Semivolatile organic compounds – from sources to the environment

Part 1: Chlorinated and brominated compounds

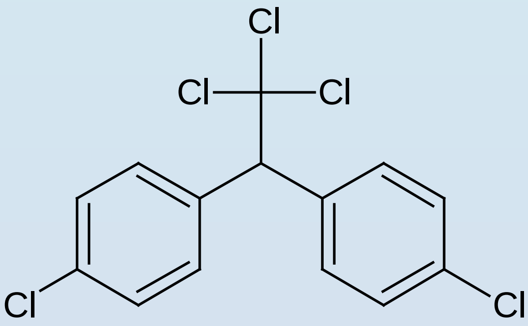
What are semivolatile organic compounds?

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

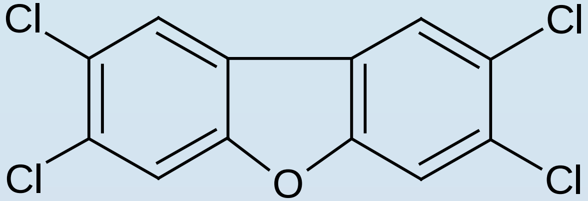
Why are they important?

- 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.

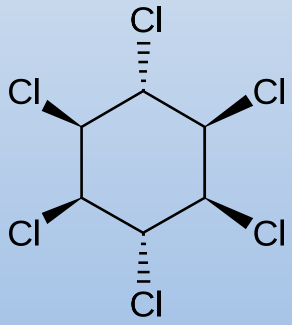
Well-known SVOCs



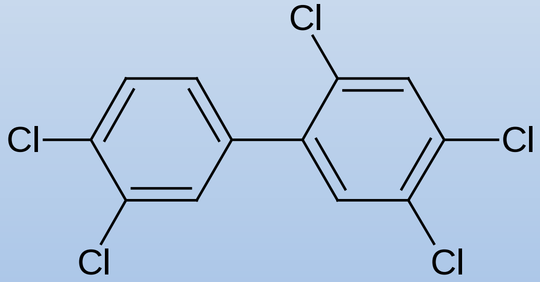
DDT
(p,p’-DDT)



Dioxin
(2,3,7,8-PCDD)



HCH
(Lindane)



PCB
(PCB 118)

Main topics

COMPOUNDS:

- Organochlorine pesticides (DDT, HCHs, etc.)
- Polychlorinated biphenyls (PCBs)
- Dioxins and furans (PCDD/Fs)
- Brominated flame retardants (PBDEs and new use FRs)

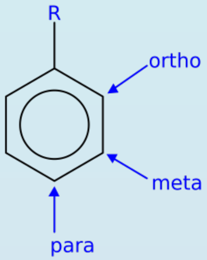
ABOUT EACH COMPOUND:

- Source of the compound
  - Industrial? Emission by-product?
- Status
  - Is the chemical still in use? Where is it legal/illegal?
- Physical-chemical properties, and why these are important
- Where do we find the chemical?
  - In the environment? In humans? How are humans exposed?

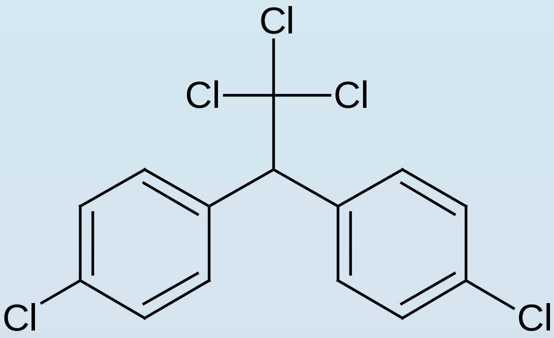
Concepts to consider:

- Costs vs. benefits of chemicals
- What evidence is needed to show that a chemical is safe? Or that a chemical is dangerous?
- What is the most effective mechanism to address concerns? How well do regulations work?
- The role of science in decisions about chemicals

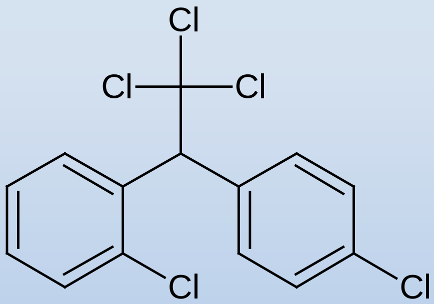
Case study 1: DDT



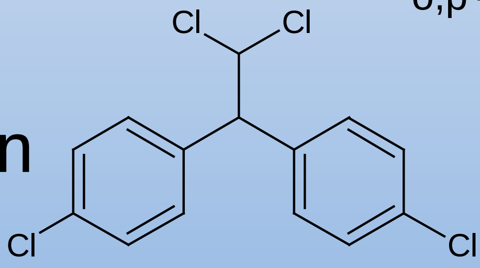
- Distinction between "chemical DDT" and "technical DDT"
- Chemical DDT – dichlorodiphenyltrichloroethane, generally ***p,p'*-DDT** – the isomer with insecticidal properties
- Technical DDT – mixture of p,p'-DDT, o,p'-DDT, DDE and DDD
- DDE and DDD are impurities in technical mixture and breakdown products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



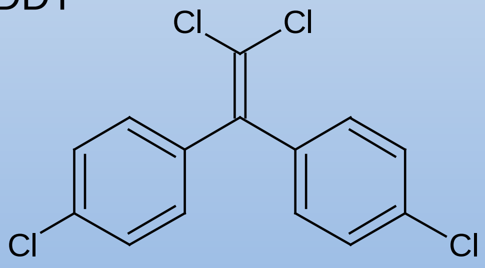
p,p'-DDT



o,p'-DDT



p,p'-DDD



p,p'-DDE

What is the composition of technical DDT?

[Contribution from the Bureau of Entomology and Plant Quarantine, Agricultural Research Administration, U. S. Department of Agriculture, and the Departments of Chemistry of Harvard University, the University of Maryland and the Ohio State University]

The Chemical Composition of Technical DDT[1]

By H. L. Haller,[2] Paul D. Bartlett,[3] Nathan L. Drake,[4] Melvin S. Newman,[5] Stanley J. Cristol,[2] Charles M. Eaker,[4] Robert A. Hayes,[2] Glen W. Kilmer,[4] Barney Magerlein,[5] George P. Mueller,[3] Abraham Schneider,[3] and William Wheatley[5]

The recent discovery of the outstanding insecticidal properties of the product known as DDT and its successful application against the body louse and other disease-carrying insects have aroused considerable interest. Numerous articles praising its merits have appeared in scientific and trade magazines, as well as in newspapers and popular magazines. These usually include the history of its introduction into this country and, as might be expected, the stories are not always in agreement. Probably the most accurate account is given by Froelicher.[6] The studies leading to the discovery of DDT as an insecticide are presented by Läuger, Martin, and Müller.[7]

The symbol "DDT" is a contraction for di-

(1) These researches were carried out under a transfer of funds to the Bureau of Entomology and Plant Quarantine from the Office of Scientific Research and Development, as recommended by the Committee on Medical Research, and under contracts between Harvard University, University of Maryland, and The Ohio State University, and the Office of Scientific Research and Development, as recommended by the National Defense Research Committee.

(2) Bureau of Entomology and Plant Quarantine, Agricultural Research Administration, U. S. Department of Agriculture, Beltsville, Md.

(3) Department of Chemistry, Harvard University, Cambridge, Mass.

(4) Department of Chemistry, University of Maryland, College Park, Md.

(5) Department of Chemistry, The Ohio State University, Columbus, Ohio.

(6) Froelicher, *Soap and Sanit. Chem.*, **20** (7), 115 (1944).

(7) Läuger, Martin and Müller, *Helv. Chim. Acta*, **27**, 892 (1944).

Table I

Composition of Technical DDT

Compound	Sample 1 (Setting point, 91.2°), %	Sample 2 (Setting point, 88.6°), %	Sample 3 (Setting point, 91.4°), %	Sample 4 (By-product oil), %
1-Trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-DDT)[a]	(*a*) 66.7, (*b*) 72.9	(*b*) 70.5, (*c*) 63.5, (*d*) 64.5, (*e*) 67.9	(*a*) 72.7, (*b*) 76.7	...
1-Trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDT)	19.0	(*c*) 7.9, (*d*) 15.3, (*e*) 20.9	11.9[b]	74.8[c]
1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (*p,p'*-DDD)	0.3	4.0	0.17[d]	...
1,1-Dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane (*o,p'*-DDD)	......	....	0.044	...
2-Trichloro-1-*o*-chlorophenylethyl *p*-chlorobenzenesulfonate	0.4	1.85	0.57	0.11
2-Trichloro-1-*p*-chlorophenylethanol	0.2	....	....	...
Bis-(*p*-chlorophenyl)-sulfone	0.6	0.1	0.034	...
α-Chloro-α-*p*-chlorophenylacetamide	......	0.01	0.006	...
α-Chloro-α-*o*-chlorophenylacetamide	......	0.007	....	...
Chlorobenzene	......	....	....	2.44
p-Dichlorobenzene	......	....	....	0.73
1,1,1,2-Tetrachloro-2-*p*-chlorophenylethane	......	....	....	+[e]
Sodium *p*-chlorobenzene-sulfonate	0.02	....	....	...
Ammonium *p*-chlorobenzene-sulfonate	......	....	0.005	...
Inorganic	0.1[f]	0.04[g]	0.01[h]	...
Unidentified and losses	6.5	5.1	10.6	19.4

[a] Letters in parentheses refer to analytical methods as follows: (*a*) Isolation from technical DDT, (*b*) recrystallization from 75% aqueous ethanol previously saturated with *p,p'*-DDT (Cristol, Hayes and Haller[10]), (*c*) fractional crystallization, (*d*) adsorption analysis and fractional crystallization, (*e*) isolation, supplemented by cryoscopic analysis on the residue. [b] This value does not represent all the *o,p'*-DDT present, as all oily fractions were not exhaustively studied. [c] Miscellaneous fractions containing *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDD. [d] Includes 0.06% of *p,p'*-DDD isolated as such and 0.11% of the corresponding olefin. [e] Isolated as nitro derivative from an oil mixture analyzing for a mixture of $C_6H_6Cl_4$ and $C_6H_5Cl_5$ and representing 2.54% of original material. [f] Qualitative tests for ferric, lead and magnesium carbonates were obtained. [g] Insoluble in boiling 95% ethanol. [h] Qualitative tests for ferric, ammonium, halide and sulfate ions were obtained.

