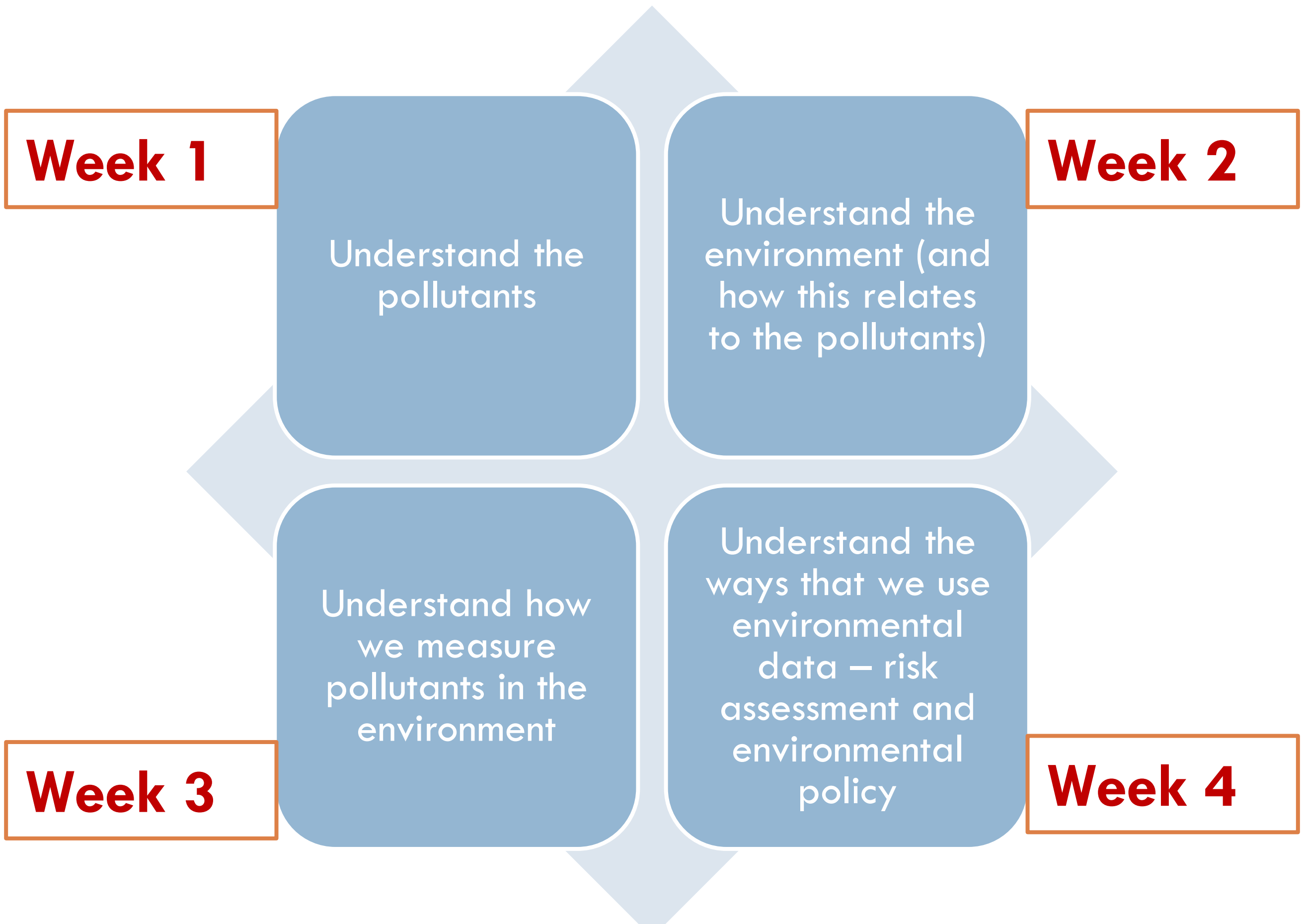
C2003 – ENVIRONMENTAL CHEMISTRY

Course goals:

After this course, students should be able to:

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



Goals in detail...

Understand the pollutants:

- characterize the main types of pollutants, mainly those that are non-degradable or persistent, have the ability to accumulate in abiotic and biotic compartments, posses a broad range of toxic effects, and can be transported to long distances
- describe basic properties of these chemicals, their occurrence, sources, and how they enter the environment
- understand relations between the chemical structure of chemical substances, their physical-chemical properties and their fate in the environment

Understand the environmental compartments (and how these relate to the pollutants):

- interpret the environmental fate of chemical substances, their environmental transport, interphase transport, phase equilibria and environmental biotic and abiotic transformation
- characterize properties of environmental compartments (atmosphere, hydrosphere, pedosphere, biosphere) and combine this knowledge with the presence and fate of chemical compounds in these compartments
- explain the relationships between the pollution sources and primary and secondary types of pollution of environmental compartments
- understand the impact of environment properties on the fate of chemicals

Understand how we measure these pollutants in the environment:

- describe purposes and principles of the activities focused on screening and monitoring of presence of anthropogenic chemicals in the environment
- distinguish between specific sampling methods for determination of volatile, non-volatile, polar and non-polar compounds in air, water, sediment, soil and biota
- review the analytical techniques for the sample preparation, clean-up and fractionation
- select the best analytical methods for the individual groups of chemicals
- compare the separation and identification techniques and their applicability for determination of various organic chemicals in the environmental samples
- define fundamentals of chromatographic and mass spectroscopy methods
- introduce the quality assurance/quality control measures - understand the whole concept of chemical analysis of the environmental samples

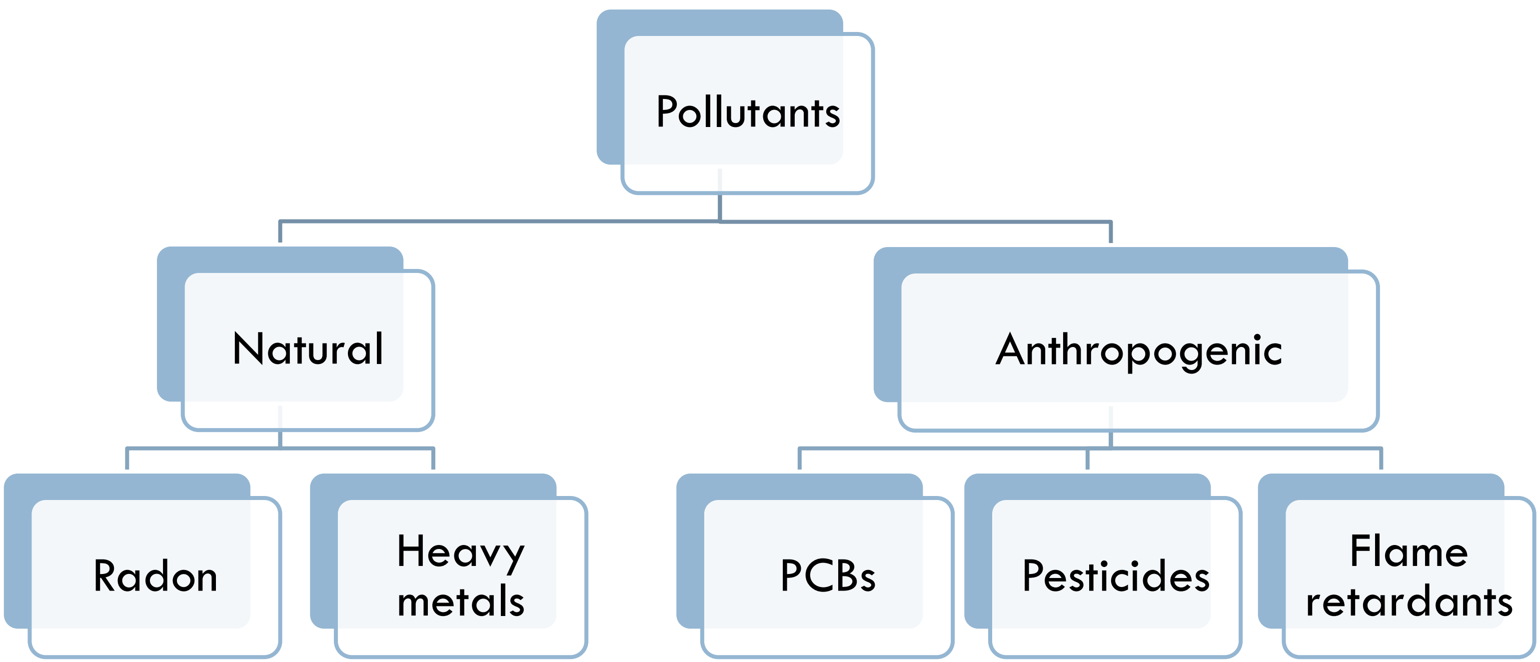
Understand the ways that we use environmental data: risk assessment and environmental policy

- characterize and discuss environmental and health impacts of pollution
- describe and discuss legislation and policy of these compounds and international conventions

What is pollution?

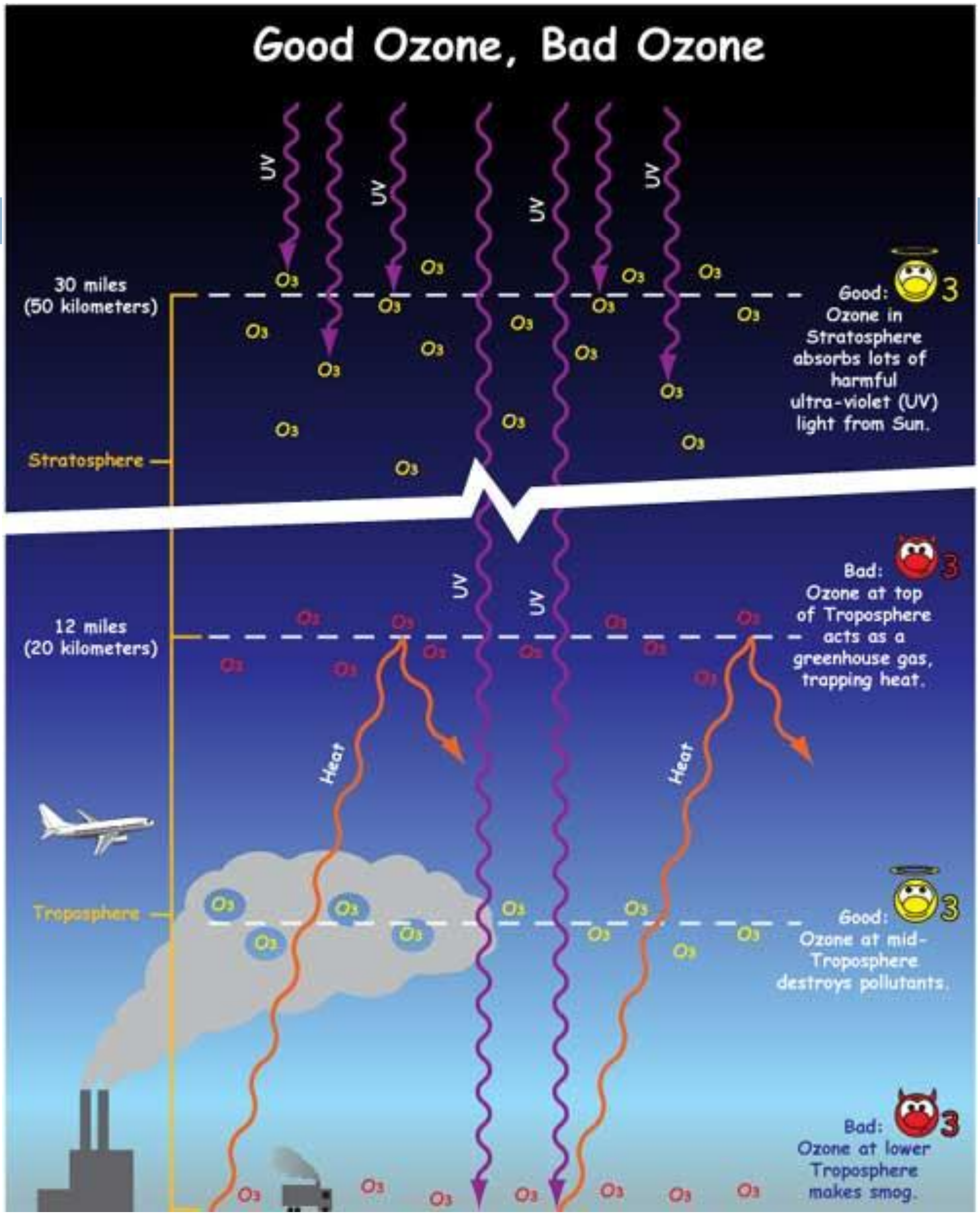
- Presence of a substance in an environmental system having a harmful effect
- The substance = *pollutant* or *contaminant*

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…



http://spaceplace.nasa.gov/greenhouse/en/

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 and understanding of the properties and behaviour of chemicals, we can better understand what the impact of humans is on the global environment

Schwarzenbach et al. *Environmental Organic Chemistry*

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.

Air pollutants

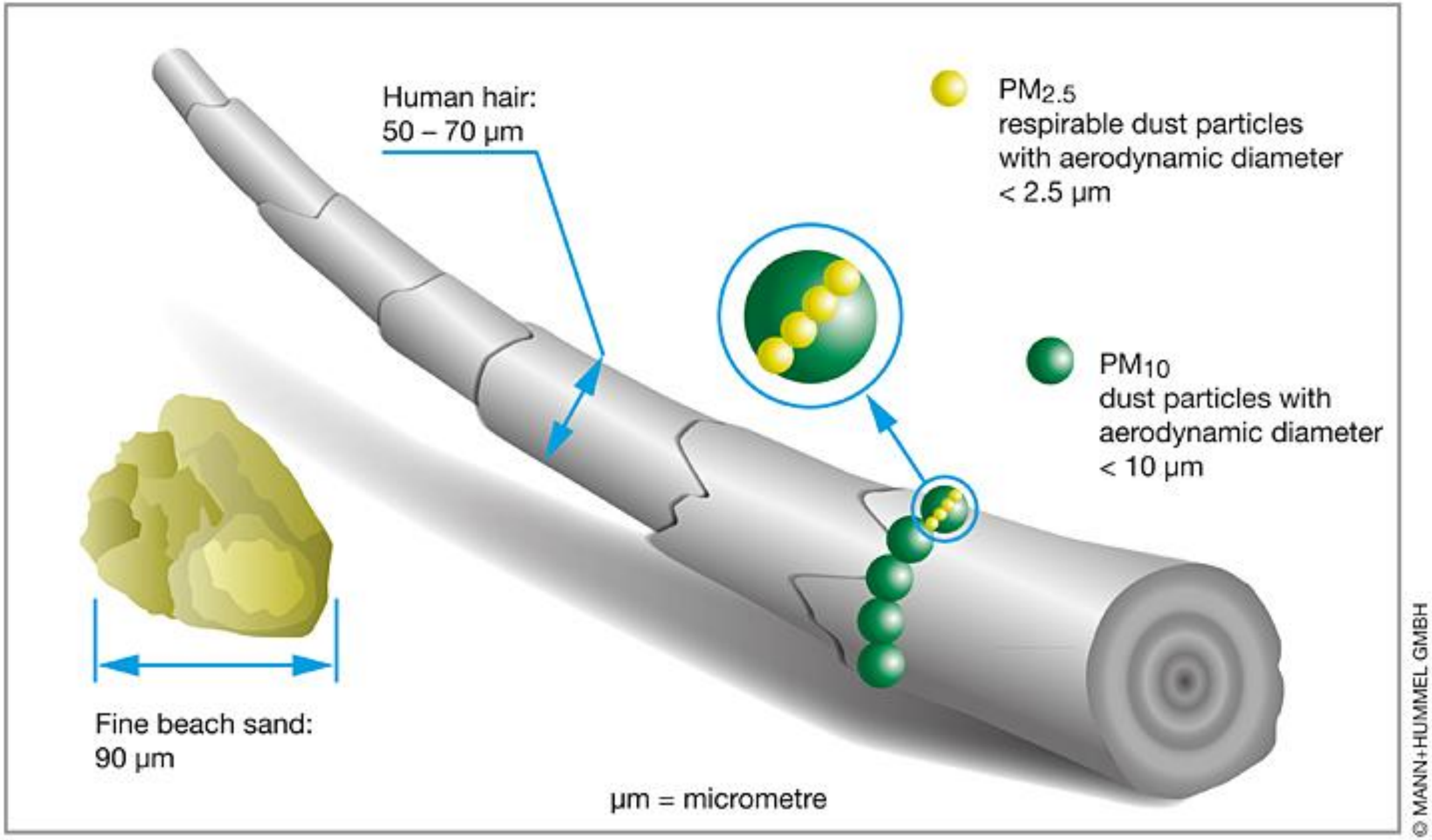
- Airborne particulate matter, volatile organic compounds (VOCs) → primarily air pollutants
- 5 major air pollutants:
  - Particulate matter
  - Ozone
  - Nitrogen dioxide
  - Sulphur dioxide
  - VOCs

