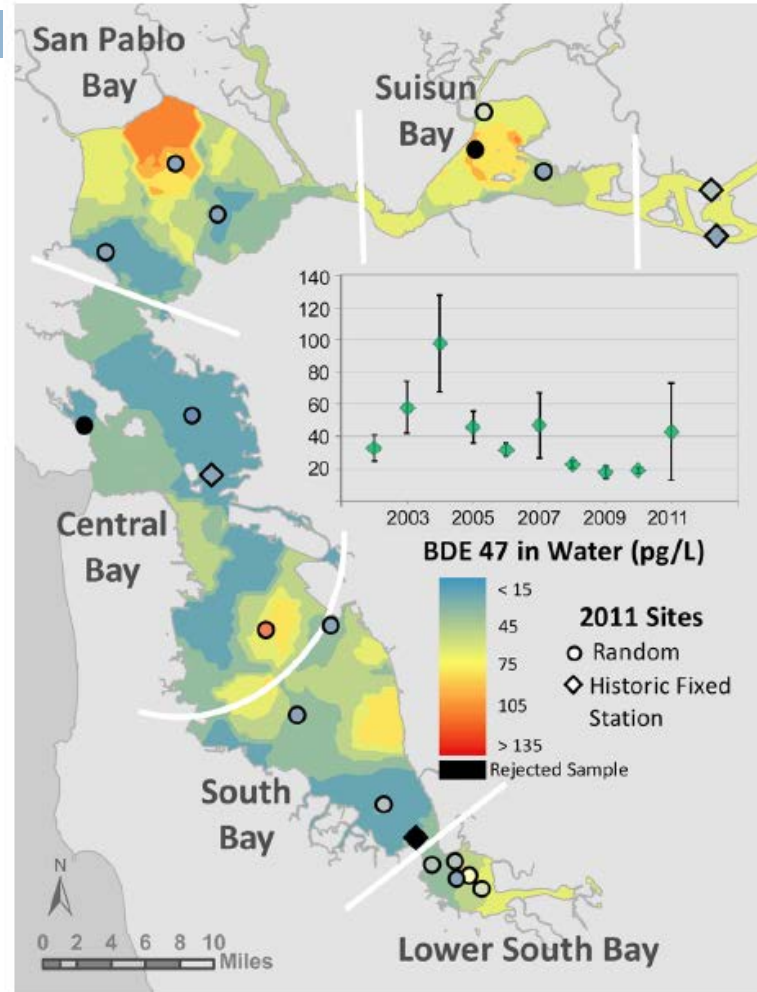
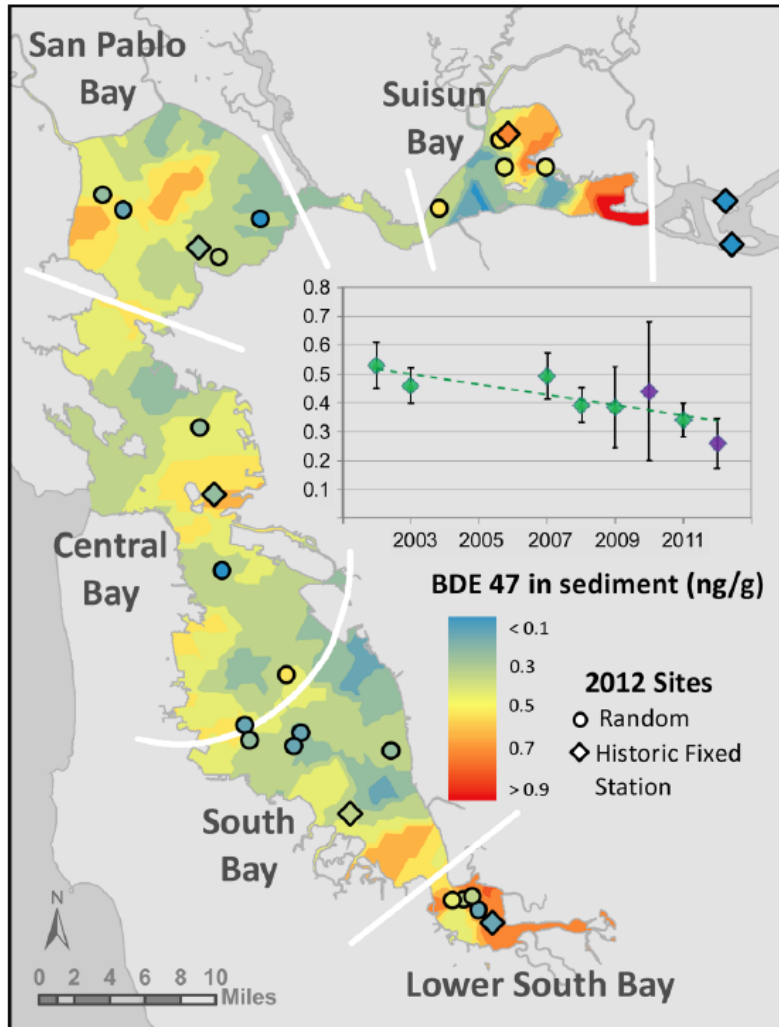