p,p'-DDT: 63-79% ← Active ingredient

o,p'-DDT: 8-21%

p,p'-DDD: 0-4%

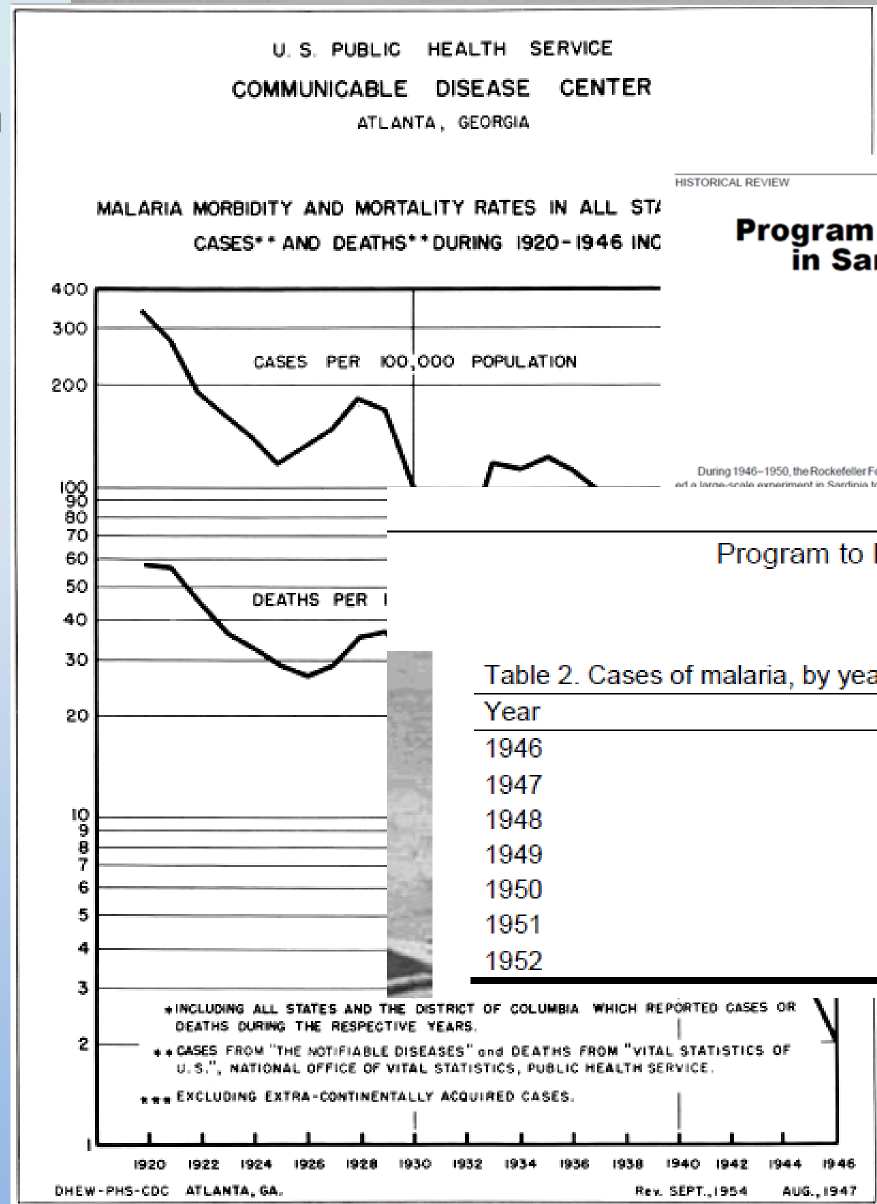
o,p'-DDD: 0-0.05%

} 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

Program to Eradicate Malaria in Sardinia

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

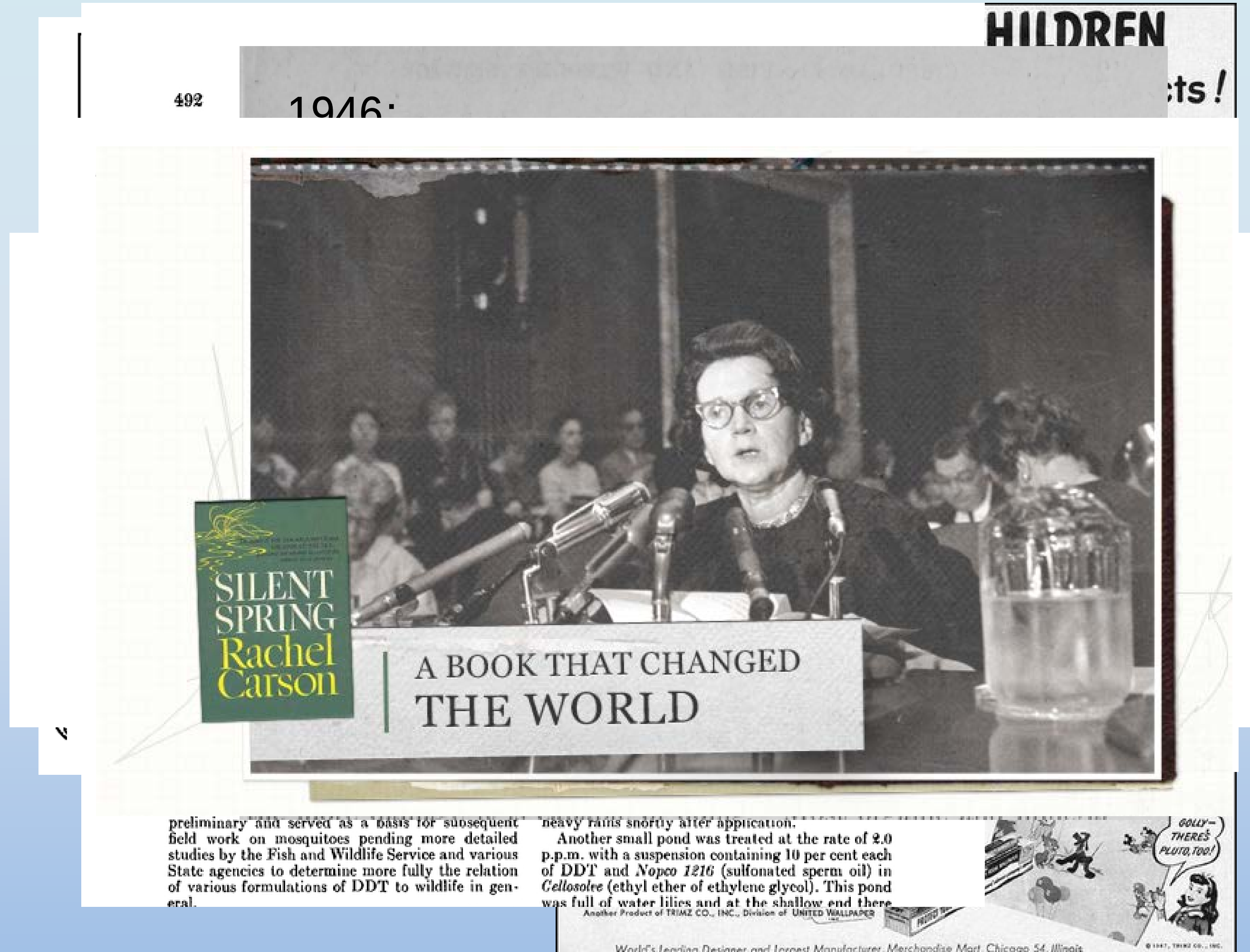
Year	No. cases (relapses)
1946	74,641
1947	39,303
1948	15,121
1949	1,314
1950	0 (44)
1951	9 (8)
1952	0

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

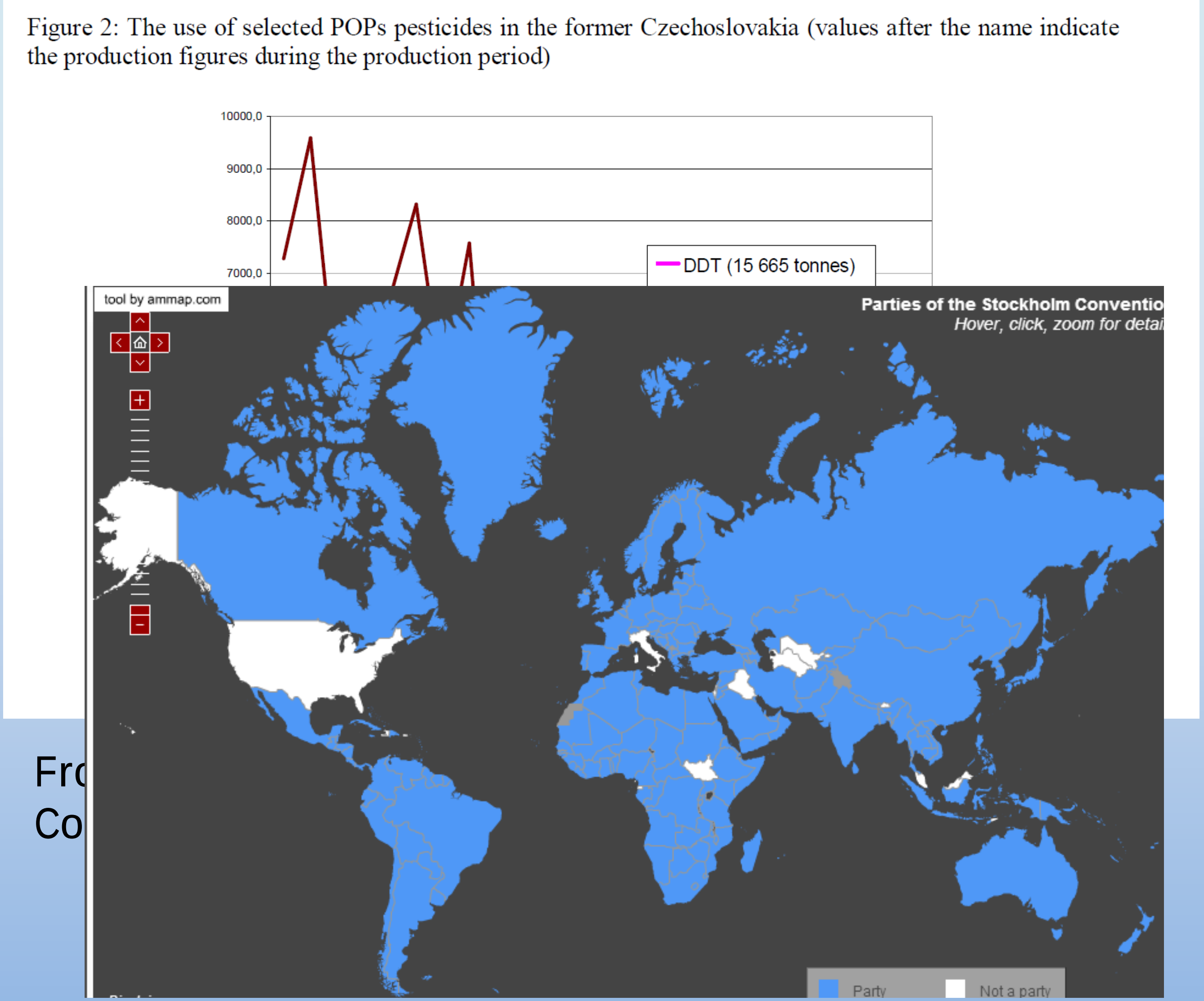


Figure 2: The use of selected POPs pesticides in the former Czechoslovakia (values after the name indicate the production figures during the production period)

Fr
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 and bioaccumulation/biomagnification!

For wildlife

- reproductive/development impairment
- Eggshell thinning in birds (DDE interferes with reproductive enzymes affecting the amount of calcium in shells)
- Very high sensitivity in bats

DDT – What are the concerns?