World Health Organization, 2005 Air Quality Guidelines

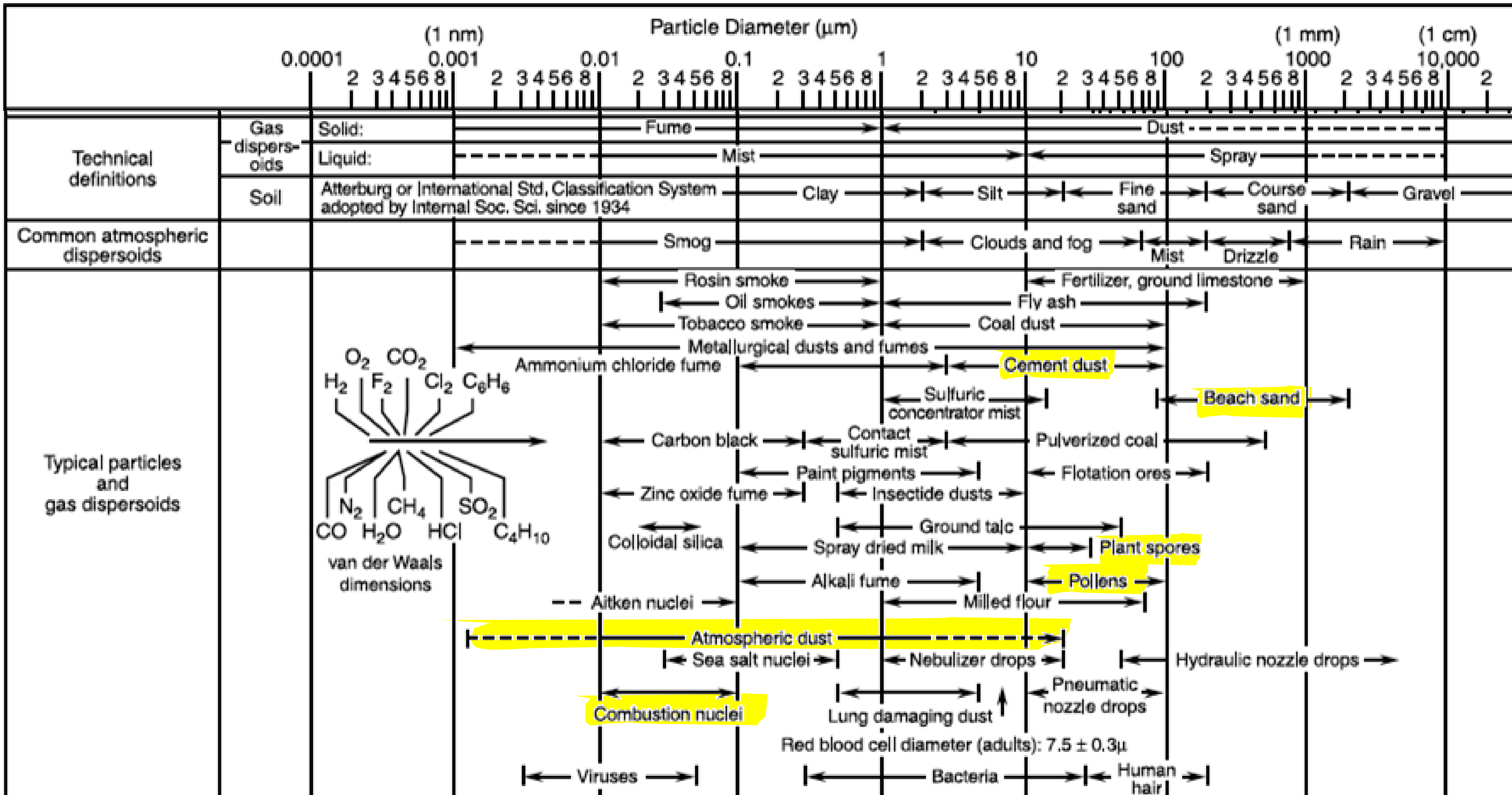
Particulate matter (PM)

- 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

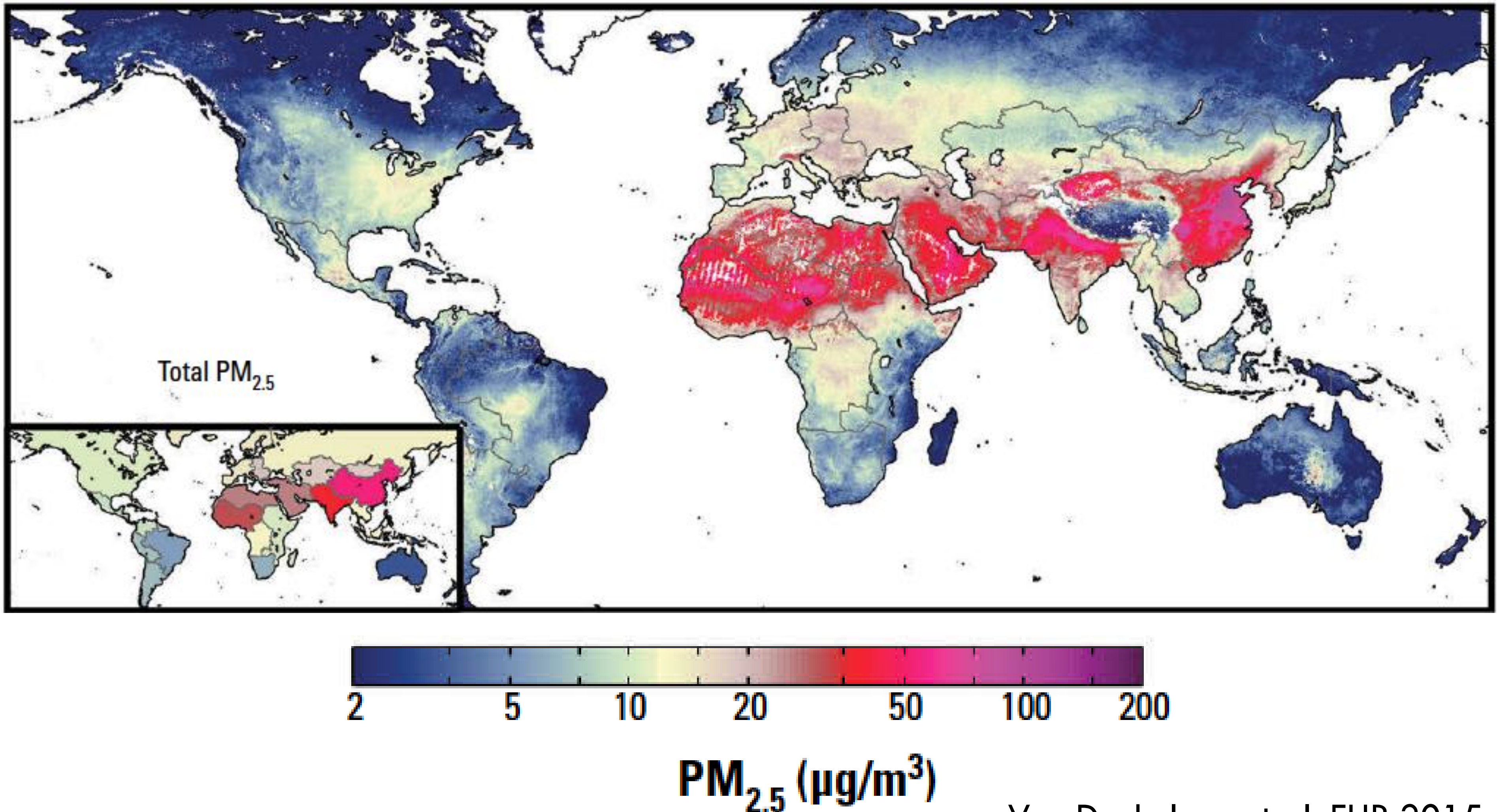


PM sizes and examples



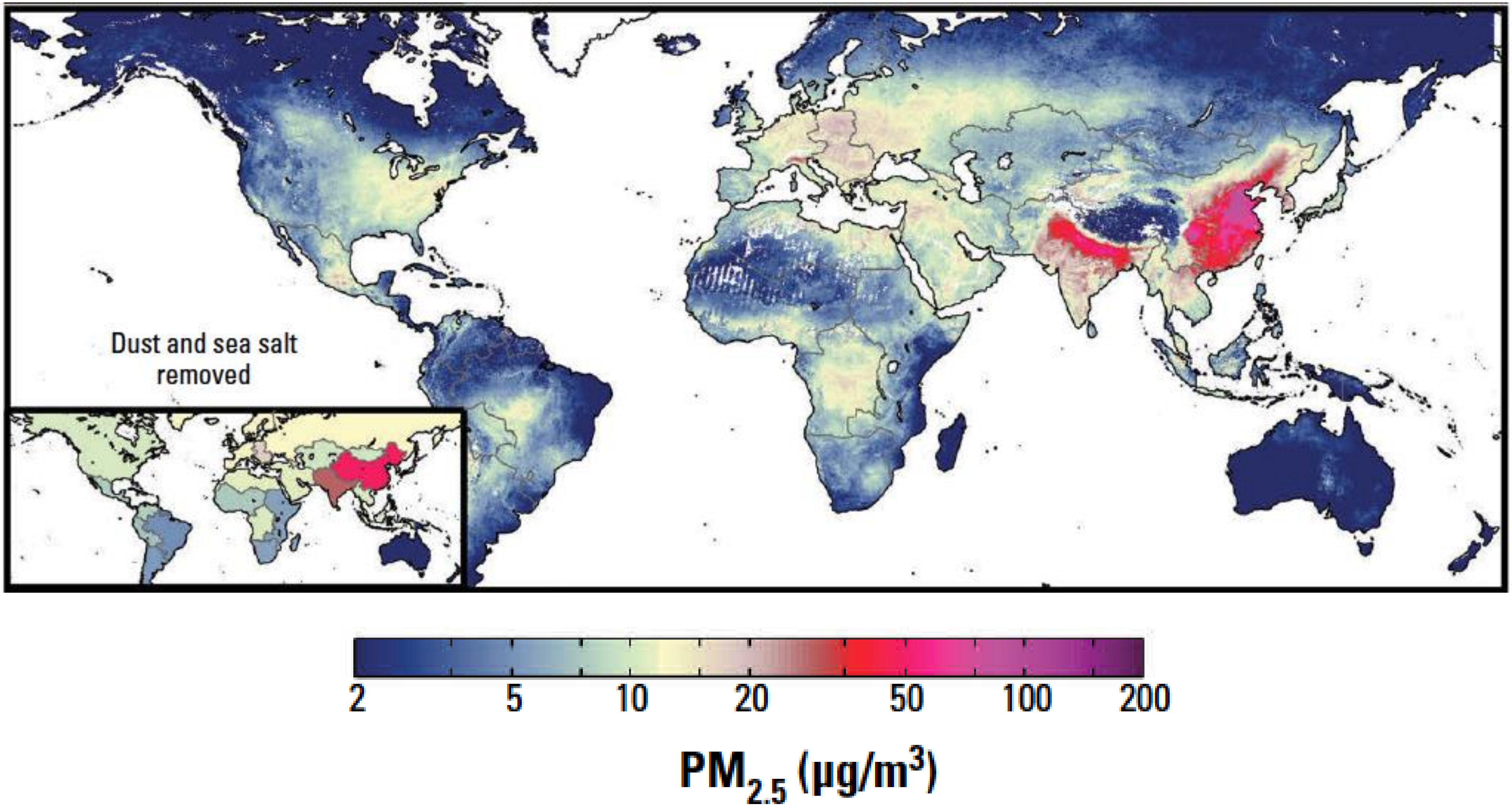
From Finlayson-Pitts and Pitts, 2000, *Chemistry of the Upper and Lower Atmosphere*

Particulate matter

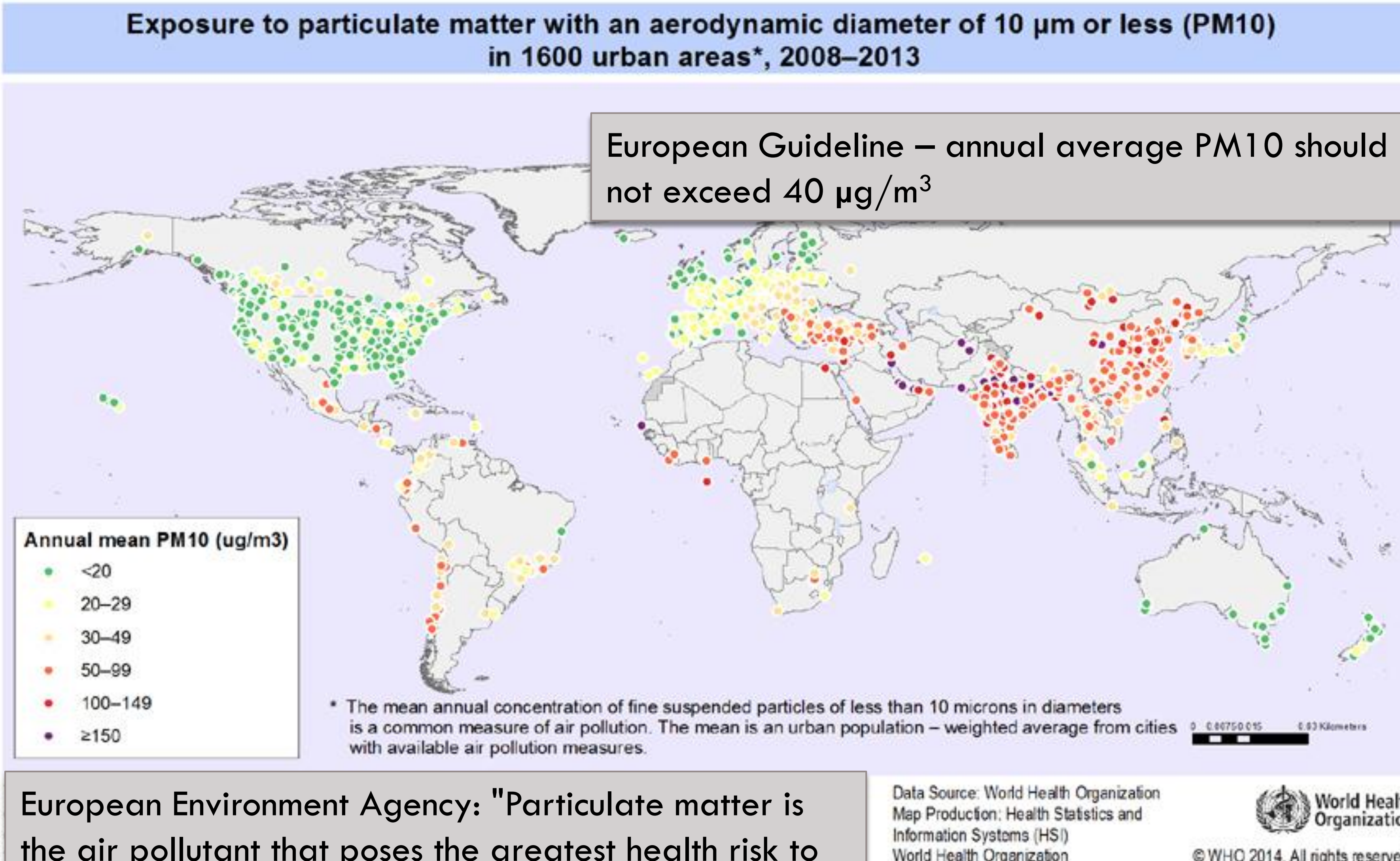


Van Donkelaar et al. EHP 2015

Particulate matter – excluding dust and sea spray



Particulate matter - exposure



European Guideline – annual average PM10 should not exceed 40 µg/m^3

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

Smog formation

- The word comes from the combination of "smoke" and "fog"…appropriate for original smog that was largely composed of soot particles from burning coal
- Today - photochemical smog ("modern" smog) – typically related to vehicle emissions
- Composed of particles and ozone and other secondary pollutants (e.g., peroxyacyl nitrates)
- 3 "ingredients" to make photochemical smog:
  - Light
  - Hydrocarbons, such as VOCs
  - A source of atmospheric radicals, such as NOx

Ingredients for smog

- VOCs – benzene, acetylene, xylene, acetone, toluene, etc.
- NOx – nitrogen oxide compounds: NO and NO_2

Sunlight can break down nitrogen dioxide (NO_2) back into nitrogen oxide (NO).

$$NO_2 + \text{sunlight} \rightarrow NO + O$$

The atomic oxygen (O) formed in the above reaction then reacts with one of the abundant oxygen molecules producing ozone (O_3).

$$O + O_2 \rightarrow O_3$$

Nitrogen dioxide (NO_2) can also react with radicals produced from volatile organic compounds in a series of reactions to form toxic products such as peroxyacetyl nitrates (PAN).