FIGURE 1. Total PBDE concentrations (Σ PBDE) in human blood, milk, and tissue (in ng/g lipid) shown as a function of the year in which the samples were taken; see Table 2. The three symbol types indicate the location from which the samples were collected. The overall regression is shown.

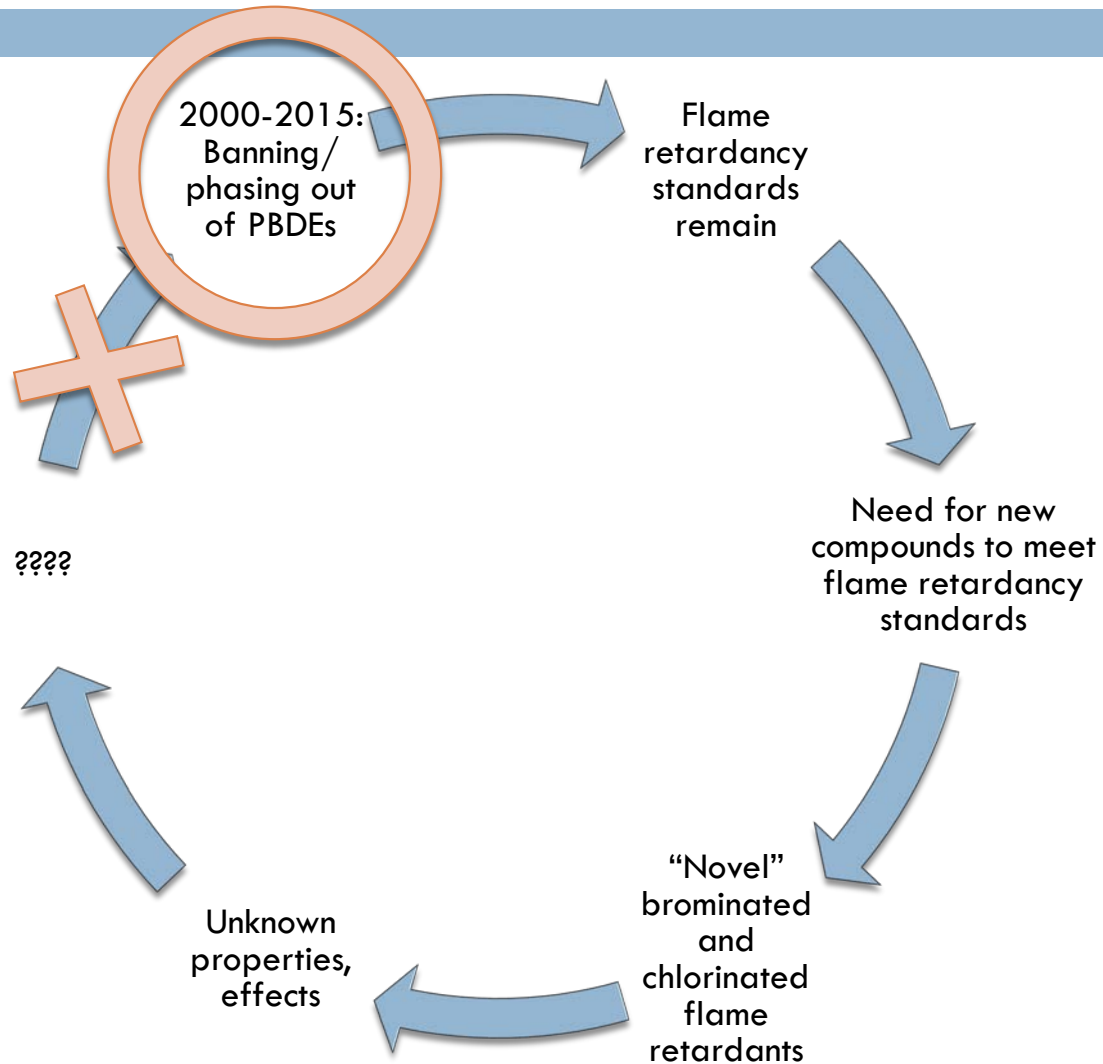
Temporal trends of PBDEs

San Francisco Bay sediment and water:

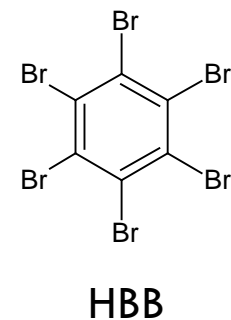
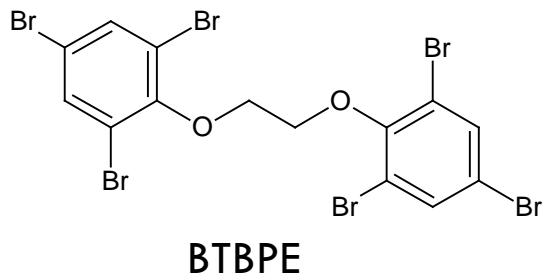
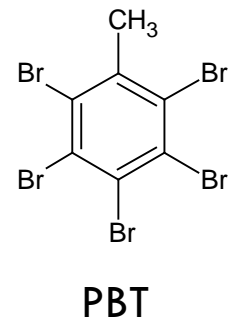
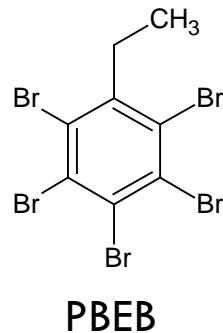
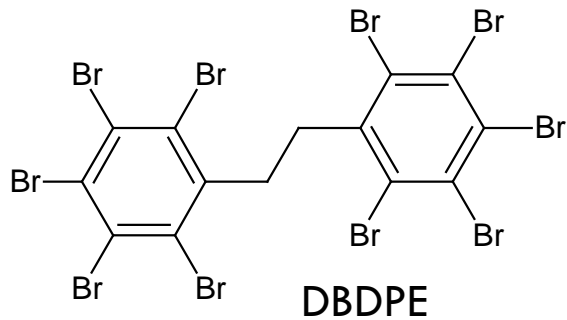
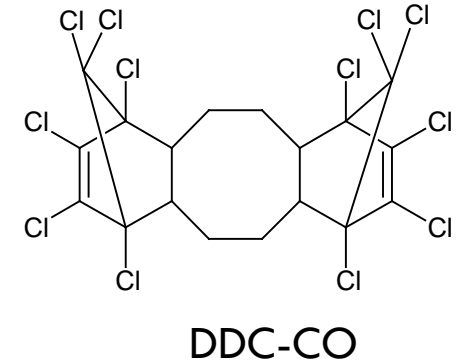
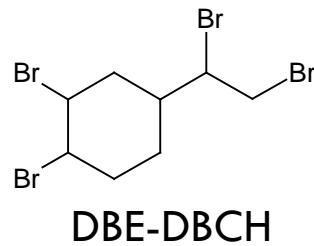
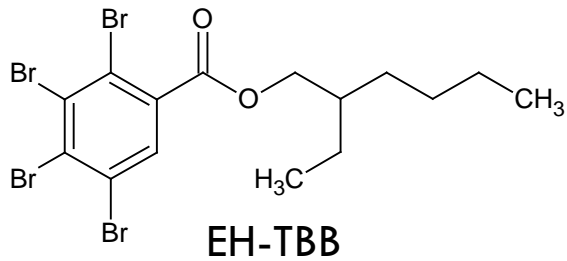


Sutton et al. 2014, Environmental Science & Technology

Replacement of banned compounds



“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.

Chemicals to know

- DDT
- PCBs
- PCDD/Fs
- PAHs
- PBDEs

What to know...

ABOUT EACH COMPOUND:

- Source/use of the compound
 - ▣ Industrial? Emission by-product?
- Status
 - ▣ Is the chemical still in use? Where is it legal/illegal?
- Where do we find the chemical?
 - ▣ In the environment? In humans? How are humans exposed?