For humans (from Eskenazi et al. 2009, Environmental Health Perspectives – good review on DDT health effects in humans)

- International Agency for Research on Cancer (IARC) – DDT is "possibly carcinogenic to humans" – mostly based on evidence that DDT caused liver tumors in lab test animals
- Some epidemiological evidence of links with liver cancer in US and Chinese populations, pancreatic cancer in Australia, breast cancer for women exposed during childhood, puberty
- Increased risk of diabetes
- Increased risk of miscarriage in pregnant women
- Birth defects, decreased sperm count in men
- Neurodevelopmental effects – delayed development, lower cognitive performance
- Thyroid effects, lowered immune responses

MANY SUBTLE HEALTH EFFECTS – NON-LETHAL, OFTEN DIFFICULT TO QUANTIFY, AFFECTING A RANGE OF BODY SYSTEMS

p,p'-DDT – physicochemical properties

- Vapour pressure: 0.00048 Pa
- Solubility: 0.00042 mol/m^3
- Henry's Law constant: 1.1 Pa m^3/mol
- $\log K_{OW}$: 6.39
- $\log K_{OA}$: 9.73

From Shen and Wania, 2005

What do the physicochemical properties tell us?

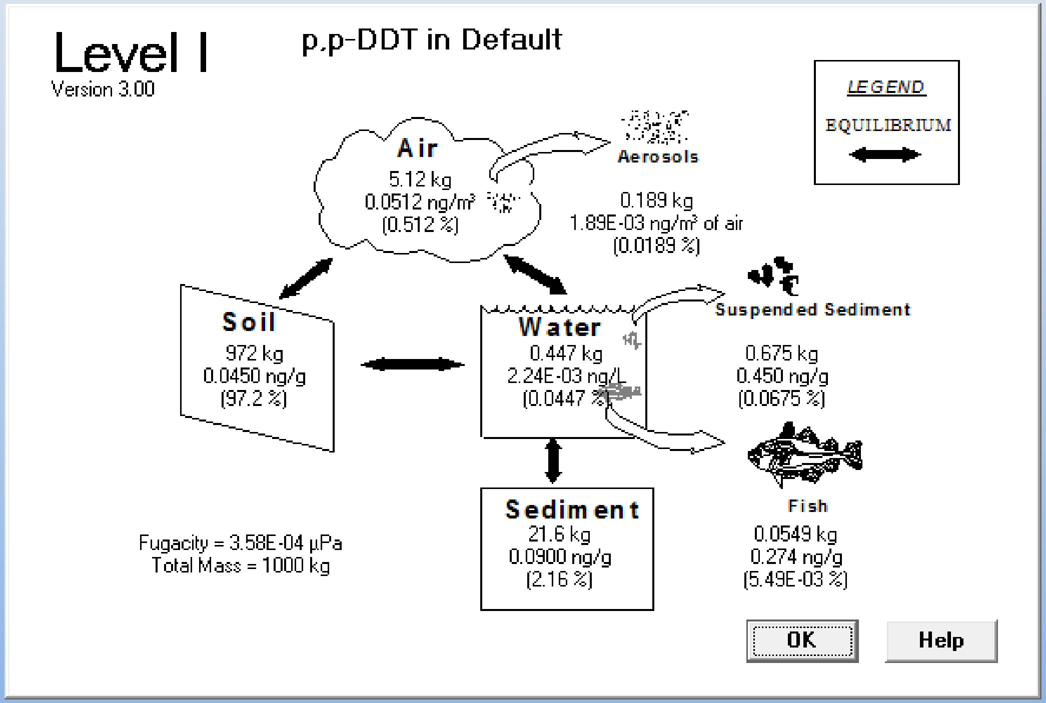
Vapour pressure: 0.00048 Pa

$\log K_{OA}$: 9.73

What fraction of the compound in air is sorbed to particles?

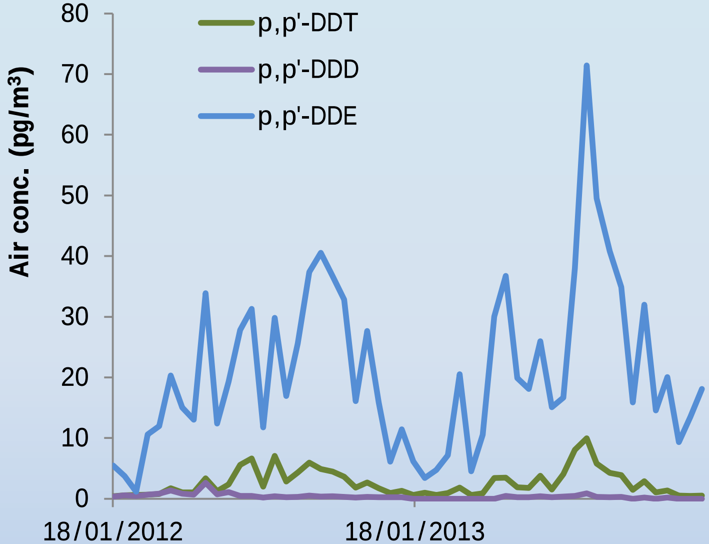
Estimated from VP: 43% on particles
Estimated from $\log K_{OA}$: 11% on particles
Measured at Košetice in 2012-2013: 13% on particles

Vapour pressure: 0.00048 Pa
Solubility: 0.00042 mol/m^3
Henry's Law constant: 1.1 Pa m^3/mol
$\log K_{OW}$: 6.39
$\log K_{OA}$: 9.73



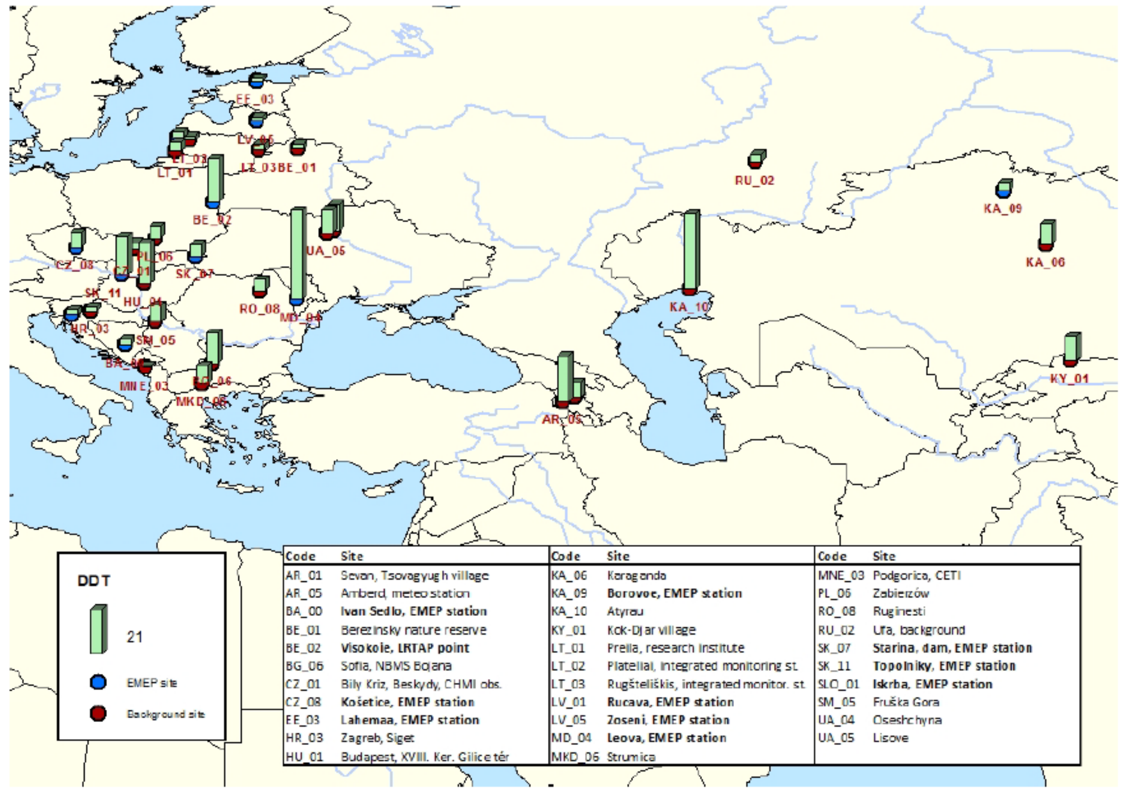
What are typical concentrations of DDT?
- in air -

2012-2013 at Košetice



From Degrendele et al. 2014

Pribylova et al. – Atmospheric Pollution Research 3 (2012) 494–505

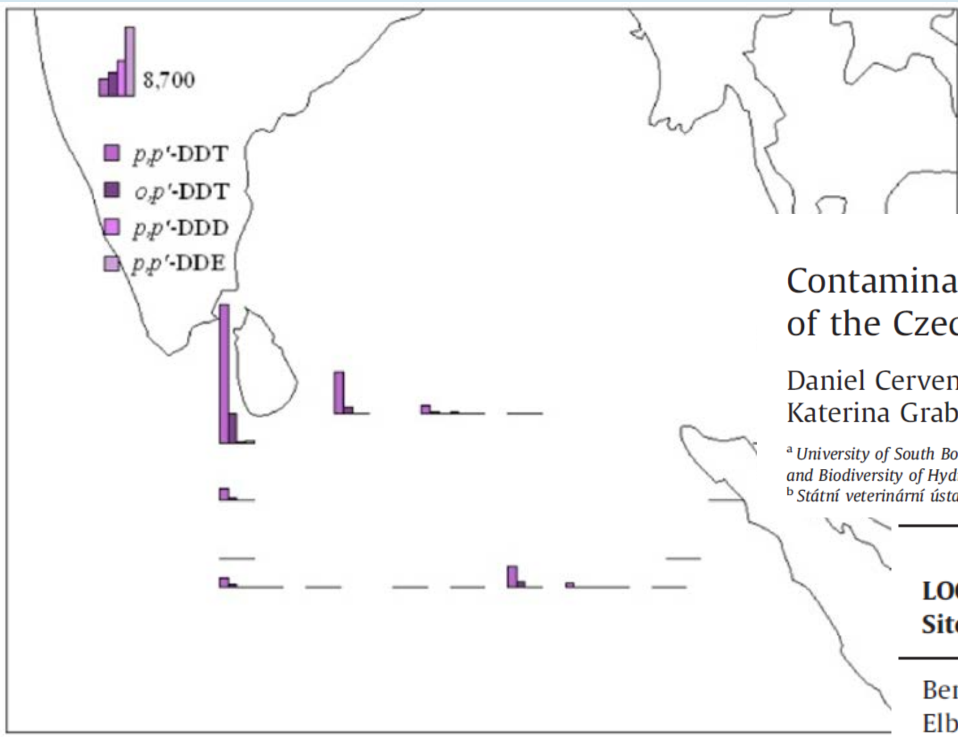


Code	Site	Code	Site	Code	Site
AR_01	Sevan, Tsovagyugh village	KA_06	Karaganda	MNE_03	Podgorica, CETI
AR_05	Amberd, meteo station	KA_09	**Borovoe, EMEP station**	PL_06	Zabierzów
BA_00	**Ivan Sedlo, EMEP station**	KA_10	Atyrau	RO_08	Ruginesti
BE_01	Berezinsky nature reserve	KY_01	Kok-Djar village	RU_02	Ufa, background
BE_02	**Visokoie, LRTAP point**	LT_01	Preila, research institute	SK_07	**Starina, dam, EMEP station**
BG_06	Sofia, NBMS Bojana	LT_02	Plateliai, integrated monitoring st.	SK_11	**Topolniky, EMEP station**
CZ_01	Bily Kriz, Beskydy, CHMI obs.	LT_03	Rugšteliškis, integrated monitor. st.	SLO_01	**Iskrba, EMEP station**
CZ_08	**Košetice, EMEP station**	LV_01	**Rucava, EMEP station**	SM_05	Fruška Gora
EE_03	**Lahemaa, EMEP station**	LV_05	**Zoseni, EMEP station**	UA_04	Oseshchyna
HR_03	Zagreb, Siget	MD_04	**Leova, EMEP station**	UA_05	Lisove
HU_01	Budapest, XVIII. Ker. Gilice tér	MKD_06	Strumica		

Figure 6. The median levels of DDTs in ambient air (PAS, ng sample^{-1}) measured at the background sites of the CEE region, 2006-2008.