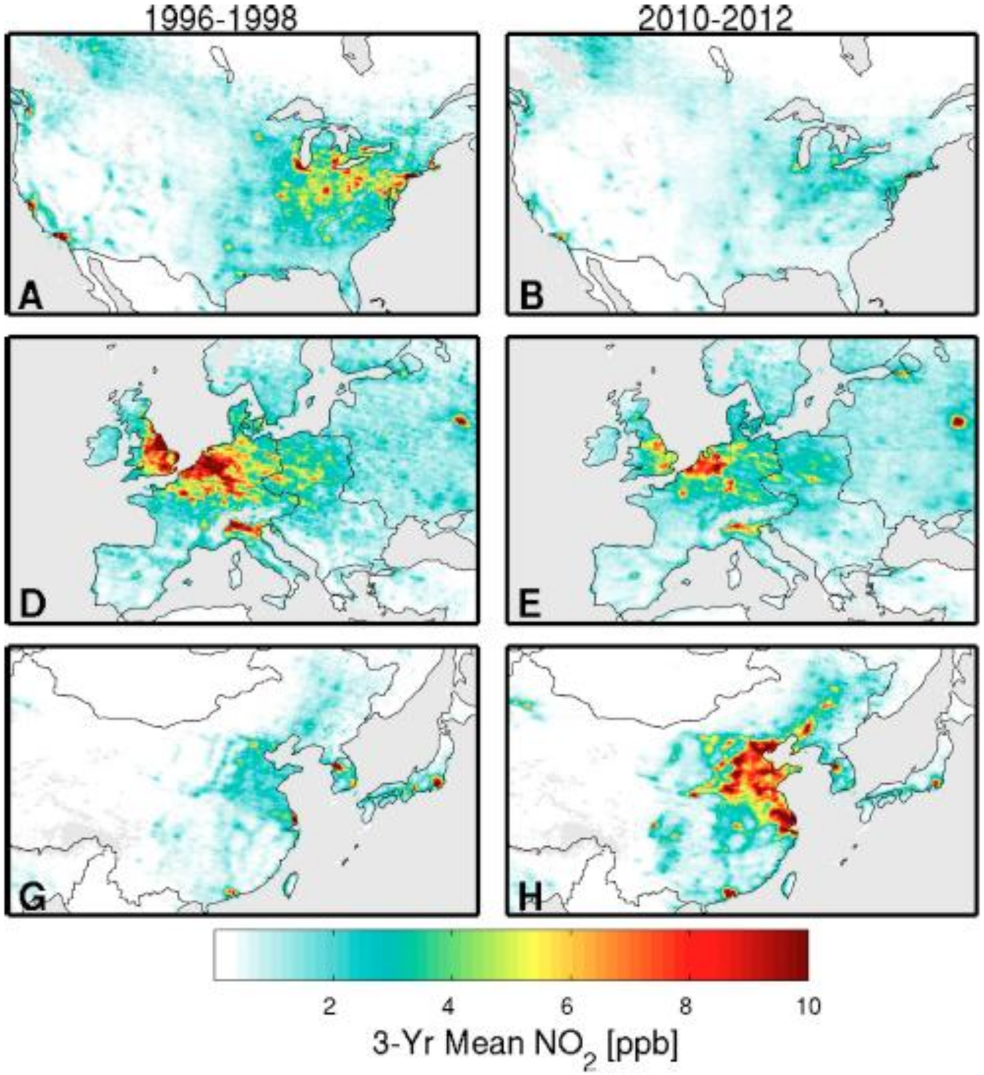
$$NO_2 + R \rightarrow \text{products such as PAN}$$

Also:

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$NO + RO_2 \rightarrow NO_2 + \text{other products}$$

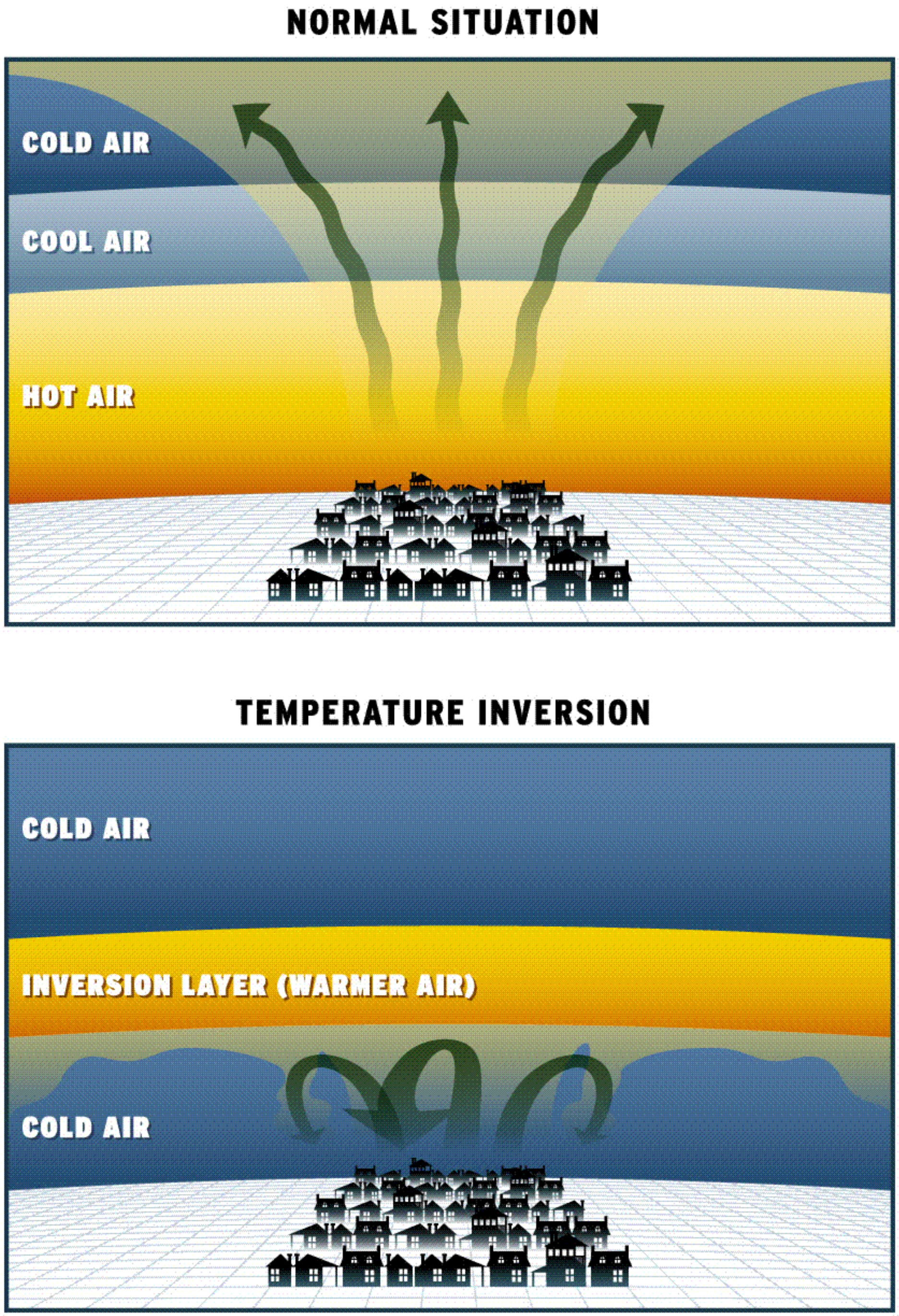
NO_2 – global distribution



Geddes et al. EHP, 2015

Case study 1: L

- 1943 – Los Angeles suffers extreme smog – irritation to eyes and breathing, visibility <3 blocks
- Smog problems continued throughout 1940s and 1950s
- Early 1950s: car emissions identified as contributing factor to smog
- LA geography made smog worse



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
  - etc.

(Persistent organic pollutants, Polycyclic aromatic hydrocarbons) + others = **SEMI-VOLATILE** ORGANIC COMPOUNDS

What are 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.

Examples of SVOCs

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

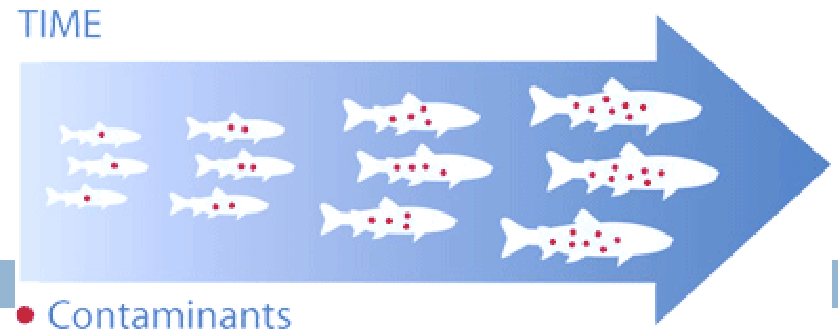
POPs / PBT

- 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 >> 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 > ~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

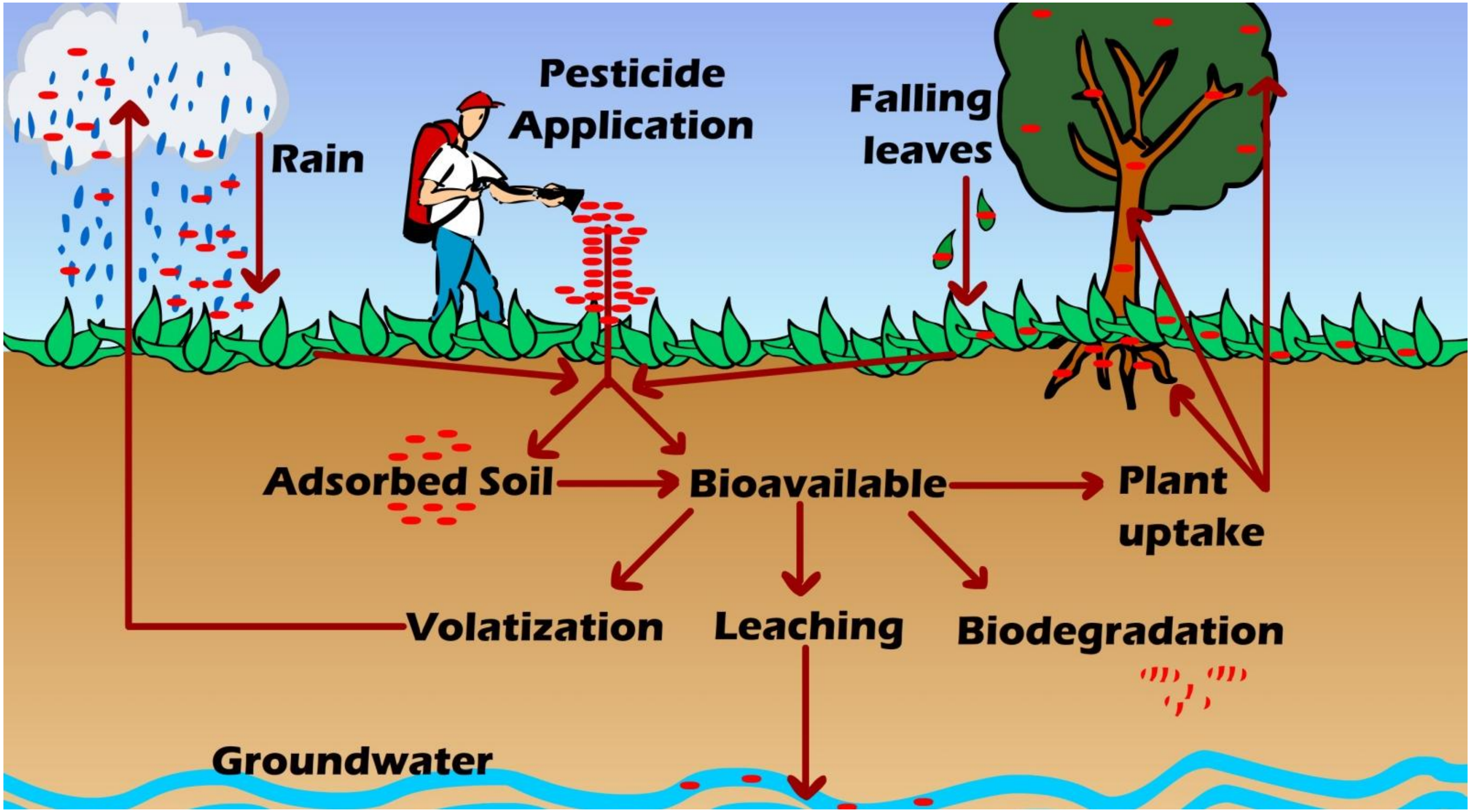
- Pesticides
- Industrial chemicals
- By-products
- Additives in consumer products

Pesticides – intentionally toxic!

Chemicals designed to kill, reduce or repel pests

- Insects → Insecticides
- Weeds → Herbicides
- Moulds → Fungicides
- Rodents → Rodenticides

How pesticides enter the environment



Langenbach. "Persistence and bioaccumulation of Persistent Organic Pollutants" 2013

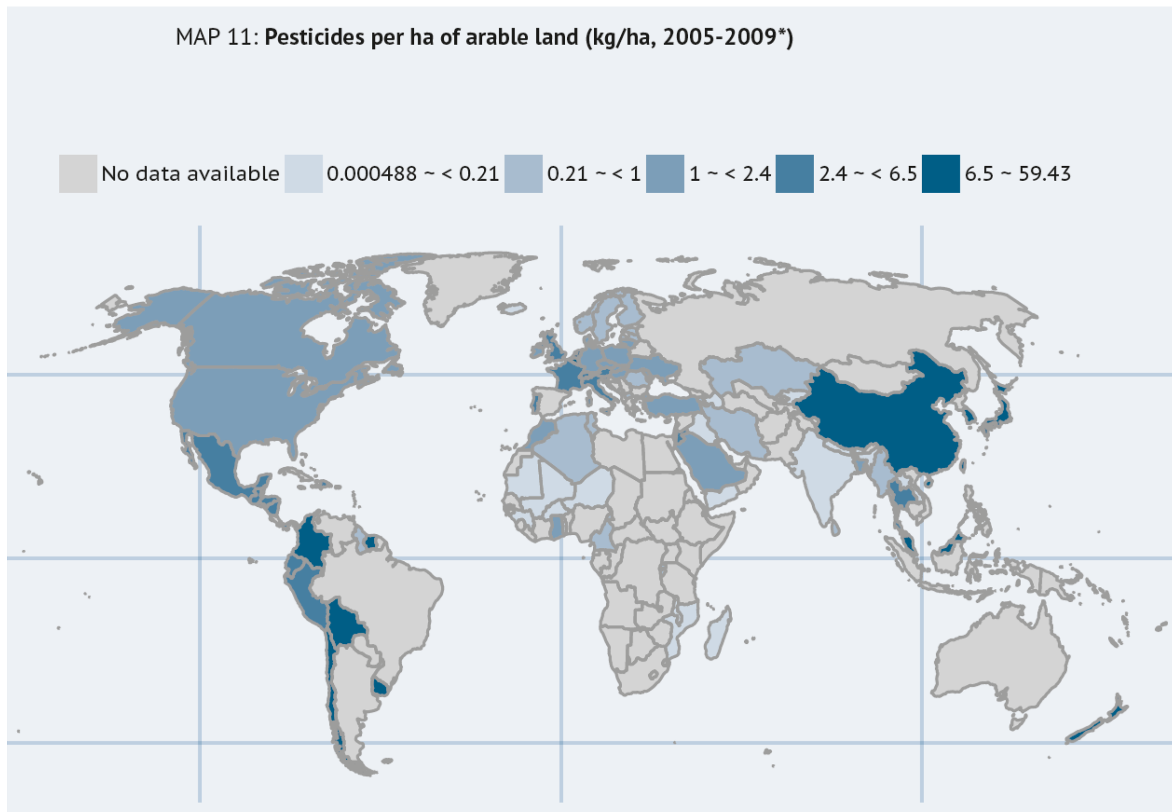
Global pesticide use

2.5 million tonnes per year (Alavanja, 2009)

Insecticide

Herbicide

Fungicide

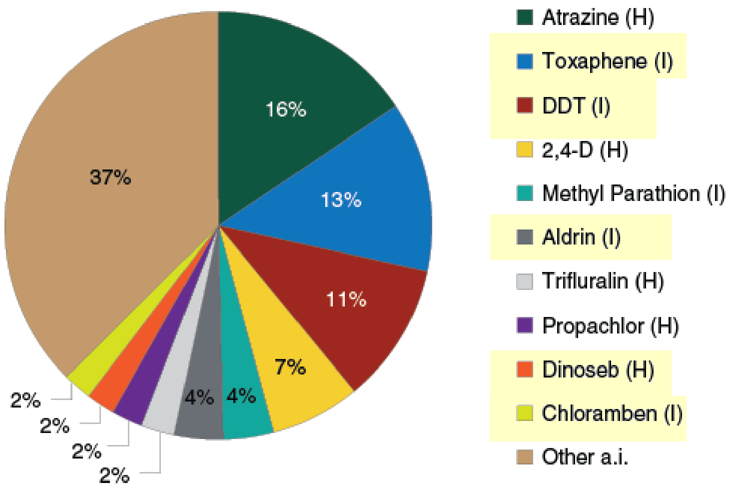


From FAO Statistical Yearbook, UN 2013

Most common pesticides

- In 1960s…

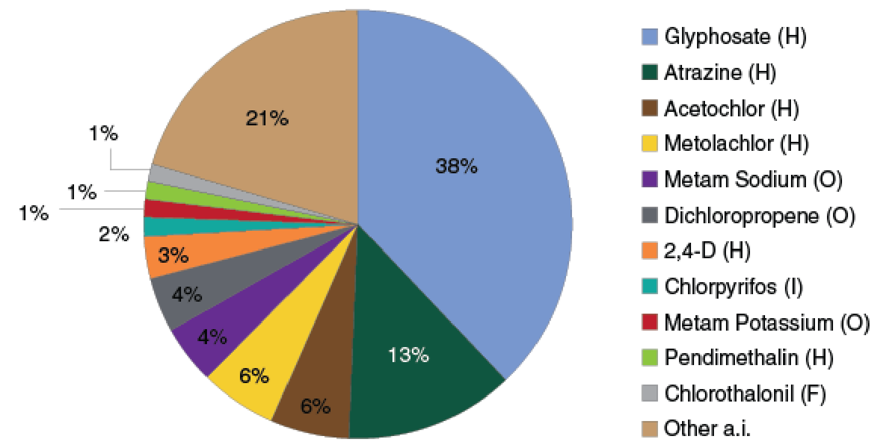
The 10 most heavily used pesticide active ingredients in 1968 included 5 insecticides and 5 herbicides (percent total pounds active ingredient applied on 21 selected crops)



Note: H = herbicide, I = insecticide.
Source: USDA, Economic Research Service using USDA, National Agricultural Statistics Service and proprietary data.

- Today…

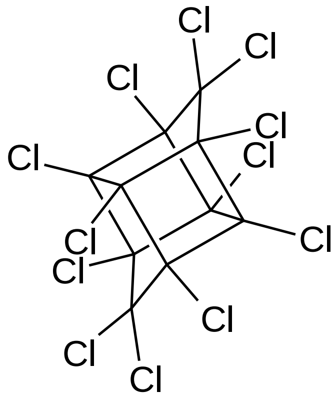
The four most heavily used pesticide active ingredients in 2008 were herbicides (percent total pounds active ingredient applied on 21 selected crops)



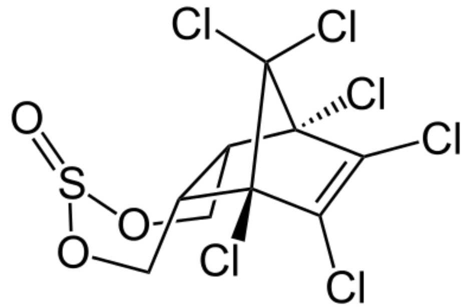
Note: H = herbicide, I = insecticide, F = fungicide, and O = other.
Source: USDA, Economic Research Service using USDA, National Agricultural Statistics Service and proprietary data.