What are typical concentrations of DDT?
- in water -

In Lake Malawi, Africa
~76 pg/L
Karlsson et al. 2000



In the Indian Ocean: 9-22000 pg/L
Huang et al. 2013

Contamination of fish in important fishing grounds of the Czech Republic

Daniel Cerveny [a,*], Vladimir Zlabek [a], Josef Velisek [a], Jan Turek [a], Roman Grabic [a], Katerina Grabicova [a], Ganna Fedorova [a], Jan Rosmus [b], Pavel Lepic [a], Tomas Randak [a]

[a] University of South Bohemia in Ceske Budejovice, Faculty of Fisheries and Protection of Waters, South Bohemian Research Center of Aquaculture and Biodiversity of Hydrocenoses, Zatisi 728/II, 389 25 Vodnany, Czech Republic
[b] Státní veterinární ústav Praha, Sidlistni 24, 165 03, Praha 6, Czech Republic

LOQs (mg kg^{-1}) **Site name**	**$\sum_6$ PCB 0.00024** (mg kg^{-1} **w.w.**)	**$\sum$ DDT 0.00005**
Berounka River – Prague	0.059	0.036
Elbe River – Obristvi	0.016	0.005
Elbe River – Pardubice	0.009	0.004
Elbe River – Svadov	0.089	0.173
Luznice River – Majdalena	0.001	0.001
Luznice River – Sobeslav	0.018	0.014
Odra River –		0.065
Otava River -		0.022
WR Dalesice	0.041	0.097
WR Hnevkovice	0.002	0.017
WR Jesenice	0.005	0.006
WR Jordan	0.004	0.006
WR Korensko	0.005	0.004

0.001-0.1 mg/kg

What are typical trends in DDTs?

SumDDT compounds in ice core from Mt. Everest glacier

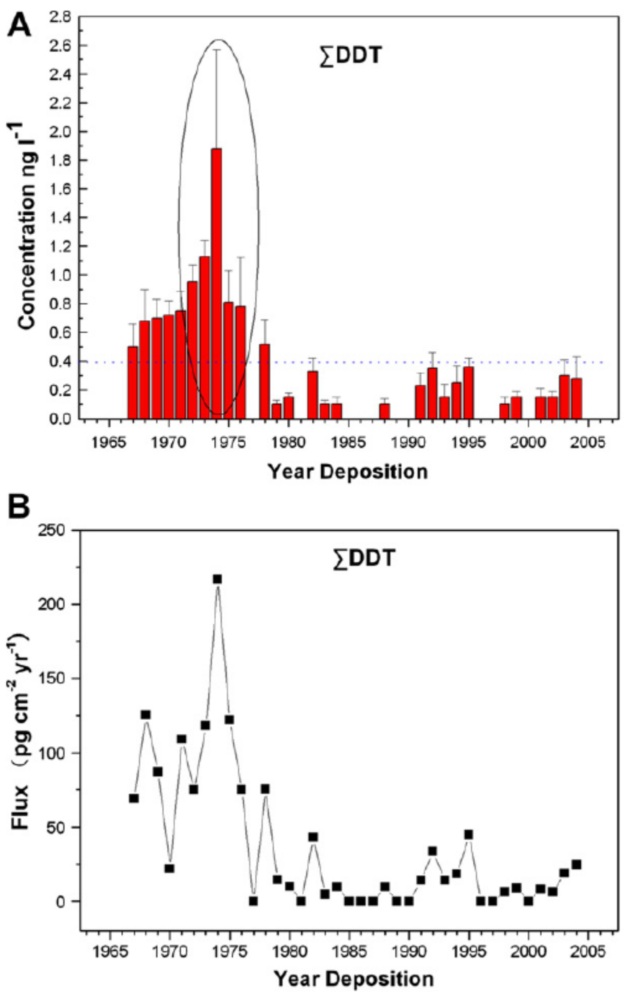


Fig. 4. Concentration (A) and deposition flux (B) of DDT in the ice core from East Rongbuk glacier (Mt.Everest, The Himalayas).

(Wang et al., Atmospheric Environment, 2008)

DDT compounds in precipitation from North America, 1995-2005

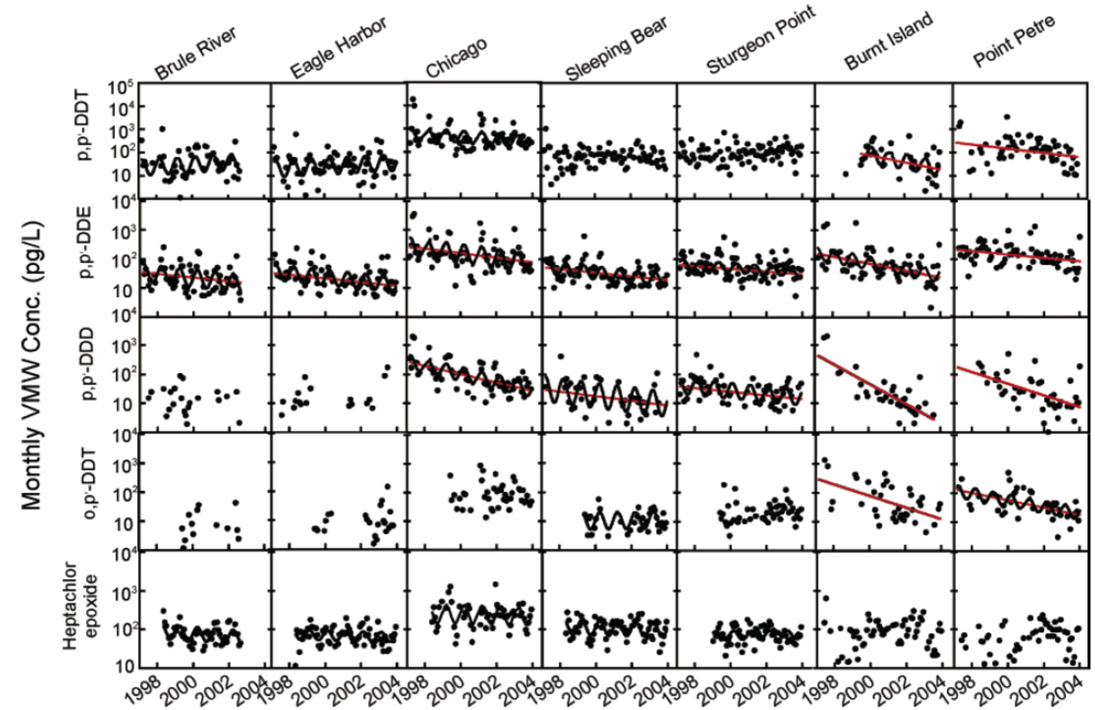
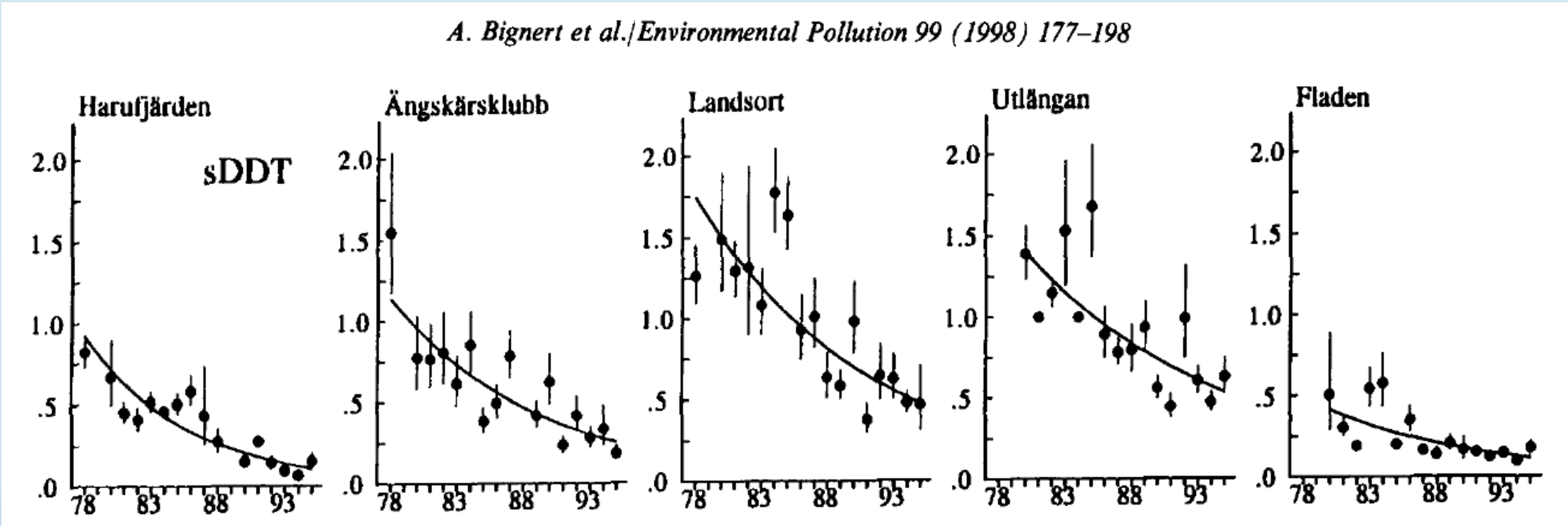


FIGURE 4. Organochlorine pesticide concentrations in precipitation collected at 7 IADN sites near the Great Lakes. The black curve is the fitted line of the sinusoidal model with the period length (a_3) set to one year. The red lines indicate long-term significant decreasing or increasing trends. Detailed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



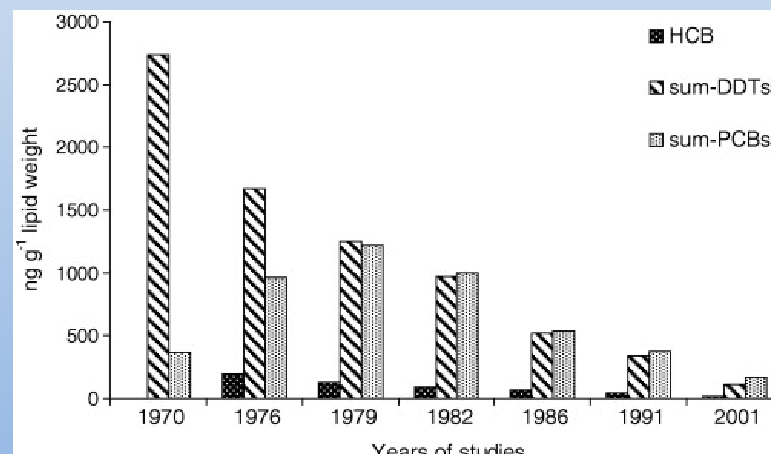
Conc. (ng/g) →

Time →

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

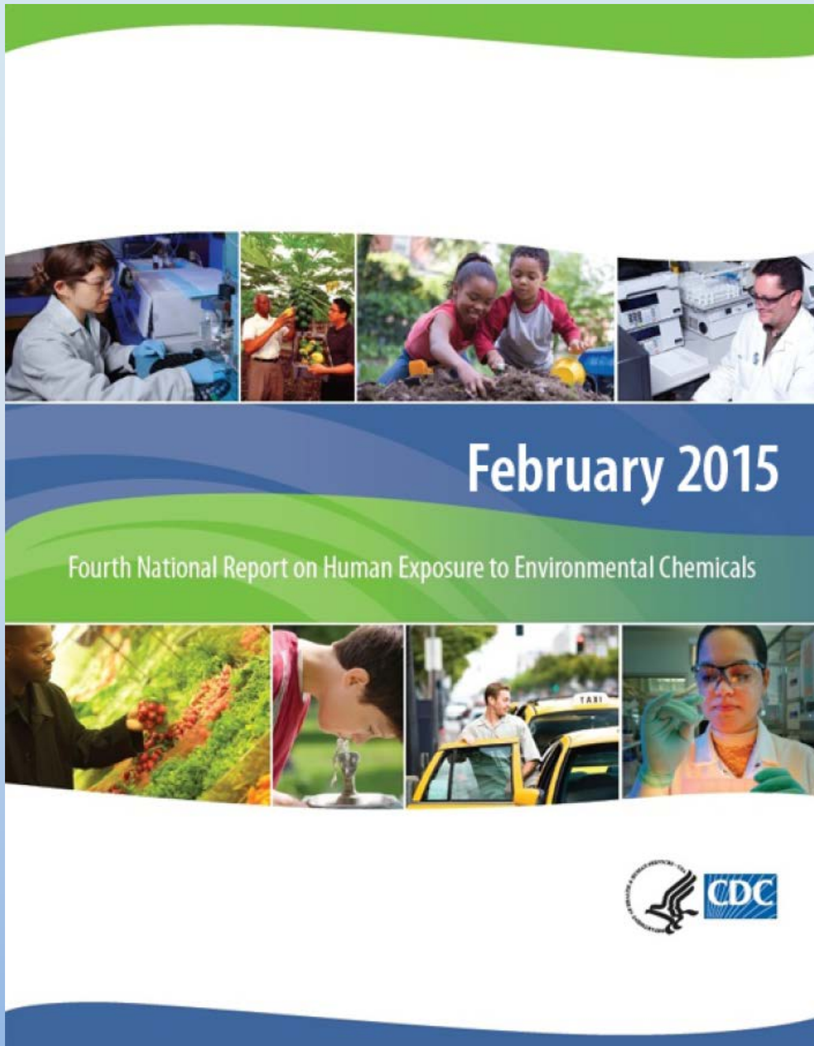
Levels and temporal trends of chlorinated pesticides, polychlorinated biphenyls and brominated flame retardants in individual human breast milk samples from Northern and Southern Norway

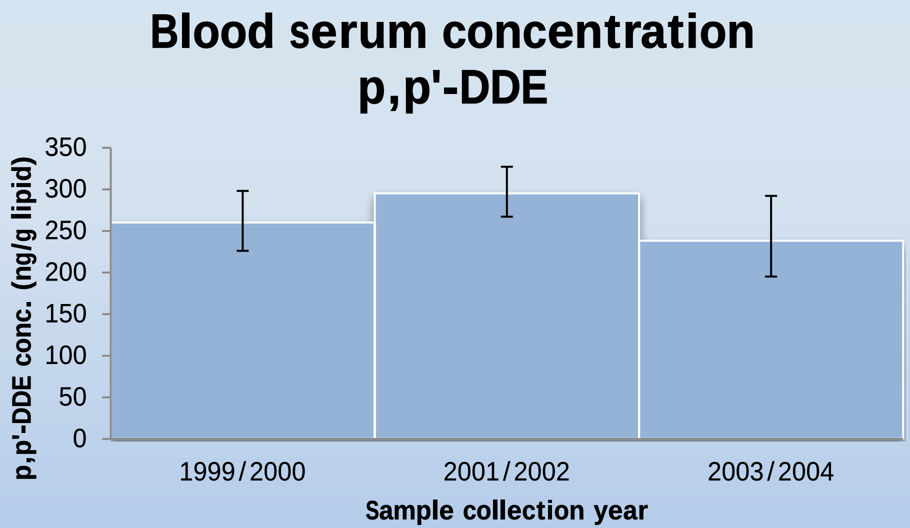
Chemosphere, Volume 73, Issue 1, 2008, 14 - 23



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

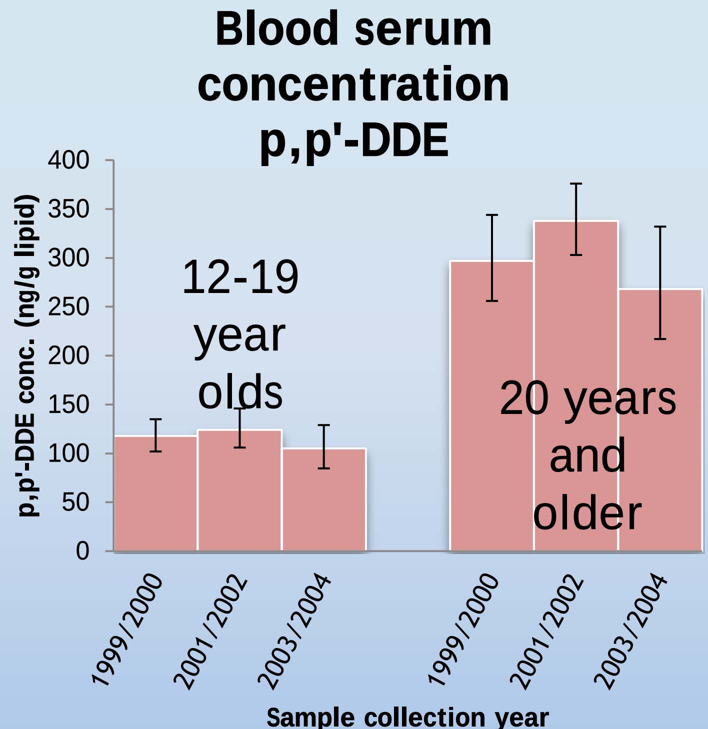
NHANES -National Health and Nutrition Examination Survey of the US Centre for Disease Control

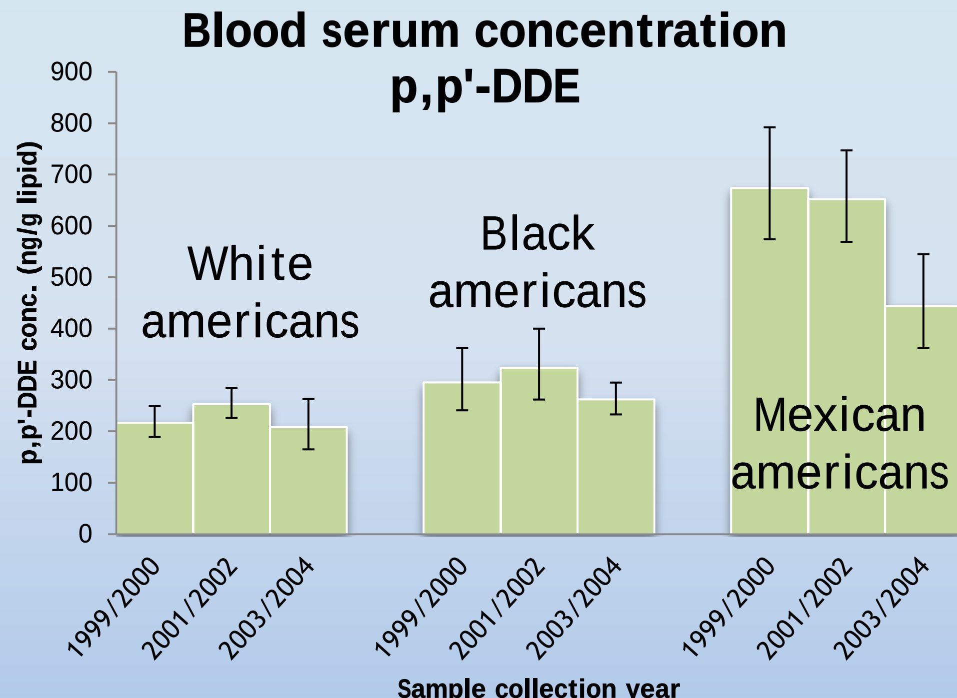




Levels are ~15x lower than in 1970s, just after ban on DDT use

Let's look a little deeper at the NHANES data...





Differences by age and differences by ethnicity. Any ideas why?

DDT – remaining questions?

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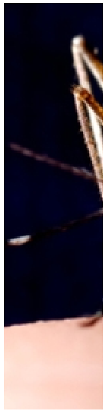
Health » Environmental Health News

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 Ethopian girl afflicted by the disease. (By Per-anders Pettersson -- Getty Images)

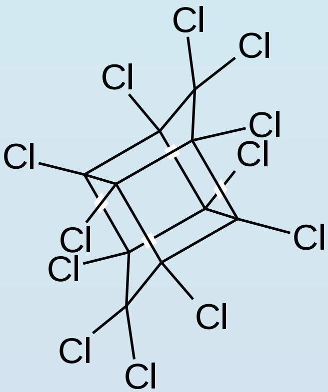
In the pantheon of poisons, DDT occupies a special place. It's the only pesticide celebrated with a Nobel Prize: Swiss chemist Paul Mueller won in 1948 for having discovered its insecticidal properties. But it's also the only pesticide condemned in pop song lyrics -- Joni Mitchell's famous "Hey, farmer, 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.

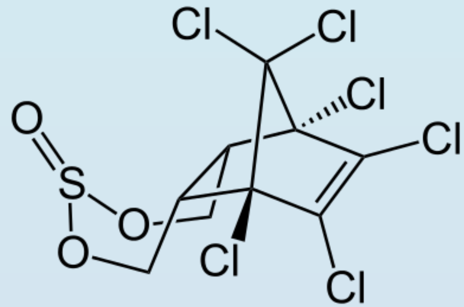
ANY QUESTIONS ABOUT DDT?

Generalizing: OCPs

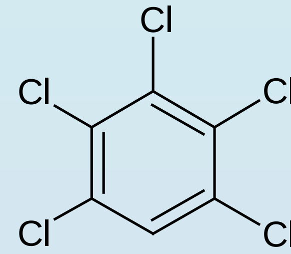
- OCPs = organochlorine pesticides
- What are the OCPs?
  - DDT
  - Hexachlorobenzene (HCB)
  - Pentachlorobenzene (PeCB)
  - Hexachlorocyclohexanes (multiple isomers)
  - Heptachlor/heptachlor epoxide
  - Aldrin/dieldrin/endrin
  - Chlordane (multiple isomers)
  - Endosulfan
  - Mirex
  - ...