Organochlorine pesticides

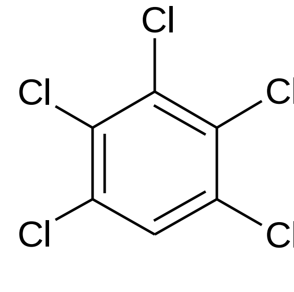
- OCPs = organochlorine pesticides
- What are the OCPs?
  - DDT
  - Hexachlorobenzene (HCB)
  - Pentachlorobenzene (PeCB)
  - Hexachlorocyclohexanes (multiple isomers)
  - Heptachlor/heptachlor epoxide
  - Aldrin/dieldrin/endrin
  - Chlordane (multiple isomers)
  - Endosulfan
  - Mirex
  - …



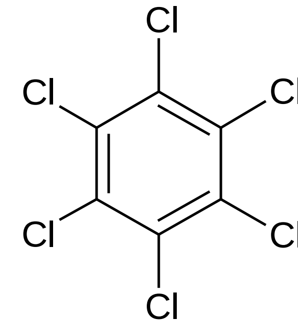
Mirex



Endosulfan

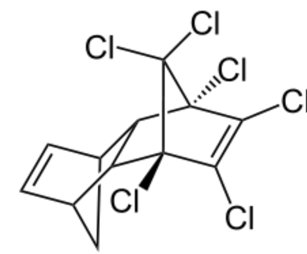


PeCB



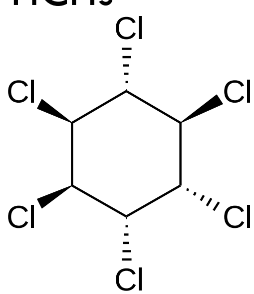
HCB

Chlorinated molecules – highly stable – therefore environmentally persistent

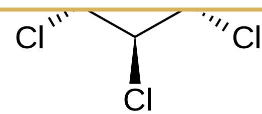


Aldrin

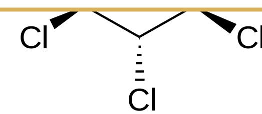
HCHs



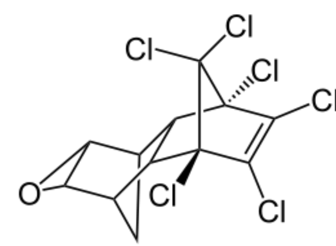
α



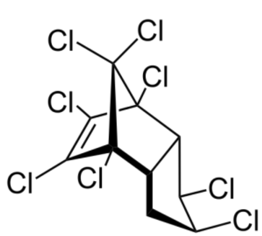
β



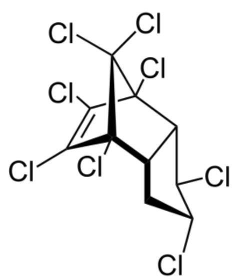
γ



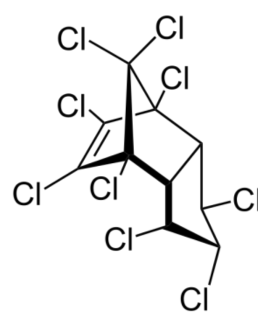
Dieldrin



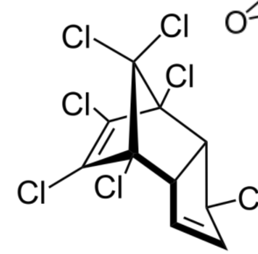
cis-chlordane



trans-chlordane

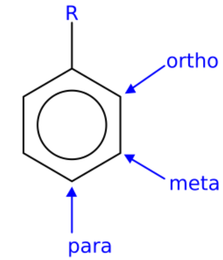


trans-nonachlor

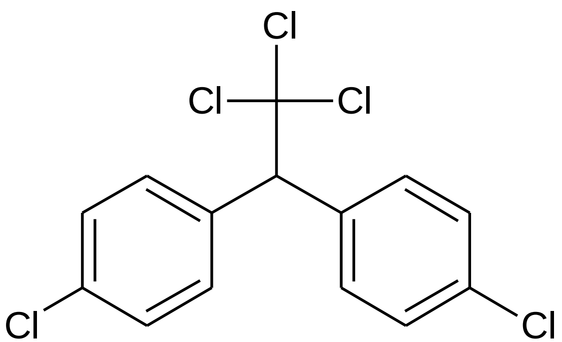


heptachlor

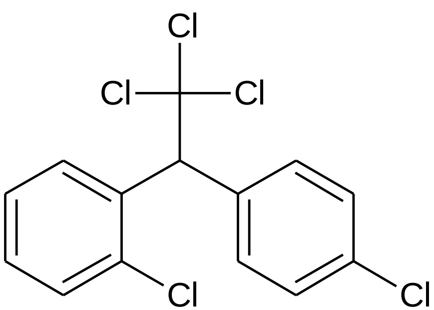
Case study 2: DDT



- DDT – **dichlorodiphenyl trichloroethane**

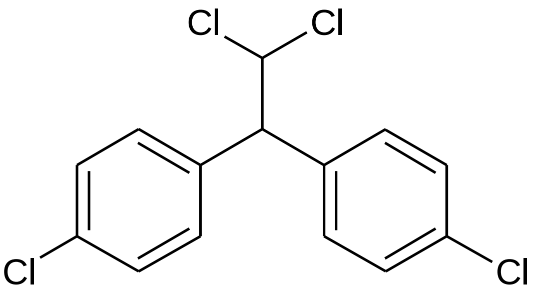


p,p'-DDT

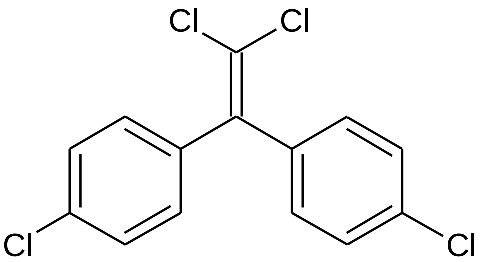


o,p'-DDT

Degradation products/metabolites are often also considered:



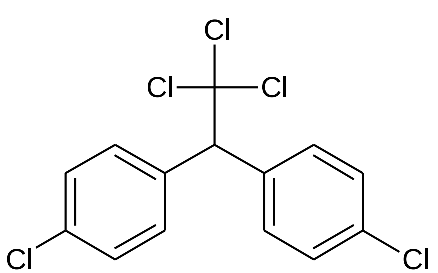
p,p'-DDD



p,p'-DDE

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

p,p'-DDT: 63-79% ← Active ingredient

o,p'-DDT: 8-21%
p,p'-DDD: 0-4%
o,p'-DDD: 0-0.05%

} Impurities

DDT – a brief history

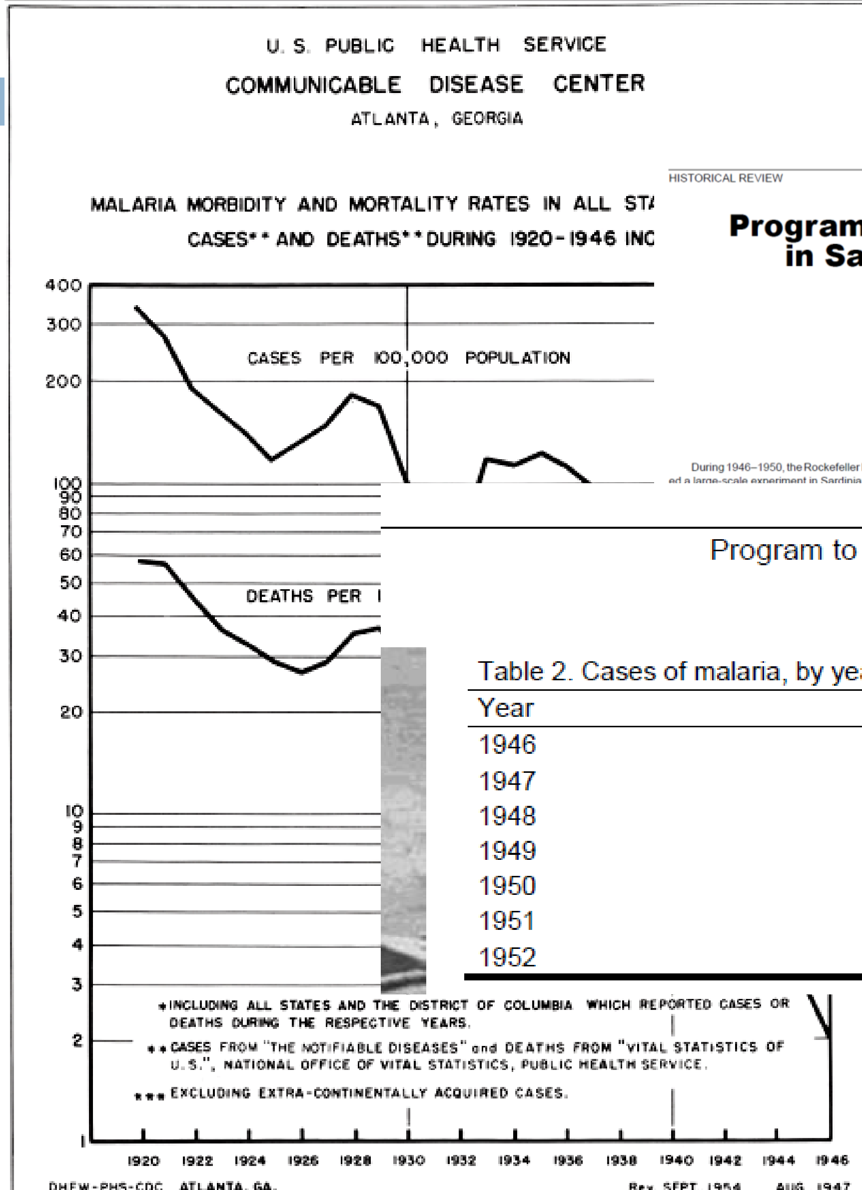
1872 – DDT was first synthesized by Austrian chemistry student

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



HISTORICAL REVIEW

Program to Eradicate Malaria in Sardinia, 1946–1950

Eugenia Tognotti

During 1946–1950, the Rockefeller Foundation conduct-

successful eradication campaigns of an invading vector, A.

Program to Eradicate Malaria in Sardinia

Table 2. Cases of malaria, by year, Sardinia, 1946–1952

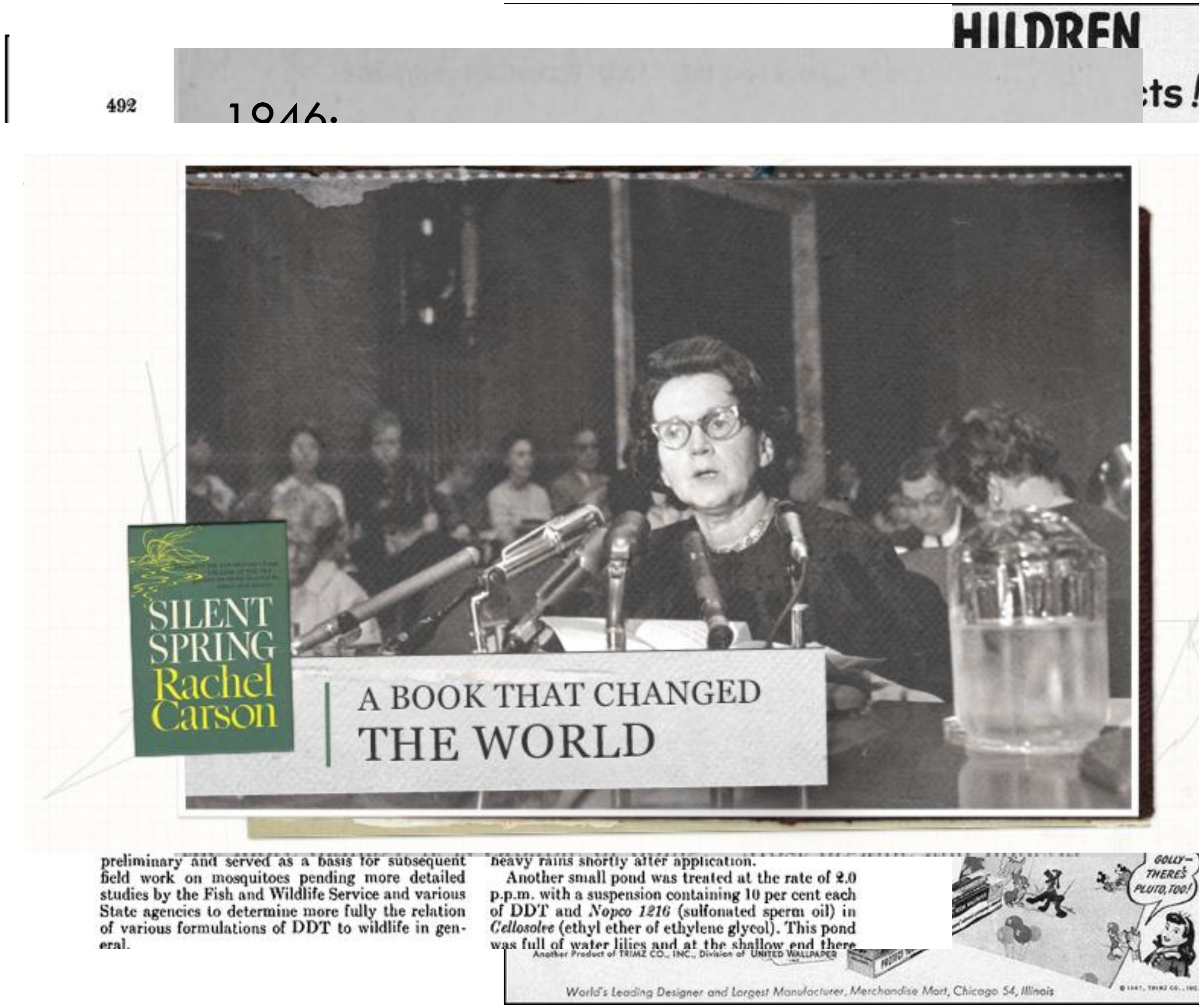
Year	No. cases (relapses)
1946	74,641
1947	39,303
1948	15,121
1949	1,314
1950	0 (44)
1951	9 (8)
1952	0

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

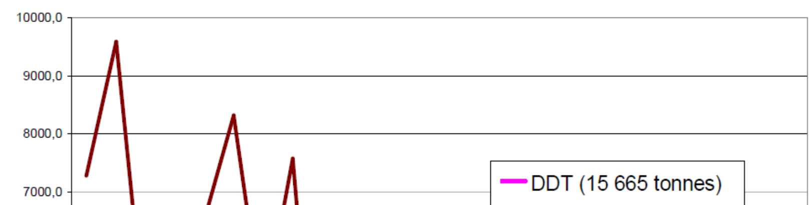
1962 - Rachel Carson's book *Silent Spring* blamed environmental destruction on DDT.

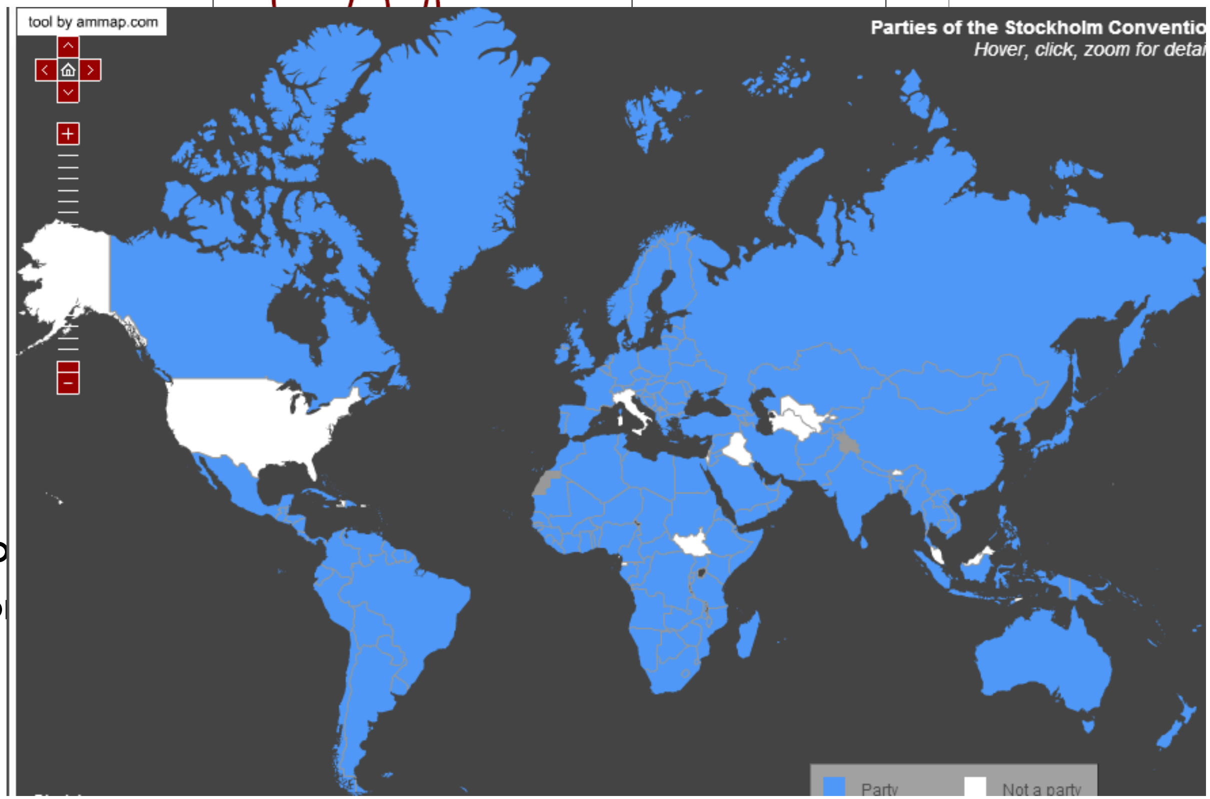


DDT – a brief history

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)





Fro
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?