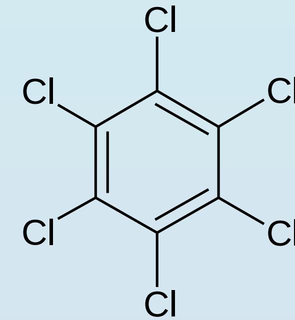
Mirex



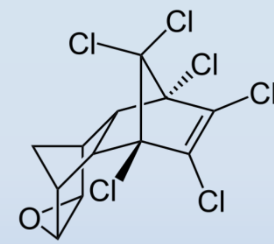
Endosulfan



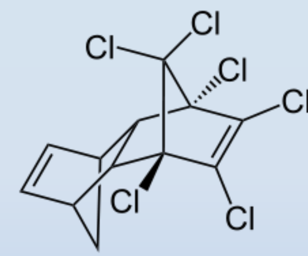
PeCB



HCB

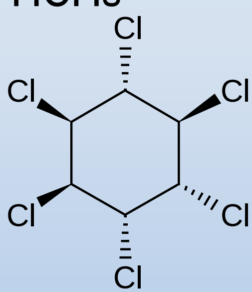


Endrin

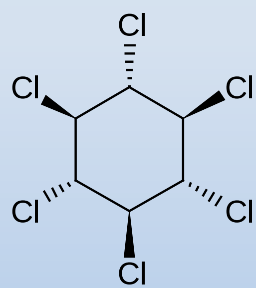


Aldrin

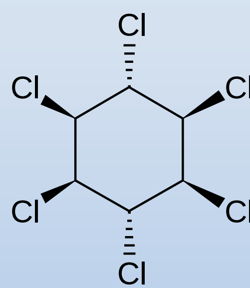
HCHs



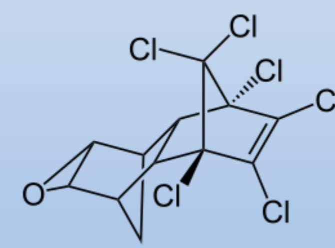
α



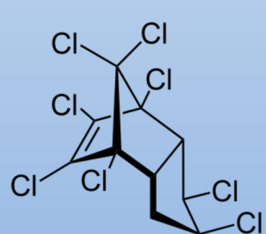
β



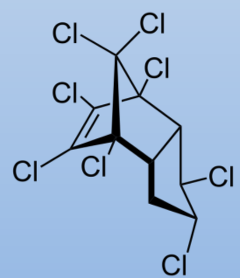
γ



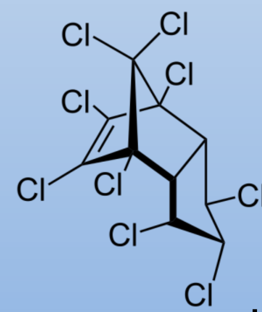
Dieldrin



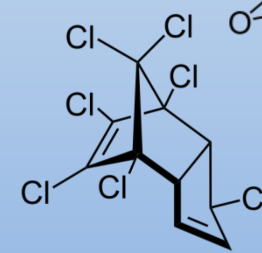
cis-chlordane



trans-chlordane



trans-nonachlor

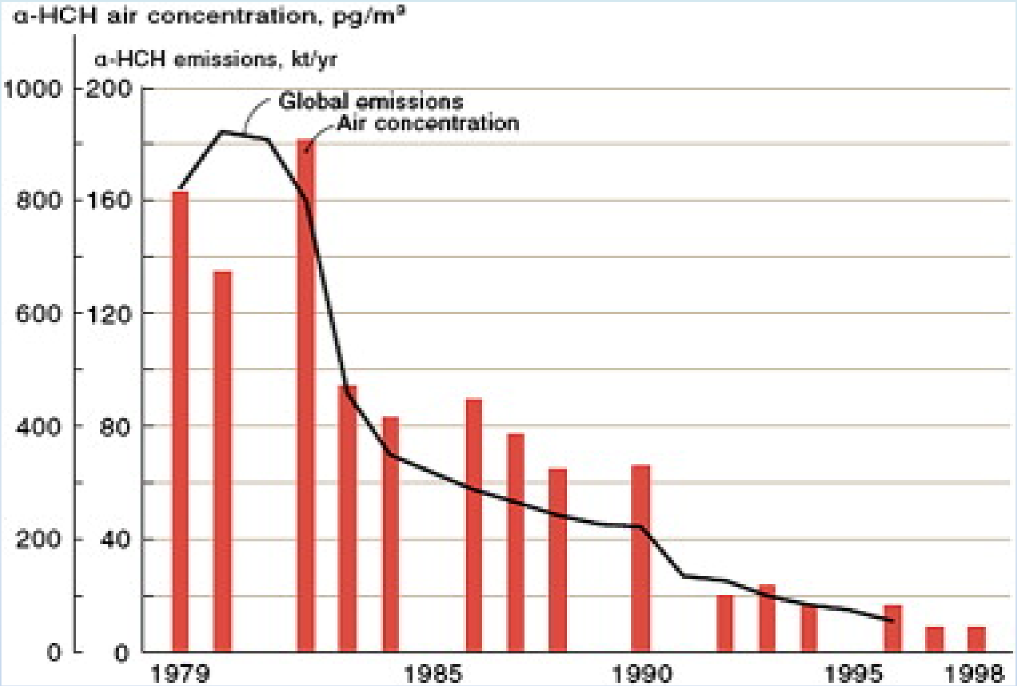


heptachlor

OCPs under the Stockholm Convention

"compounds recognized as causing adverse effects on humans and the ecosystem"

- **Aldrin**
- **Chlordane**
- **DDT and metabolites**
- **Endrin**
- **Dieldrin**
- **Endosulfan**
- **α-, β-, γ-HCH**
- **HCB**
- **PeCB**
- **Toxaphene**
- **Mirex**



Global emissions of α-HCH and its mean concentrations in Arctic air from 1979 to 1996 assembled from published data

Rainer Lohmann , Knut Breivik , Jordi Dachs , Derek Muir

Global fate of POPs: Current and future research directions

Environmental Pollution, Volume 150, Issue 1, 2007, 150 - 165

Phys-chem properties

- Vapour pressure

VP= 0.01 Pa (PeCB) to 0.0002 Pa (ß-endosulfan)

- Octanol-water partitioning coefficient: $\log K_{OW}$ = 5.5 (dieldrin) to 6.9 (p,p'-DDE)
- Octanol-air partitioning coefficient: $\log K_{OA}$ = 6.7 (PeCB) to 10.0 (p,p'-DDD)
- Air-water partitioning coefficient:

  $\log K_{AW}$ = -1.5 (PeCB) to -4.7 (ß-endosulfan)

Chemicals divided according to partitioning properties

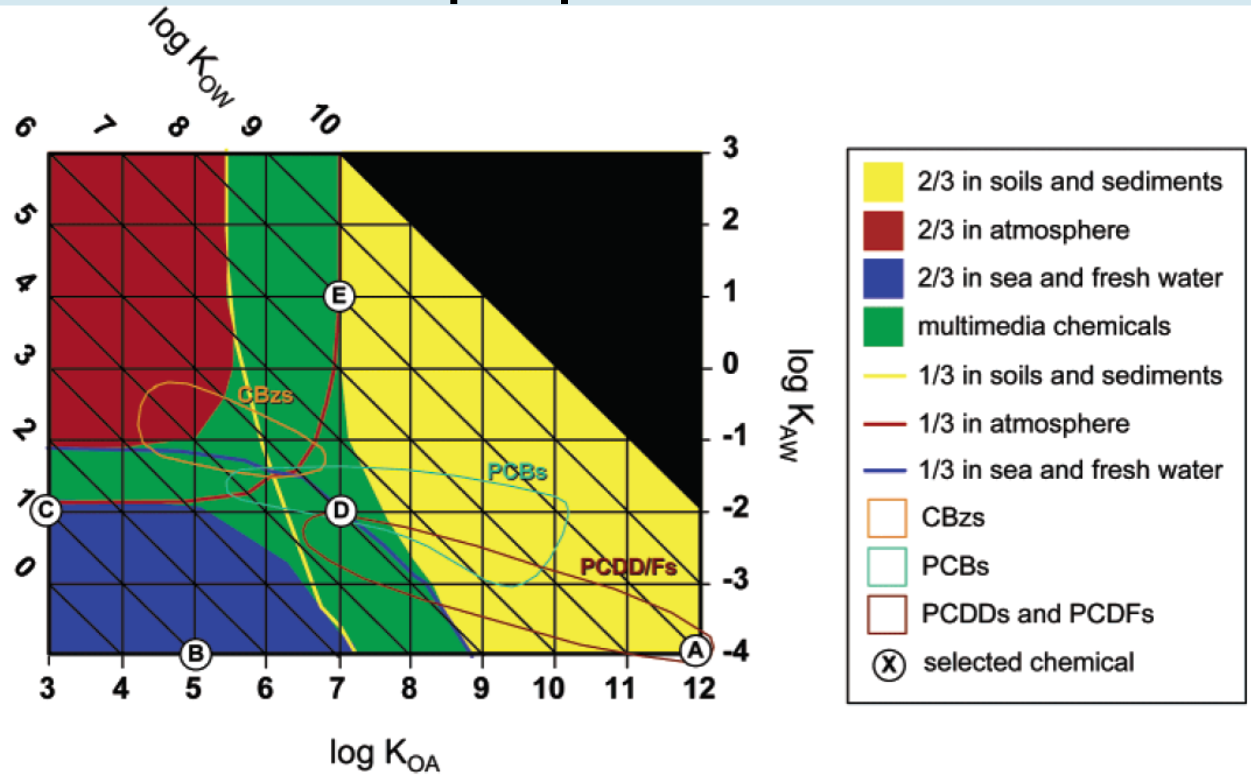
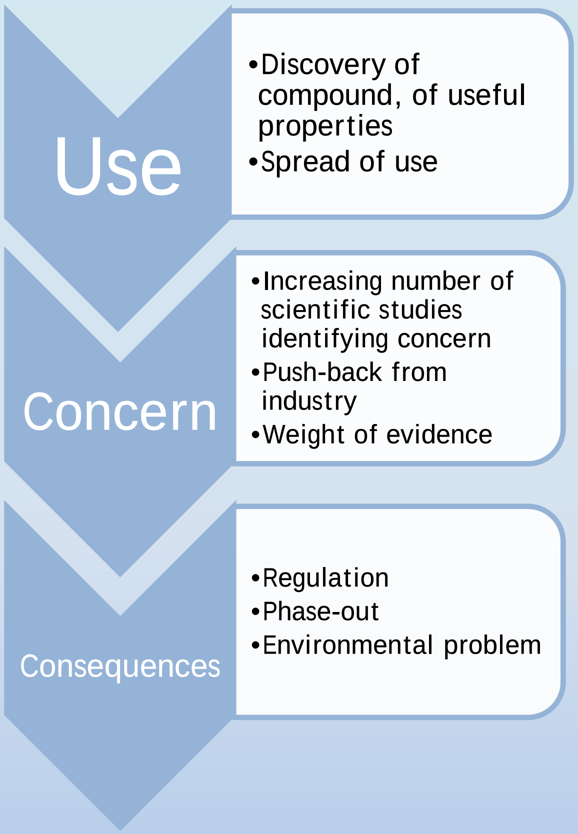


FIGURE 3. Primary environmental compartments for hypothetical chemicals defined by their partitioning properties log K_{AW}, log K_{OA}, and log K_{OW}. The distribution between media was calculated with the Globo-POP model assuming 10 years of steady emissions of perfectly persistent chemicals into air, water, and soil (1/3 each) using a zonal emission distribution matching that of the human population. Chemicals with a log $K_{OW} > 10$ are unlikely to exist. The white circles locate the five chemicals used in the sensitivity analysis within that chemical space. Closed curves indicate the partitioning properties of the chlorobenzenes (CBzs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs).

From Wania, 2003, Environmental Science and Technology

Any questions about OCPs?

Polychlorinated biphenyls - PCBs



-High chemical and physical stability, even at high temperatures

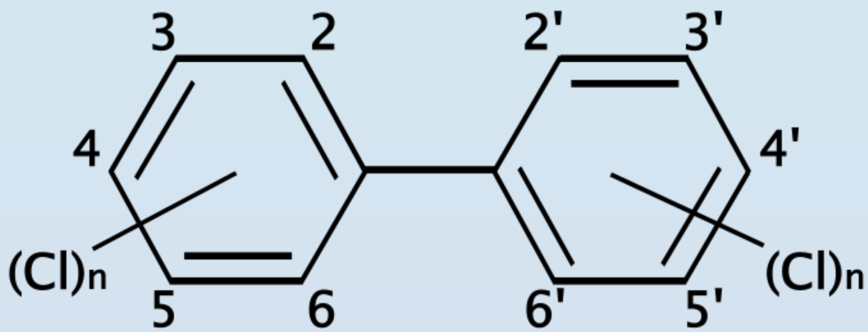
→Desirable property!

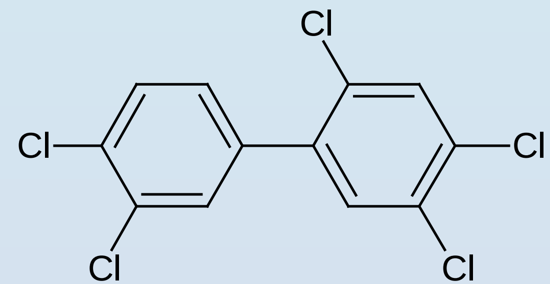
-Industrially produced in 10 countries for a range of uses

- 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

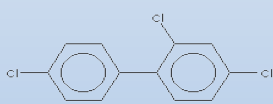




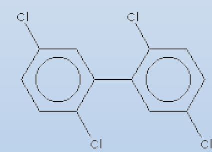
2,3',4,4',5-Pentachlorobiphenyl
PCB 118

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

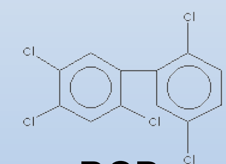
Indicator PCBs – 7 congeners:



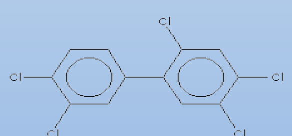
PCB 28



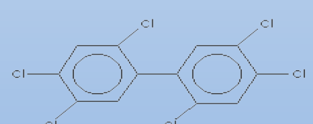
PCB 52



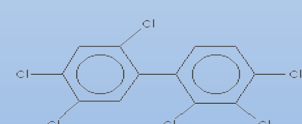
PCB 101



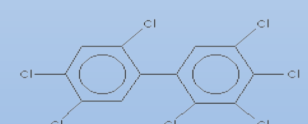
PCB 118



PCB 153



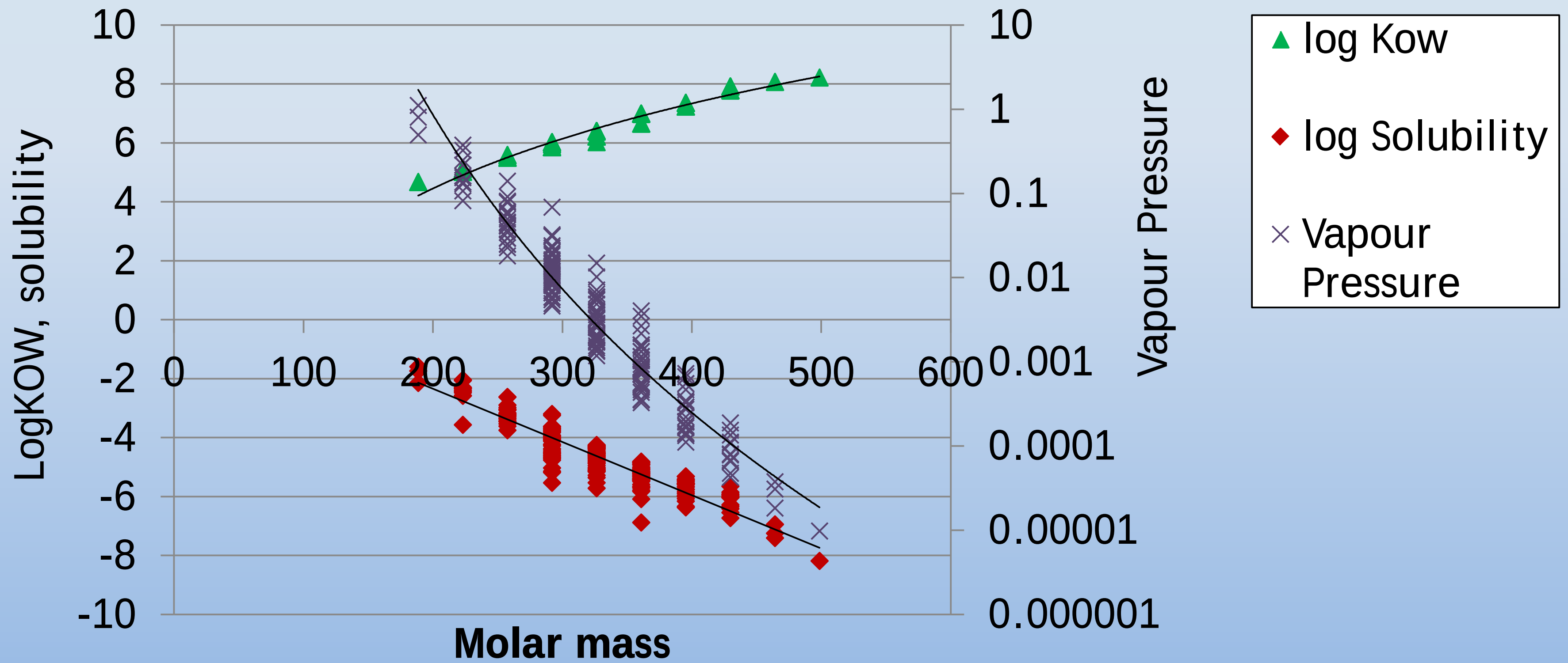
PCB 138



PCB 180

PCBs – Physical-chemical properties

- Trend in phys-chemical properties with chlorination

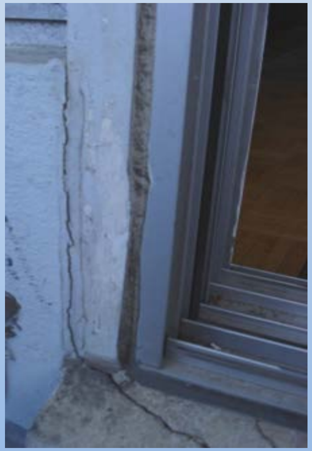


From Paasivirta et al. 2009

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



Building sealants?

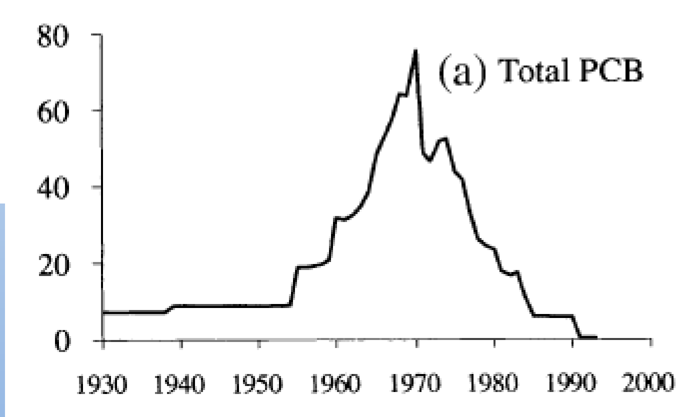
- Caulking material used to waterproof joints between masonry/concrete parts of buildings
- PCBs added as plasticizer to caulking to allow for expansion during temperature change
- Added at a concentration of at least 10 mg/g (1%) (Kohler et al., 2005)

PCB production

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

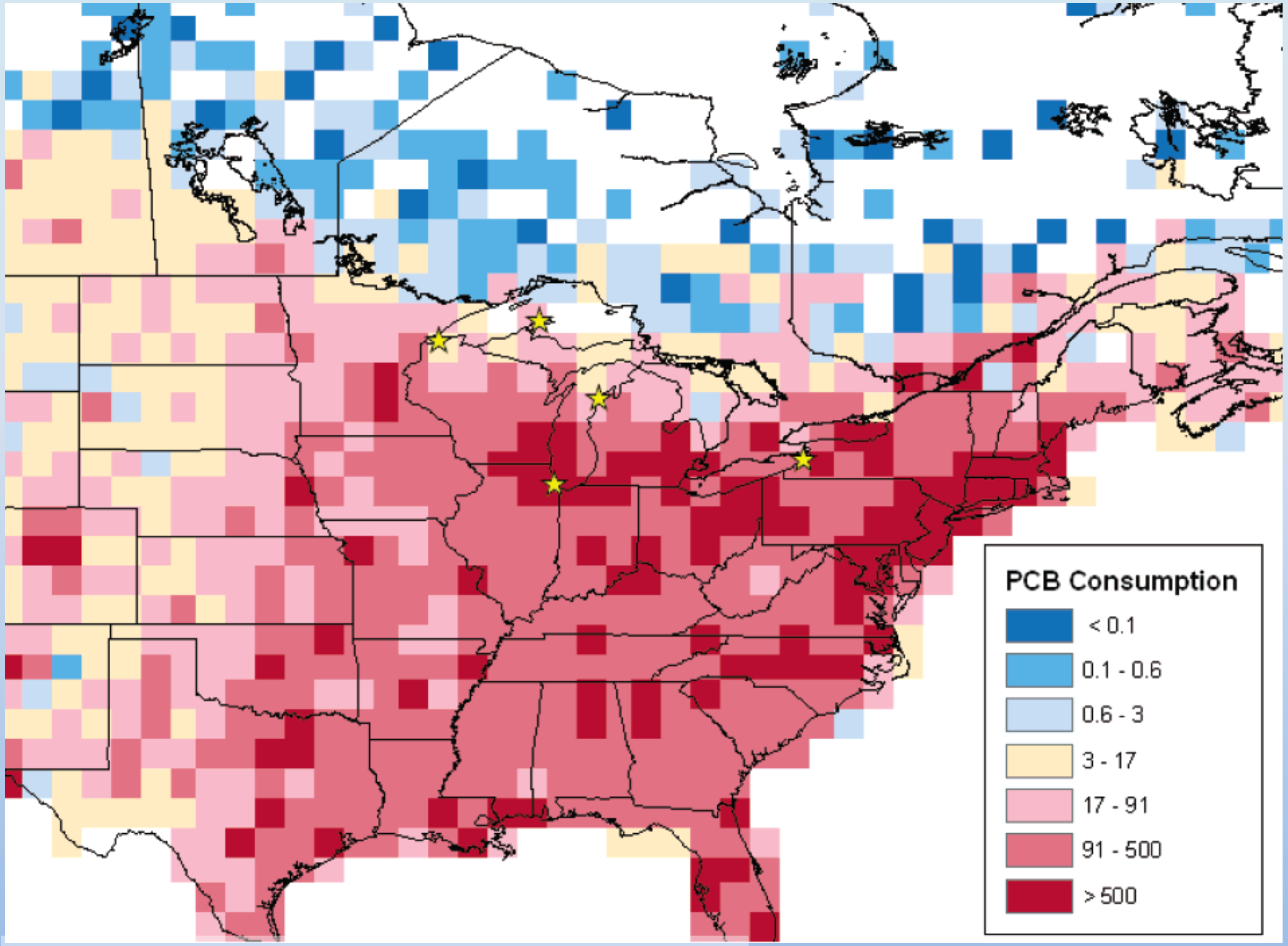
Table 1
Total PCB production in t as reported in the literature