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

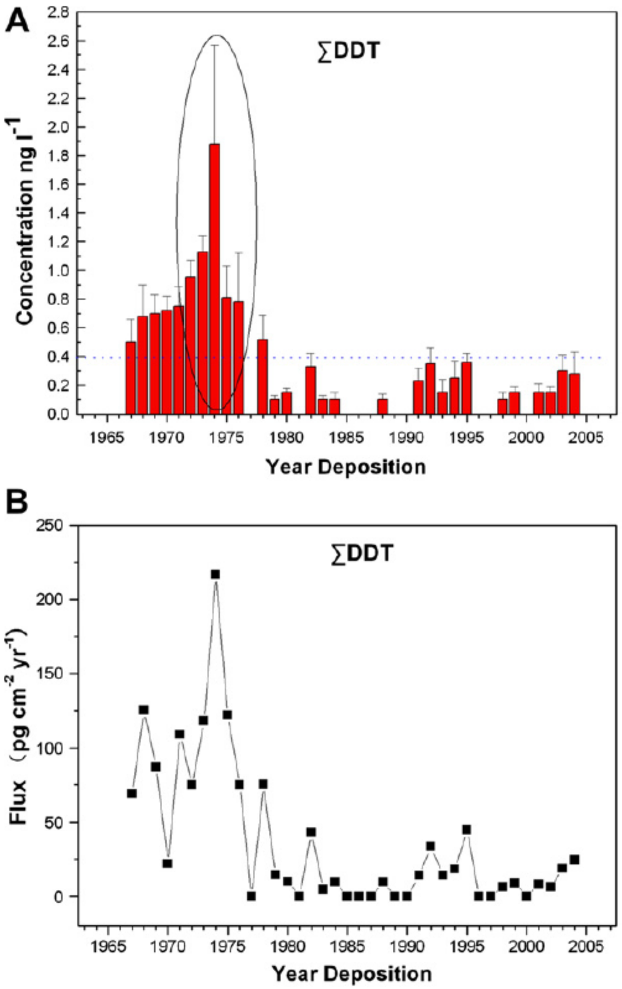


Fig. 4. Concentration (A) and deposition flux (B) of DDT in the ice core from East Rongbuk glacier (Mt.Everest, The Himalayas).

(Wang et al., Atmospheric Environment, 2008)

DDT compounds in precipitation from North America, 1995-2005

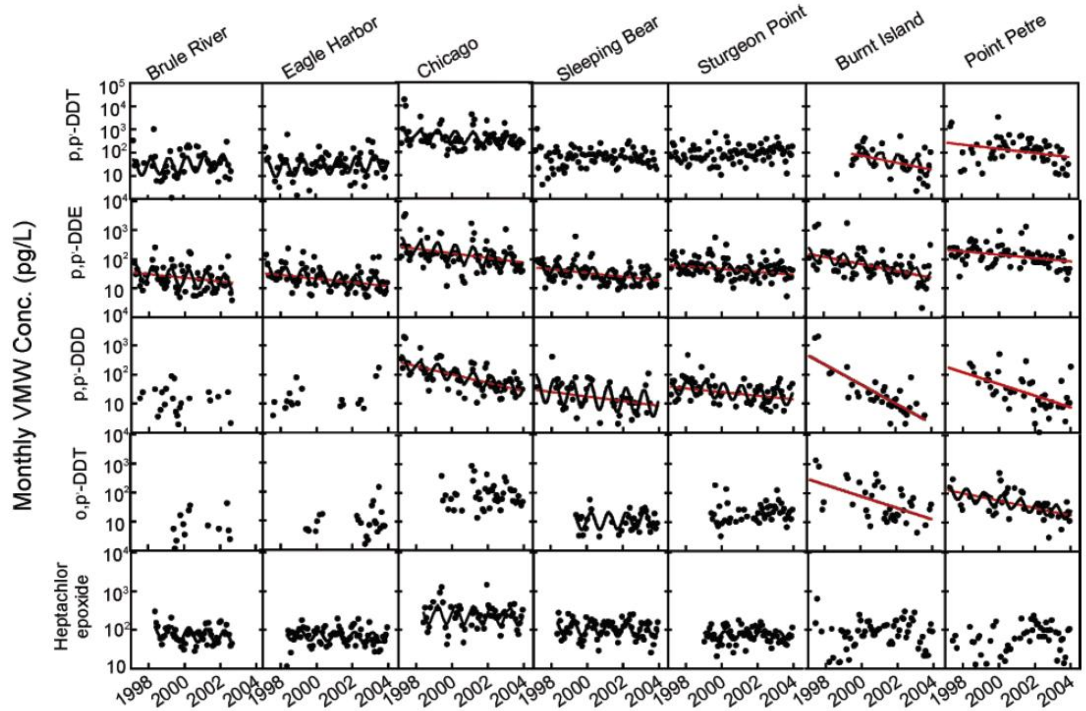


FIGURE 4. Organochlorine pesticide concentrations in precipitation collected at 7 IADN sites near the Great Lakes. The black curve is the fitted line of the sinusoidal model with the period length (a_3) set to one year. The red lines indicate long-term significant decreasing or increasing trends. Detailed information on the fitted parameters is in the Supporting Information.

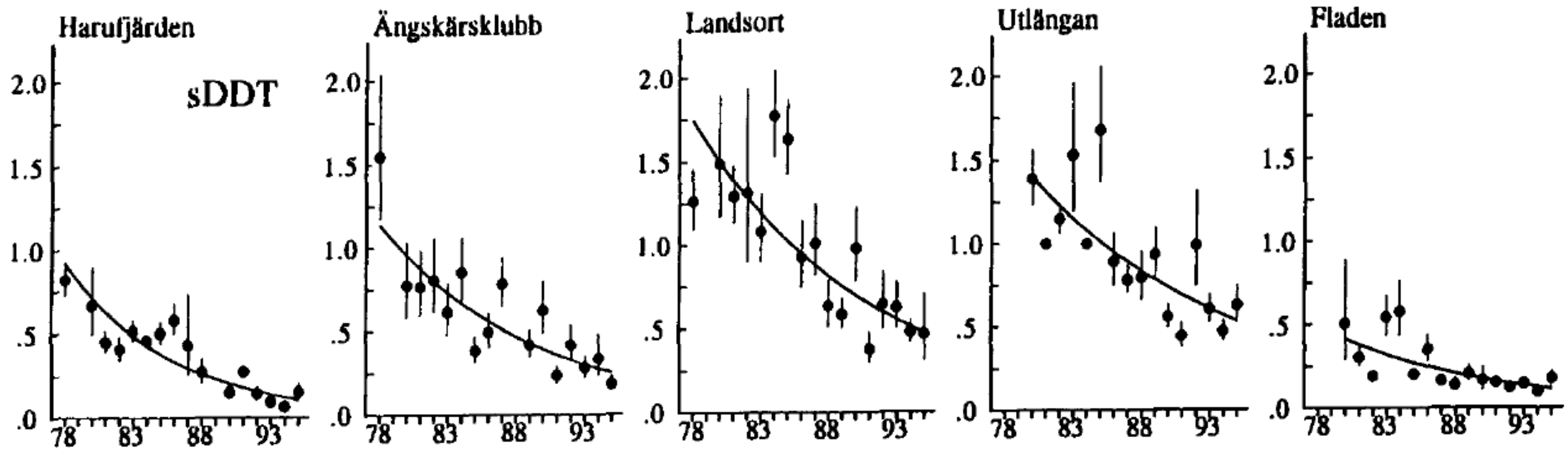
(Sun et al., Environmental Science and Technology, 2006)

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

Conc. (ng/g) →

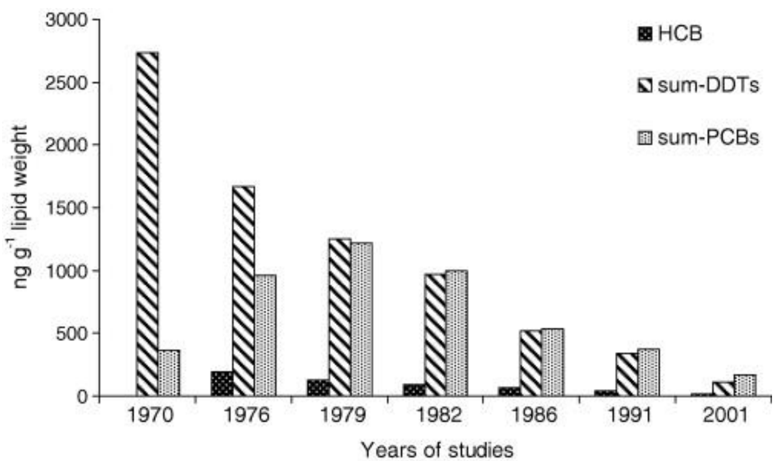


Time →

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?

Health » Environmental Health News

Should DDT Be Used to C Malaria?

DDT should be used "with caution" in combating malaria, a pan

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

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)

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.

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 2011[2]
- Replacement pesticides should have lower *persistence* and *bioaccumulative* potential

1 Van den Berg, EHP 2009; 2 FAO Statistics (faostat.fao.org);

Currently used pesticides

- Glyphosate ("Round-up")
  - Herbicide
  - In use since 1970s
  - Most widely use 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
- Chlopyrifos
  - Most widely used insecticide
  - 170000 tonnes per year (~7% of world pesticide market)

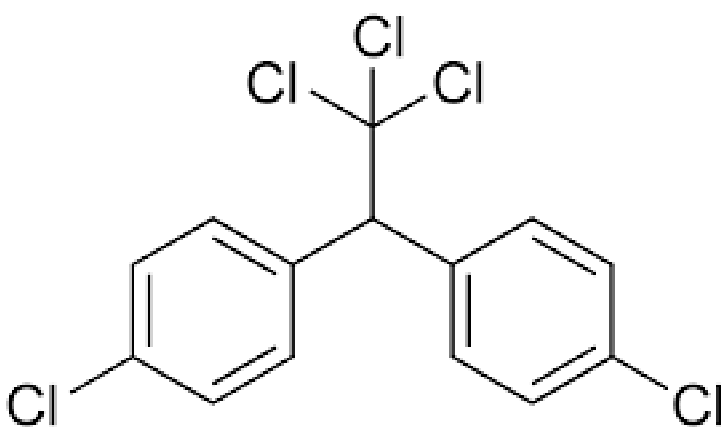
Comparing 2 insecticides: Chlorpyrifos vs. DDT

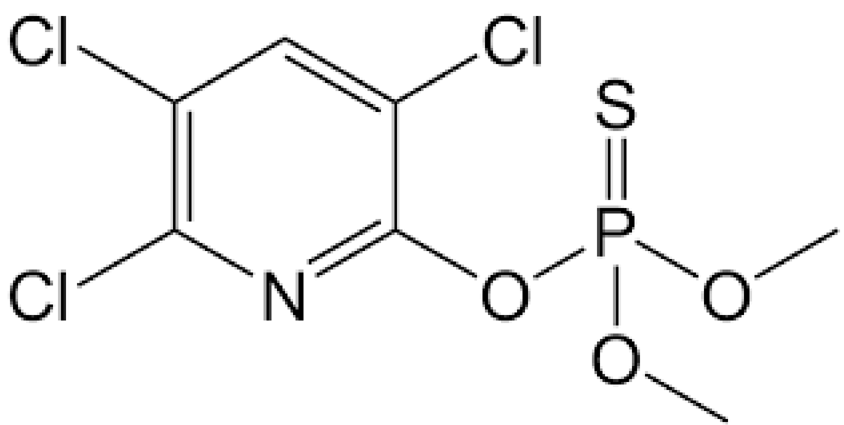
DDT

- 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





Data from Pesticide Information Profiles, Extoxnet, Cornell University; and Mackay et al. 2014

Any questions about pesticides?

Examples of SVOCs

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

Polychlorinated biphenyls - PCBs

Use
- Discovery of compound, of useful properties
- Spread of use

Concern
- Increasing number of scientific studies identifying concern
- Push-back from industry
- Weight of evidence

Consequences
- Regulation
- Phase-out
- Environmental problem

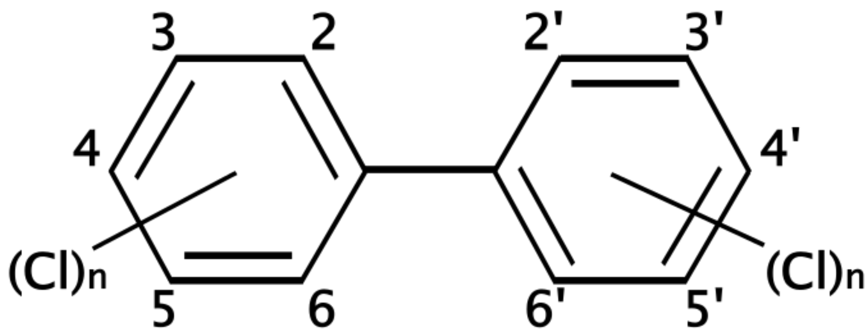
-High chemical and physical stability, even at high temperatures

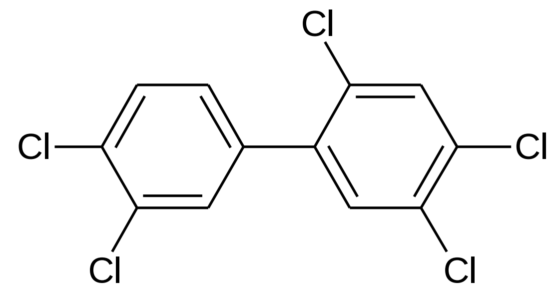
→Desirable property!

- 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

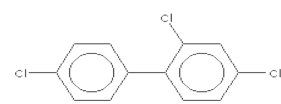




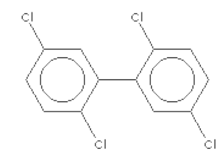
2,3',4,4',5-Pentachlorobiphenyl
PCB 118

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

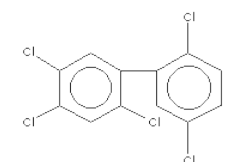
Indicator PCBs – 7 congeners:



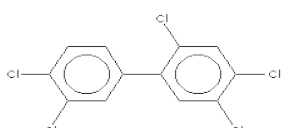
PCB
28



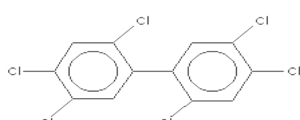
PCB
52



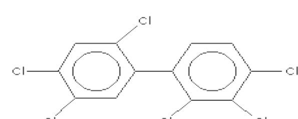
PCB
101



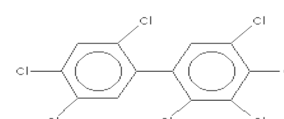
PCB
118



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

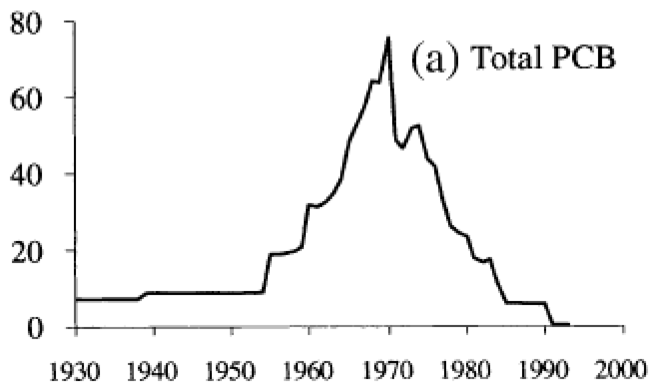

Sanexen Environmental Services

PCB production

K. Breivik et al. / The Science of the Total Environment 290 (2002) 181–198 183

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)
		39	1990	141 800	AMAP (2000)
		72	1993	32 000	AMAP (2000)
		60	1979	8000	Jiang et al. (1997)
		30	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

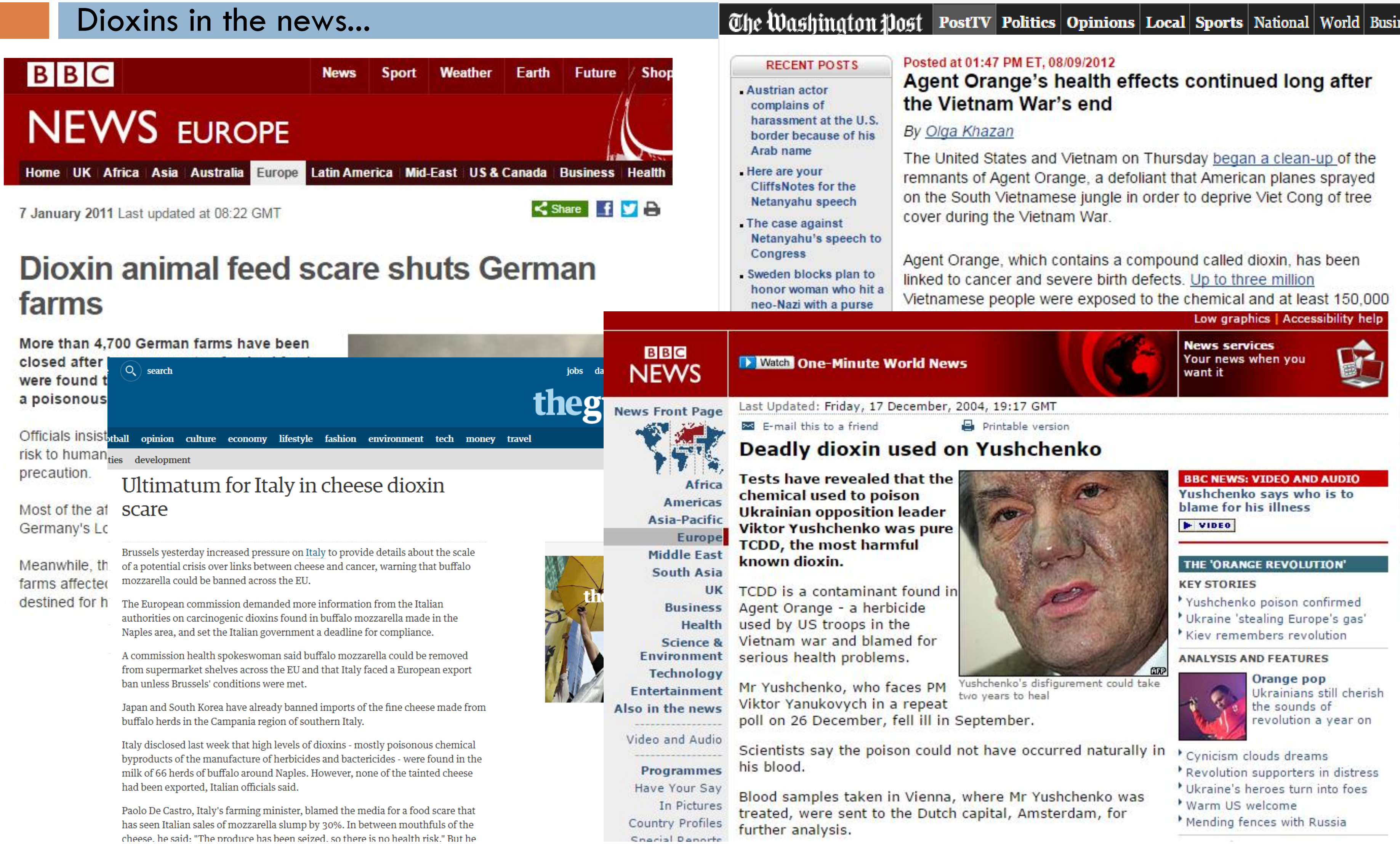
- Pesticides
- Industrial chemicals
- By-products
- Additives in consumer products

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

Dioxins and furans

Dioxins in the news…



BBC NEWS EUROPE

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 … were found … a poisonous …

Officials insist … risk to human … precaution.

Most of the af… Germany's Lo…

Meanwhile, th… farms affecte… destined for h…

the guardian

Ultimatum for Italy in cheese dioxin scare

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

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 …

BBC NEWS

Last Updated: Friday, 17 December, 2004, 19:17 GMT

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.

Yushchenko's disfigurement could take two years to heal

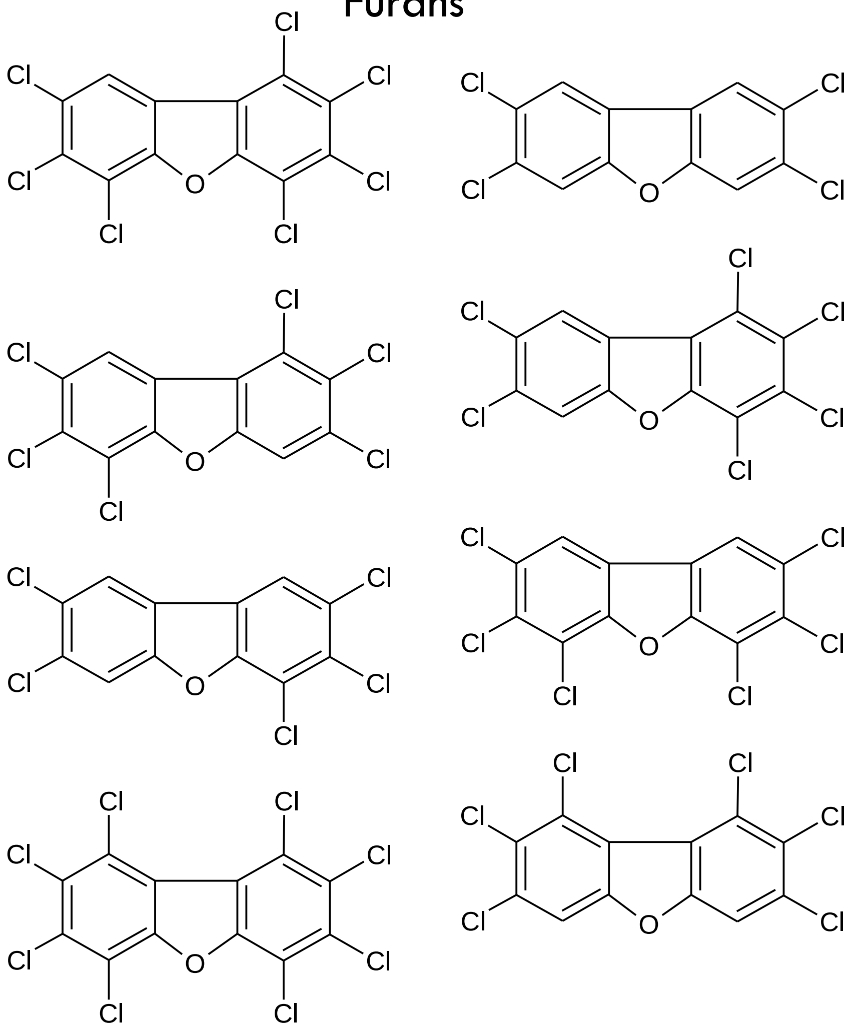
Mr Yushchenko, who faces PM Viktor Yanukovych in a repeat poll on 26 December, fell ill in September.

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

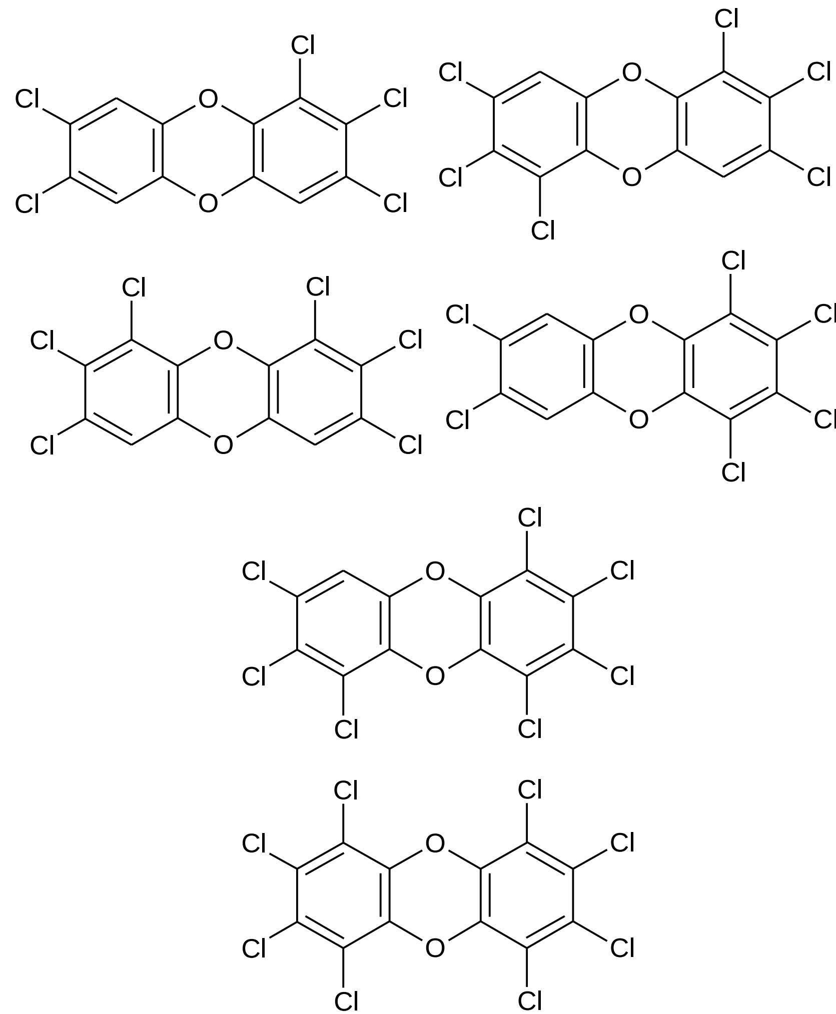
Blood samples taken in Vienna, where Mr Yushchenko was treated, were sent to the Dutch capital, Amsterdam, for further analysis.

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

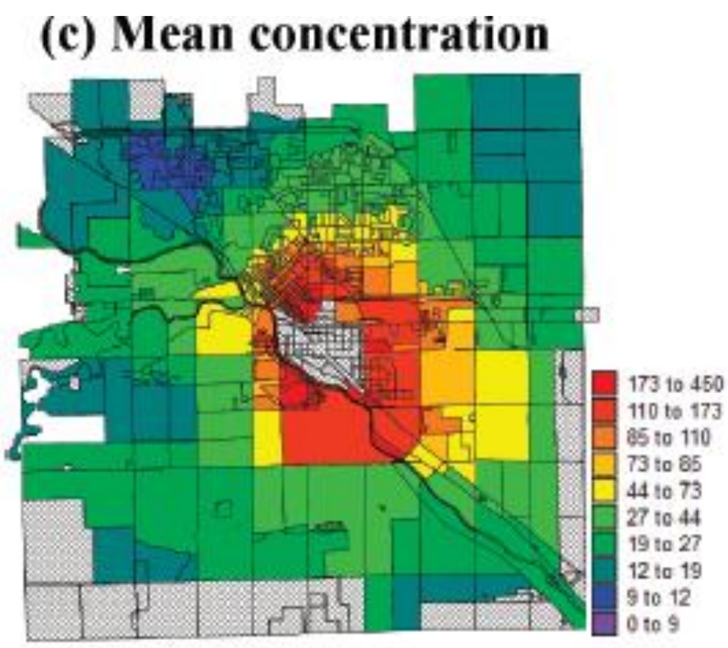
Secondary sources are:

- Australia – metal production
- Cambodia and Sri Lanka – waste incineration and heat and power generation

Spatial patterns of PCDD/Fs

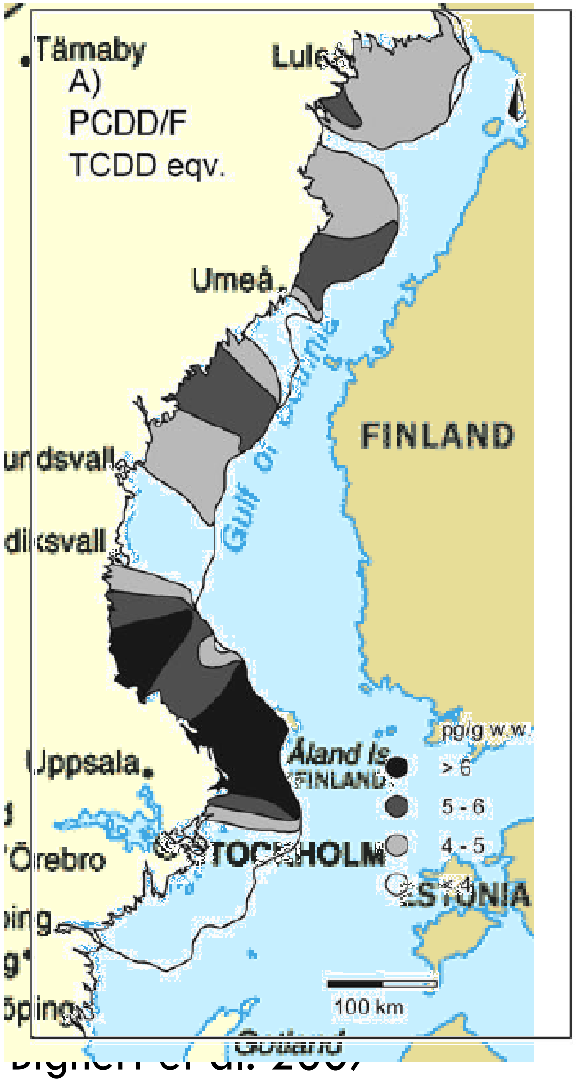
- Higher concentrations closer to sources, in highly developed, industrialized areas
- Concentrations patterns in air, soil, sediment and biota mirror each other
- Trends on a large scale – globally – and small scale - locally

Local scale – PCDD/Fs in soil around an incinerator



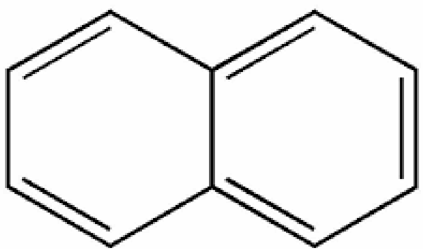
Goovaerts et al. 2008

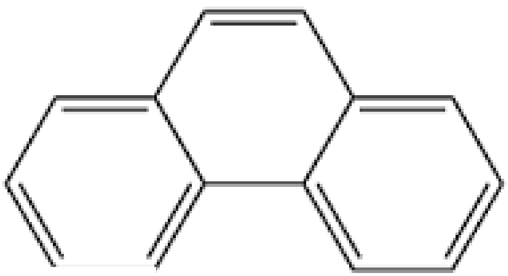
Regional scale – PCDD/Fs in fish from the coast of Sweden

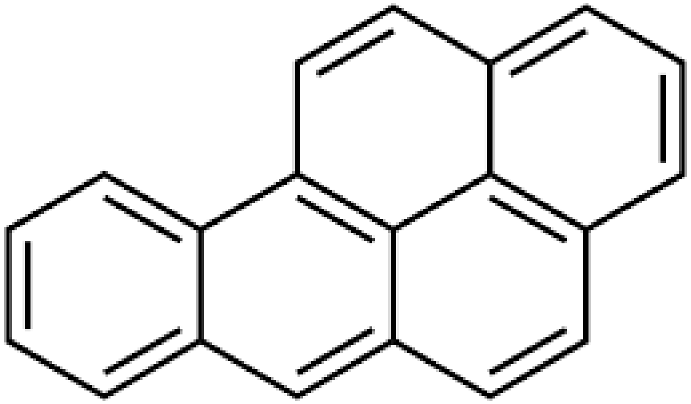


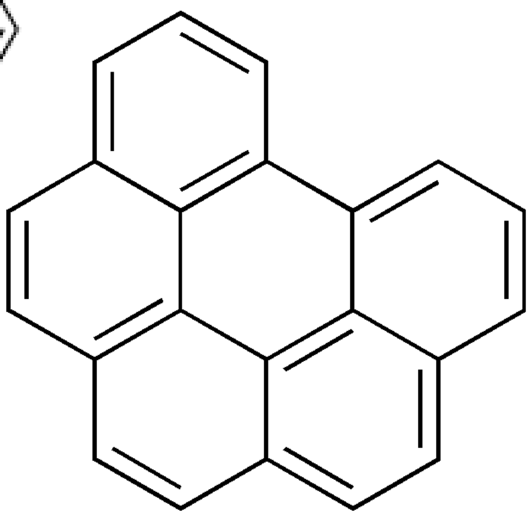
Polycyclic Aromatic Hydrocarbons (PAHs)

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



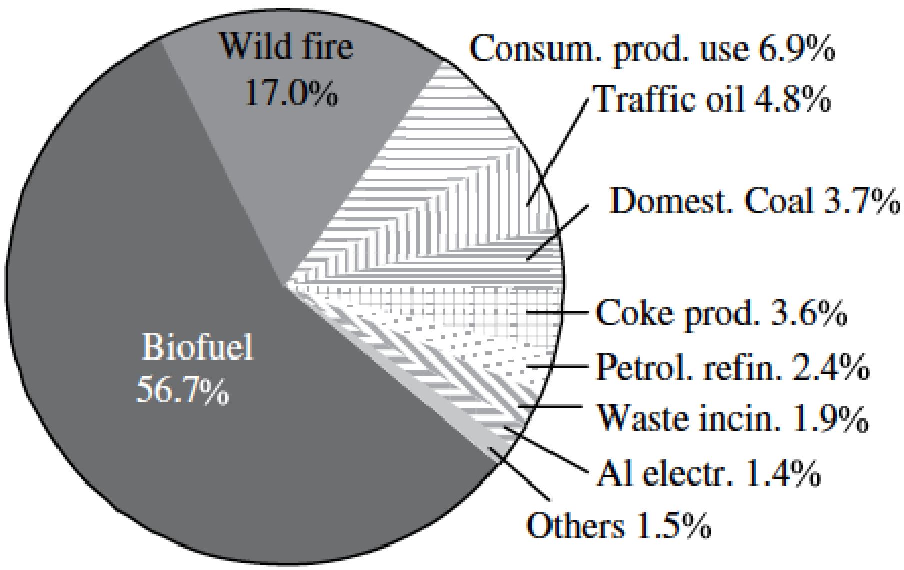




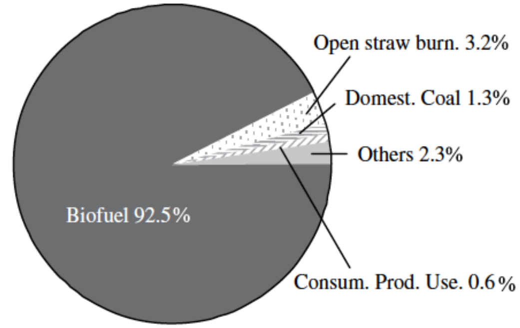


PAH Sources

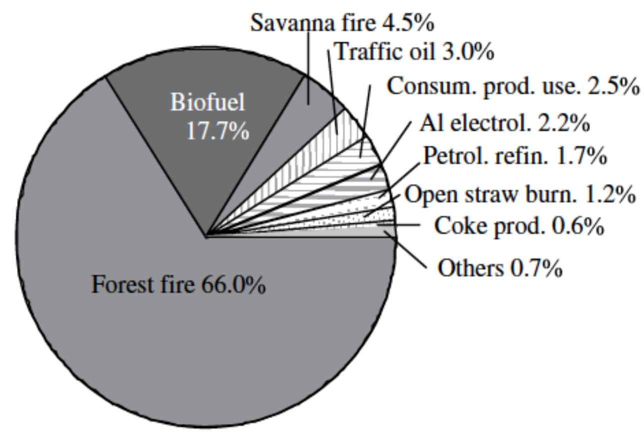
PAH16:



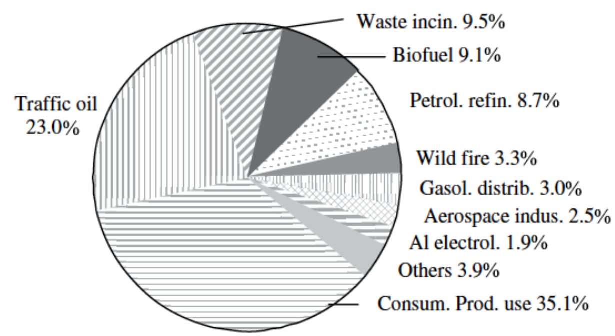
Global (530 Gg/y)



India (90 Gg/y)



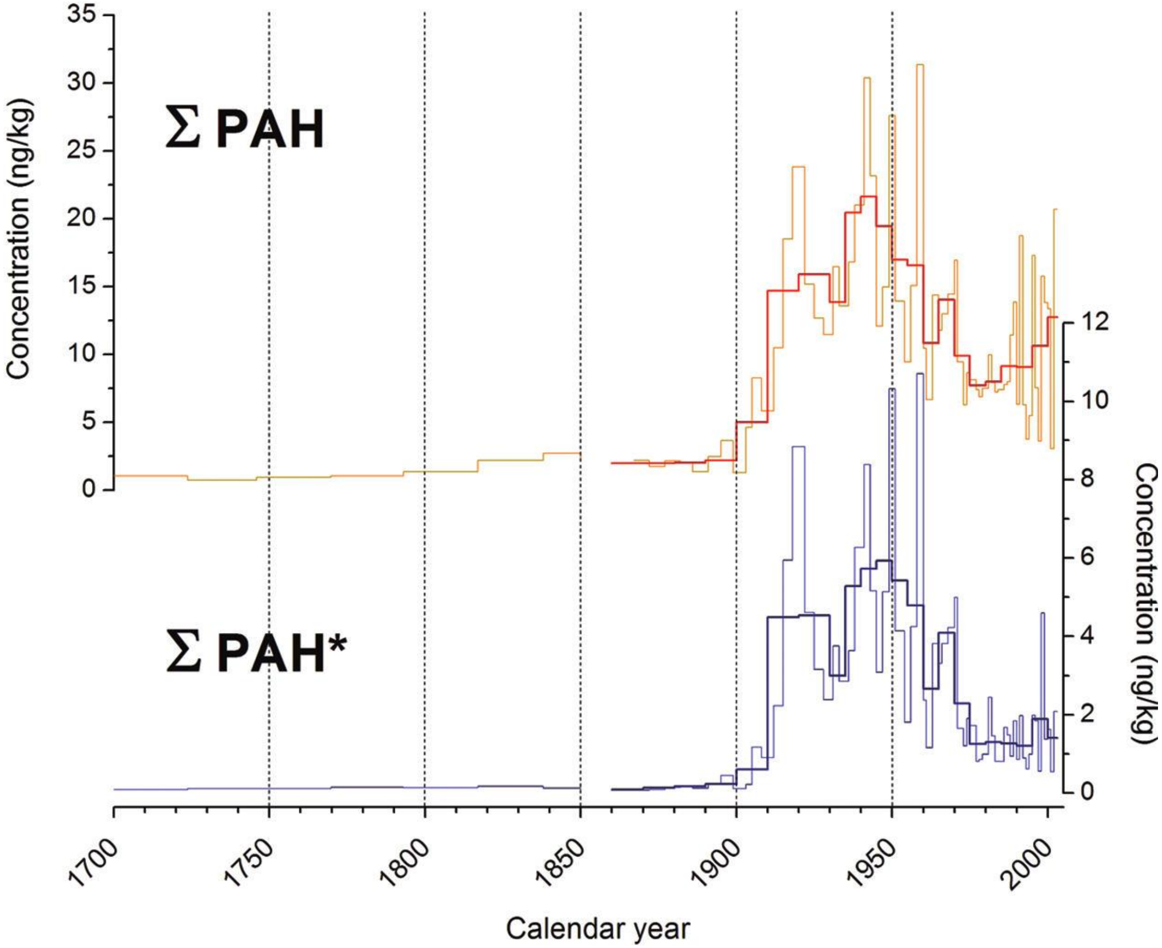
Brazil (19 Gg/y)



USA (32 Gg/y)

Zhang and Tao, Atmospheric Env. 2009

PAHs over the past 300 years



Gabrieli et al. 2010

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

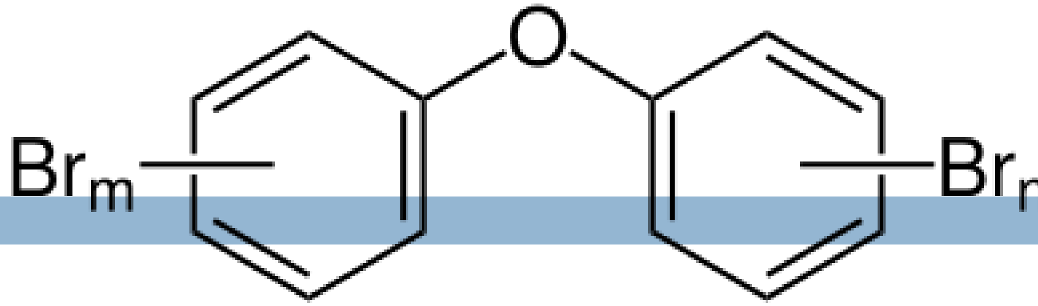
Plasticizers – additive chemicals that increase the flexibility, softness, fluidity of a material. Largely used in plastics.

Flame retardants

http://www.jptarpaulins.com/

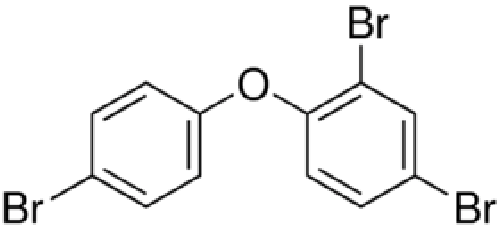
- To slow the spread of flames
- Organic or inorganic
- Wide range of applications (furniture, electronics, industrial/workplace textiles and protective equipment, vehicles)
- Required by fire safety regulations

PBDEs

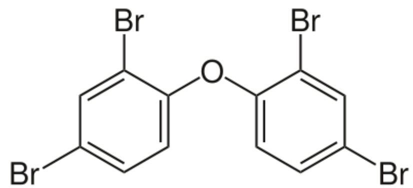


- Polybrominated diphenyl ethers
- Flame retardants
- Classified by either technical mixture or congener group
  - Confusing!! E.g., penta-BDE can refer to either the technical mixture called “Penta” or could refer to a PBDE with 5 bromines
  - Commercial mixtures sometimes distinguished as “c-penta”

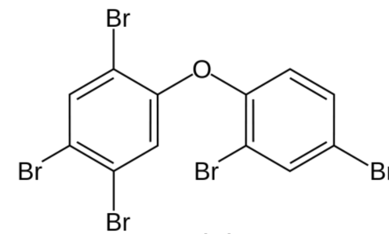
PBDE naming - congeners



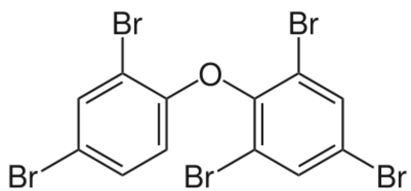
BDE-28
Tribromodiphenyl ether



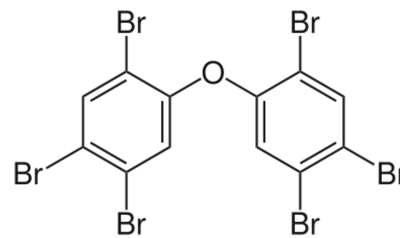
BDE-47
Tetrabromodiphenyl ether



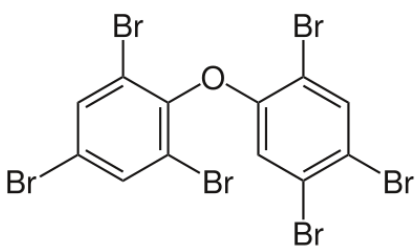
BDE-99
Pentabromodiphenyl ether



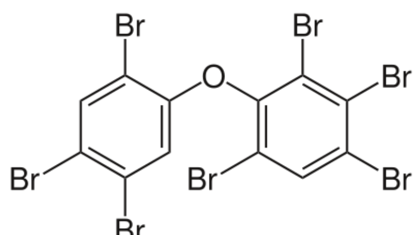
BDE-100
Pentabromodiphenyl ether



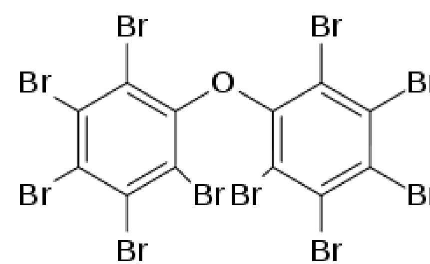
BDE-153
Hexabromodiphenyl ether



BDE-154
Hexabromodiphenyl ether



BDE-183
Heptabromodiphenyl ether



BDE-209
Decabromodiphenyl ether

Polybrominated Diphenyl Ethers: Uses

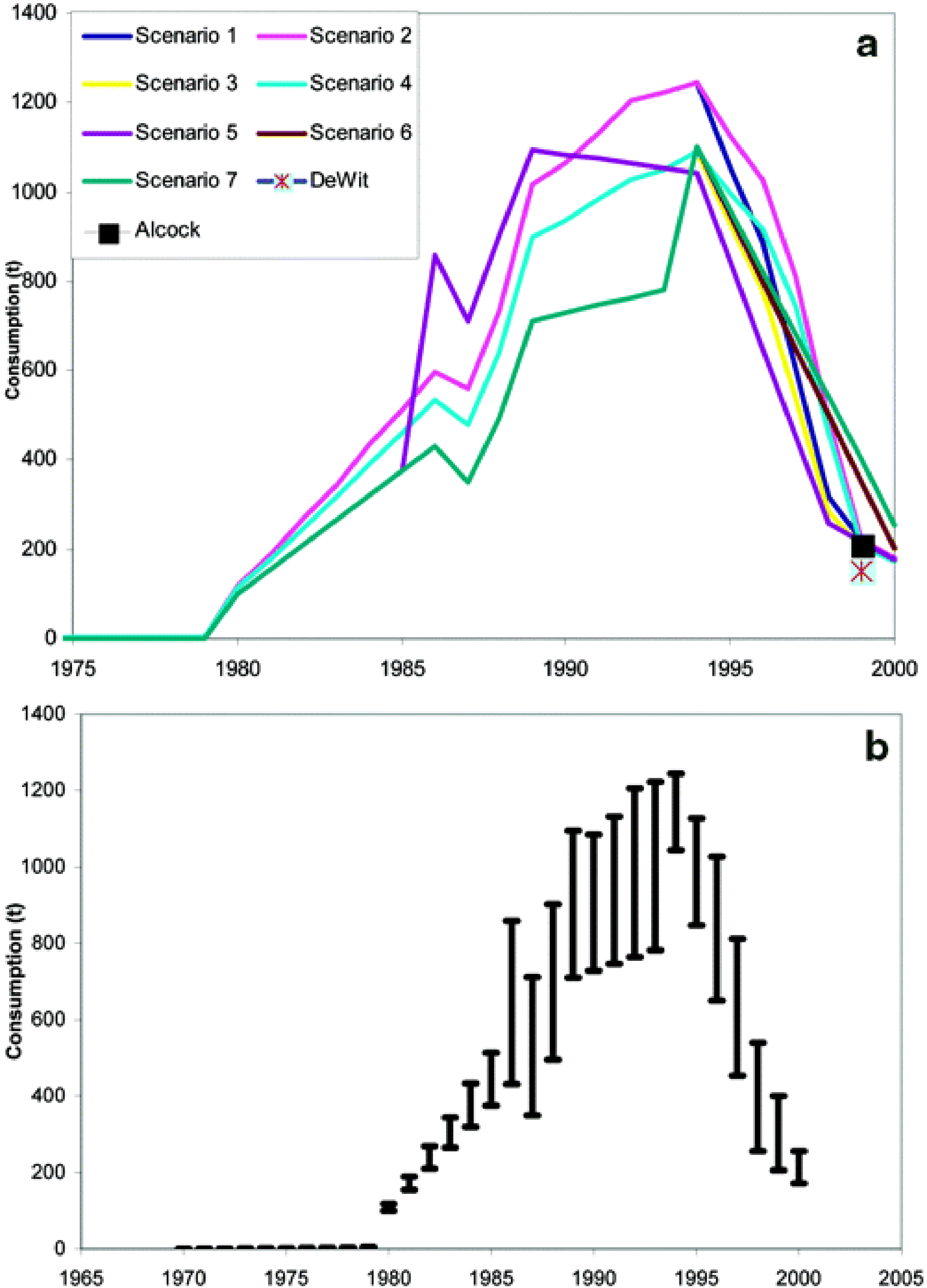
Penta	Textiles, PUF, paint, household plastic products, automotive parts banned under Stockholm Convention
Octa	ABS plastic for computers, casings, circuit boards, small appliances banned under Stockholm Convention
Deca	Electrical & electronic equipment, casings for TVs, computers, textile backings (e.g., 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

Review: Birnbaum & Staskal 2004 EHP 112:9-17.

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

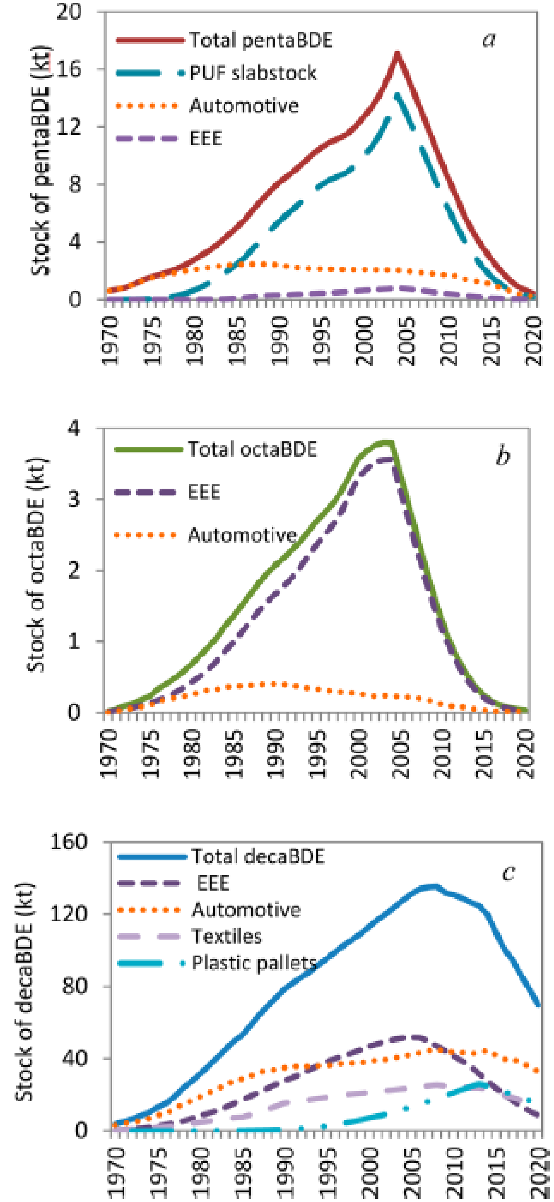


Figure 2. Stock of each PBDE commercial mixture in in-use products in the U.S. and Canada from 1970 to 2020, (a) pentaBDE in EEE, automotive vehicles, and PUF slabstock used in furniture, (b) octaBDE in automotive vehicles and EEE, and (c) decaBDE in plastic pallets, textiles, EEE, and automotive vehicles.

Abbasi et al. 2015
Environ Sci Technol

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

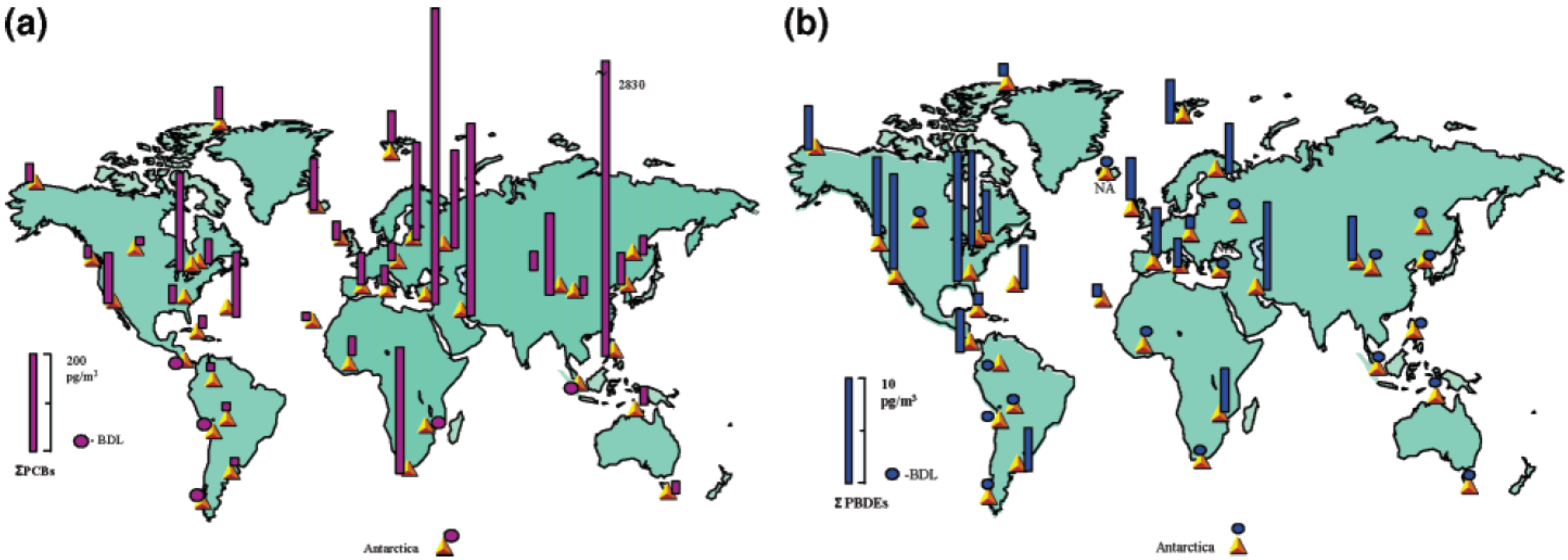


FIGURE 4. Air concentrations (pg/m³) of (a) PCBs and (b) PBDEs between December 2004 and March 2005 at GAPS sites. See Table S1 for BDL values.

From Pozo et al. 2006

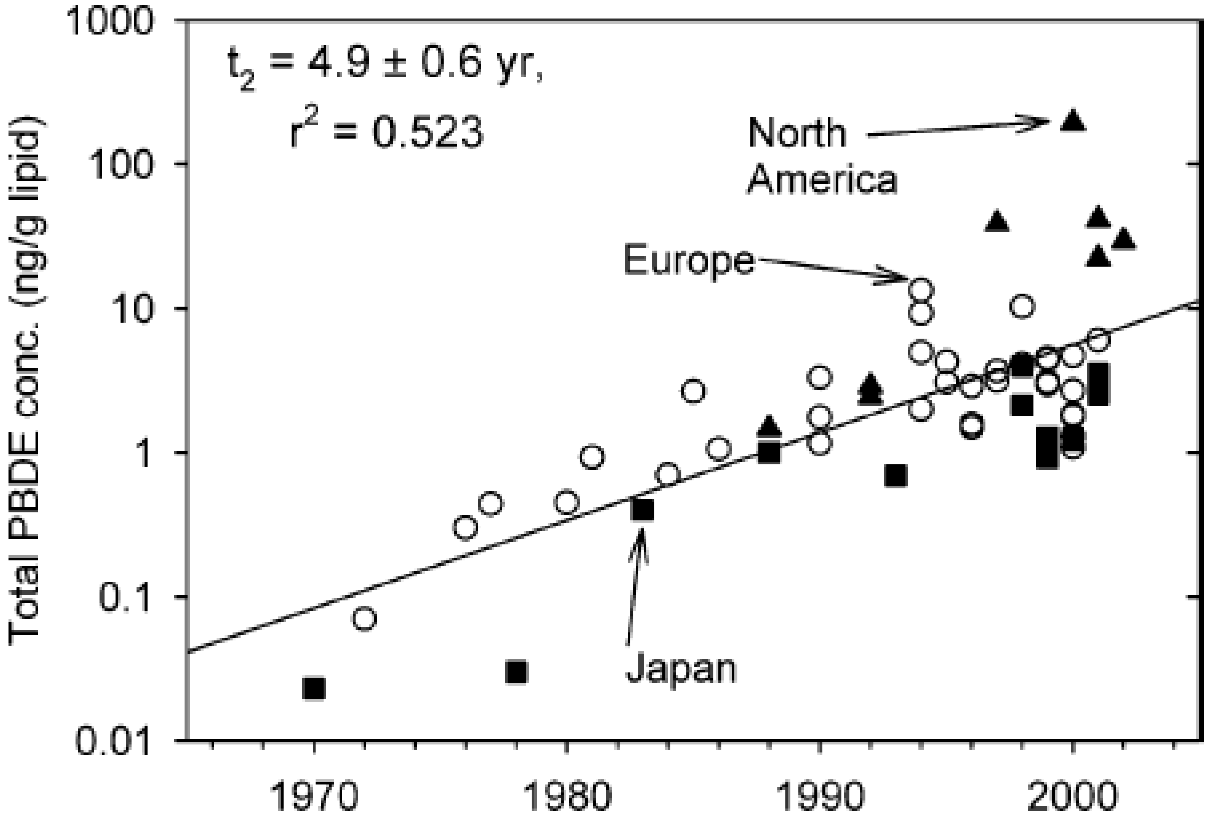
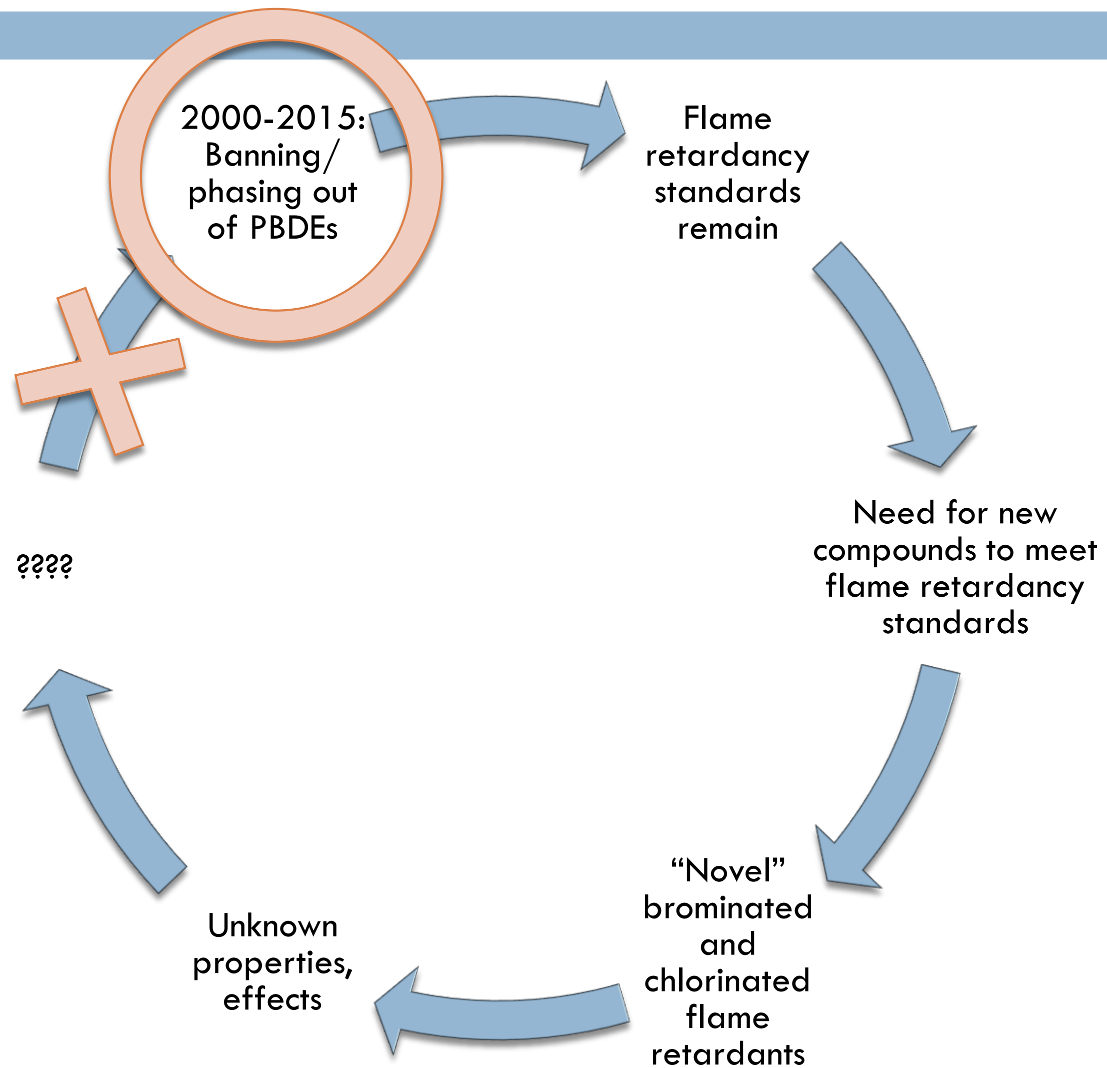


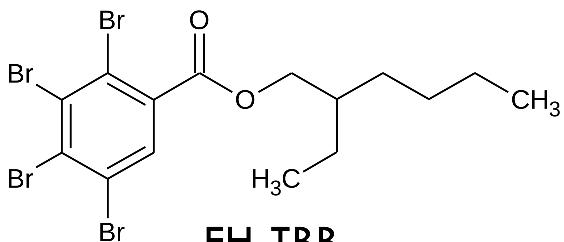
FIGURE 1. Total PBDE concentrations (∑PBDE) in human blood, milk, and tissue (in ng/g lipid) shown as a function of the year in which the samples were taken; see Table 2. The three symbol types indicate the location from which the samples were collected. The overall regression is shown.

Hites 2004 Environmental Science & Technology

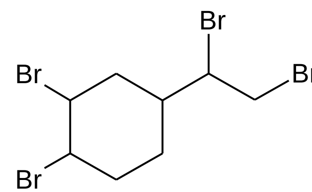
Replacement of banned compounds



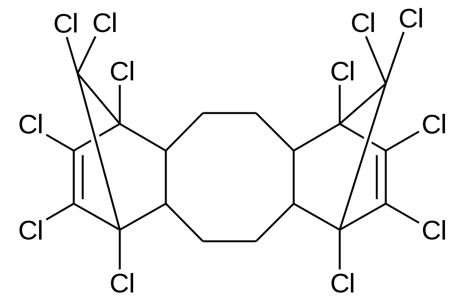
“Novel” flame retardants - NFRs – replacements for PBDEs



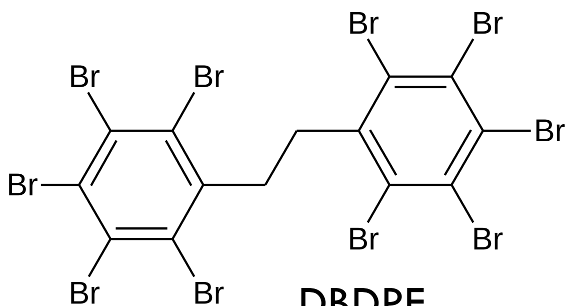
EH-TBB



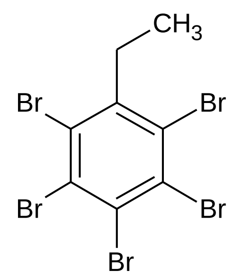
DBE-DBCH



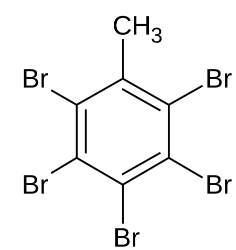
DDC-CO



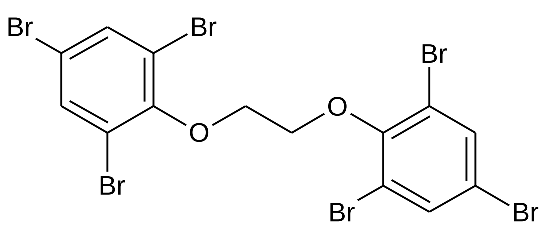
DBDPE



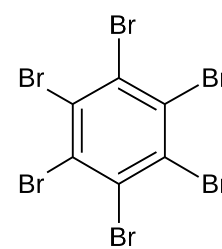
PBEB



PBT



BTBPE



HBB

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.

Stapleton et al. Environmental Science and Technology, 2009

Plasticizers - Phthalate esters

- One of the most broadly uses 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

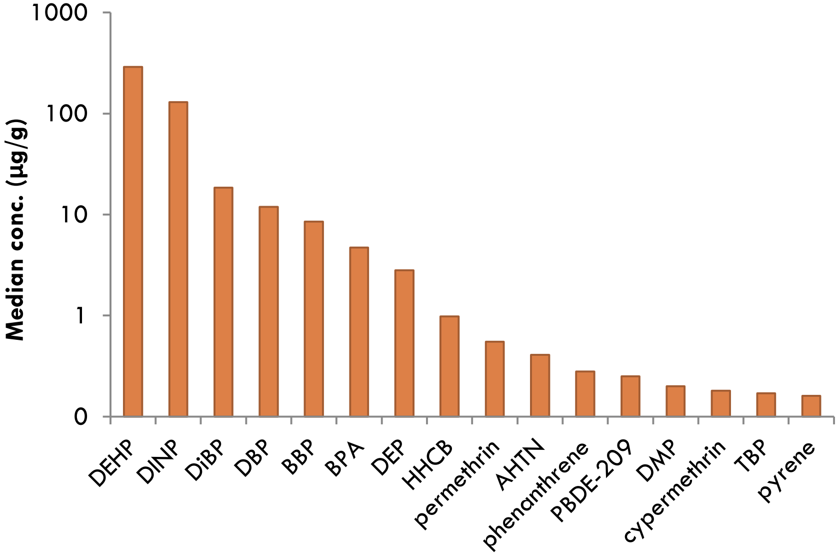
- Through eating, drinking foods that were in contact with phthalate-containing plastics
- Use of personal care products containing phthalates (dermal absorption)
- Inhaling air or ingesting dust containing phthalates

Phthalates

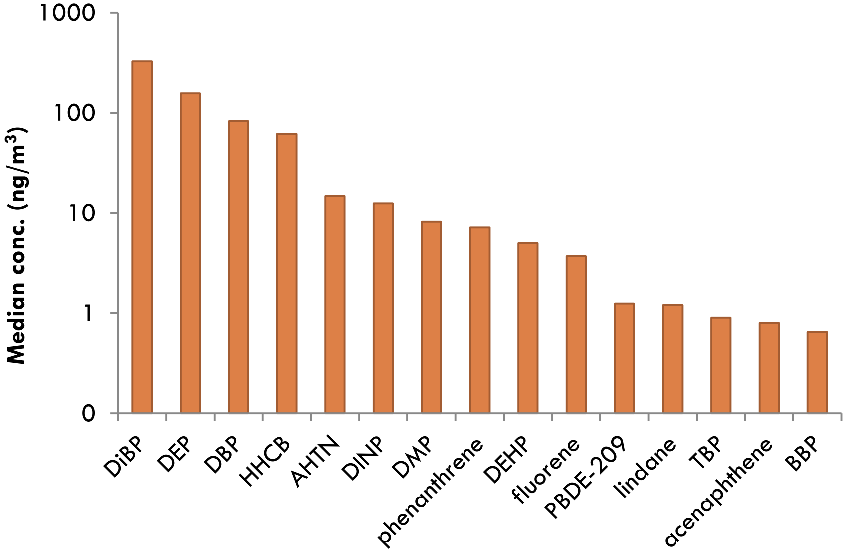
- Usually the highest concentration synthetic compound found in indoor dust and air
- Levels typically 10-100x higher than other SVOCs

Dust and air samples from 30 homes, Western France[1]:

Median conc. in settled dust (µg/g)



Median conc. in indoor air (ng/m³)



[1] Blanchard et al. 2014 *Environ Sci Tech*

Phthalates exposure

Journal of Exposure Science and Environmental Epidemiology **22**, 468-475 (September/October 2012)
|doi:10.1038/jes.2012.33

Consumer product exposures associated with urinary phthalate levels in pregnant women

Jessie P Buckley, Rachel T Palmieri, Jeanine M Matuszewski, Amy H Herring, Donna D Baird, Katherine E Hartmann and Jane A Hoppin

Abstract

Human phthalate exposure is ubiquitous, but little is known regarding predictors of urinary phthalate levels. To explore this, 50 pregnant women aged 18–38 years completed two questionnaires on potential phthalate exposures and provided a first morning void. Urine samples were analyzed for 12 phthalate metabolites. Associations with questionnaire items were evaluated via Wilcoxon tests and t-tests, and r-squared values were calculated in multiple linear regression models. Few measured factors were statistically significantly associated with phthalate levels. Individuals who used nail polish had higher levels of mono-butyl phthalate (P=0.048) than non-users. Mono-benzyl phthalate levels were higher among women who used eye makeup (P=0.034) or used makeup on a regular basis (P=0.004). Women who used cologne or perfume had higher levels of di-(2-ethylhexyl) phthalate metabolites. Household products, home flooring or paneling, and other personal care products were also associated with urinary phthalates. The proportion of variance in metabolite concentrations explained by questionnaire items ranged between 0.31 for mono-ethyl phthalate and 0.42 for mono-n-methyl phthalate. Although personal care product use may be an important predictor of urinary phthalate levels, most of the variability in phthalate exposure was not captured by our relatively comprehensive set of questionnaire items.

Indoor Air 2013; 23: 32–39
wileyonlinelibrary.com/journ
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jörn Lundgren,[1]

Lyngby, Denmark; [3]Public Health
obert Wood Johnson Medical

ort interval over which it has occurred
that the increase is caused by changes
onmental exposures rather than genetic
(Etzel 2003; Strachan 2000). Changes
or environments warrant special atten-
cause indoor air constitutes a domi-
posure route. Increased exposures to
s and/or adjuvants (enhancing factors)
ch be partially responsible for the
e. Multidisciplinary reviews of the

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.

EU REACH Legislation

DHP – reproductive toxin

DEHP – serious effects on environment

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

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."

Chemicals to know

- Particulate matter
- DDT
- PCBs
- PCDD/Fs
- PAHs
- PBDEs
- phthalates

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?