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)
[illegible]	[illegible]	…39	1990	141 800	AMAP (2000)
[illegible]	[illegible]	…72	1993	32 000	AMAP (2000)
[illegible]	[illegible]	…60	1979	8000	Jiang et al. (1997)
[illegible]	[illegible]	…30	1993	1 324 131	



over 1 million tonnes globally

PCB use in North America



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

Large quantities of PCBs demanding ESM in Central and Eastern European

PCB production in CEE countries

Country	Trademarks example	Former production [tonnes]	Production period
Former Czechoslovakia	Delor, Deloterm, Hydelor	21,500	1959 – 1984
Poland	Tarnol, Chlorofen	679	1971 – 1976
Former Soviet Union	Sovol	53,000	1939 – 1993
	Sovtol	57,000	1939 – 1993
	Trichlorobiphenyl	70,000	1963 – 1993
Total		**202,179**	

PCB liquids were mostly exported for manufacture of transformers and capacitors to Western European countries, Cuba, Pakistan and Vietnam. However, the CEE regional electric equipment industry was also important in the former Czechoslovakia, former East Germany, the former Soviet Union and the former Yugoslavia.

However, the CEE regional electric equipment industry was also important in the former Czechoslovakia, former East Germany, the former Soviet Union and the former Yugoslavia.

Legislation

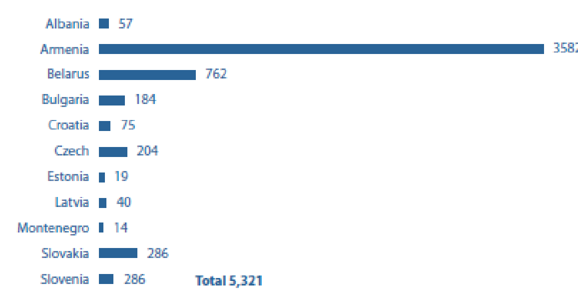
All CEE countries are quite advanced in the process of implementing the Stockholm Convention at the national level, having established legal frameworks for PCBs. Each country has developed or is currently finalizing their National Implementation Plan (NIP) under the Stockholm Convention. The implementation of general PCB obligations that are set in revised national regulations and legal acts have led to better environmentally sound PCB waste management 20 – 30 years ago. Law enforcement through officially designated environmental inspection bodies exists, while illegal handling and improper management practices are penalised.

However, there are different groups of countries including European Union member states, European Union pre-accession countries, former United Soviet Socialistic Republics or countries of former Yugoslavia that show unequal approaches and standards for environmental policies.

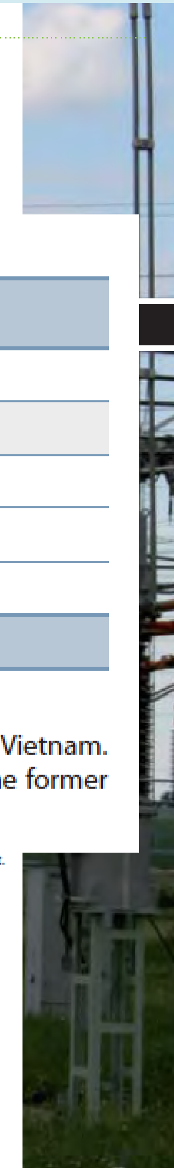
Countries in the CEE Region have their deadlines for decontamination or disposal of PCBs and PCB contaminated equipment set, mainly based on the obligations of the Stockholm Convention or on the European Council Directive 96/59/EC on the disposal of PCBs and polychlorinated terphenyls (PCTs). Wastes, equipment and liquids are considered to contain or be contaminated with PCBs if the PCB concentration is higher than 50 mg/kg ~ 50 ppm ~ 0,005 % by weight in the whole CEE Region.

actually contaminated equipment. The other countries have identified only the main stakeholders of PCB equipment.

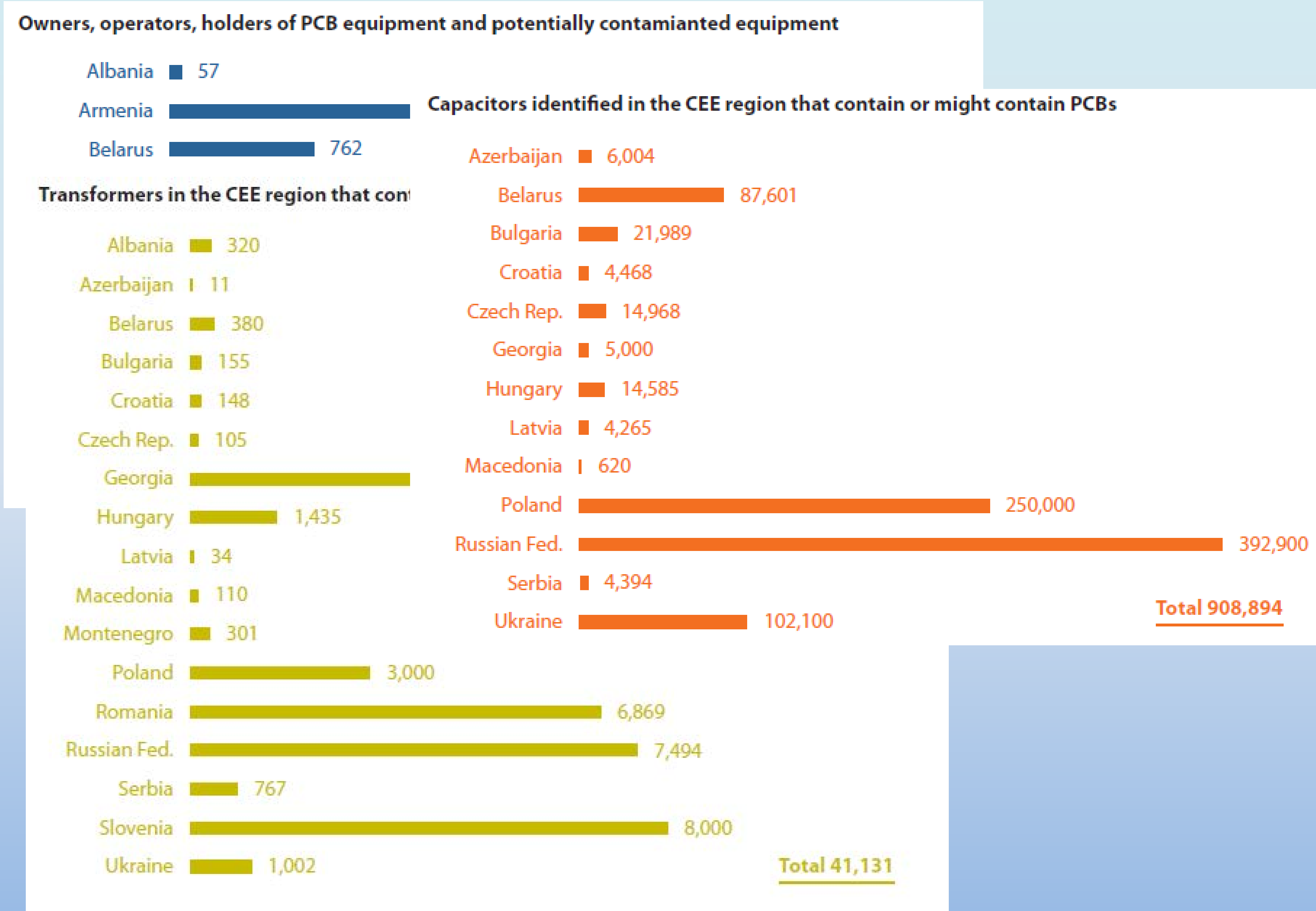
Owners, operators, holders of PCB equipment and potentially contamianted equipment



(cont. on page 44...)



From PCBs Elimination Network Magazine, Stockholm Convention, 2010


Owners, operators, holders of PCB equipment and potentially contamianted equipment
Albania 57
Armenia
Belarus 762
Transformers in the CEE region that con
Albania 320
Azerbaijan 11
Belarus 380
Bulgaria 155
Croatia 148
Czech Rep. 105
Georgia
Hungary 1,435
Latvia 34
Macedonia 110
Montenegro 301
Poland 3,000
Romania 6,869
Russian Fed. 7,494
Serbia 767
Slovenia 8,000
Ukraine 1,002
Total 41,131
Capacitors identified in the CEE region that contain or might contain PCBs
Azerbaijan 6,004
Belarus 87,601
Bulgaria 21,989
Croatia 4,468
Czech Rep. 14,968
Georgia 5,000
Hungary 14,585
Latvia 4,265
Macedonia 620
Poland 250,000
Russian Fed. 392,900
Serbia 4,394
Ukraine 102,100
Total 908,894

Slovakia

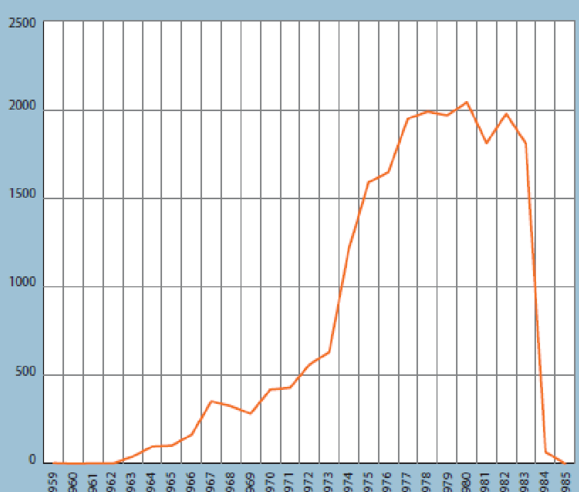
Now we have to address the PCB mess

By Katarína Dercová, Hana Dudášová, Lucia Lukáčová, Anton Kočan, Jana Chovancová, Martin Murín, Alena Pilváčová

One of the eight world's largest PCB producers

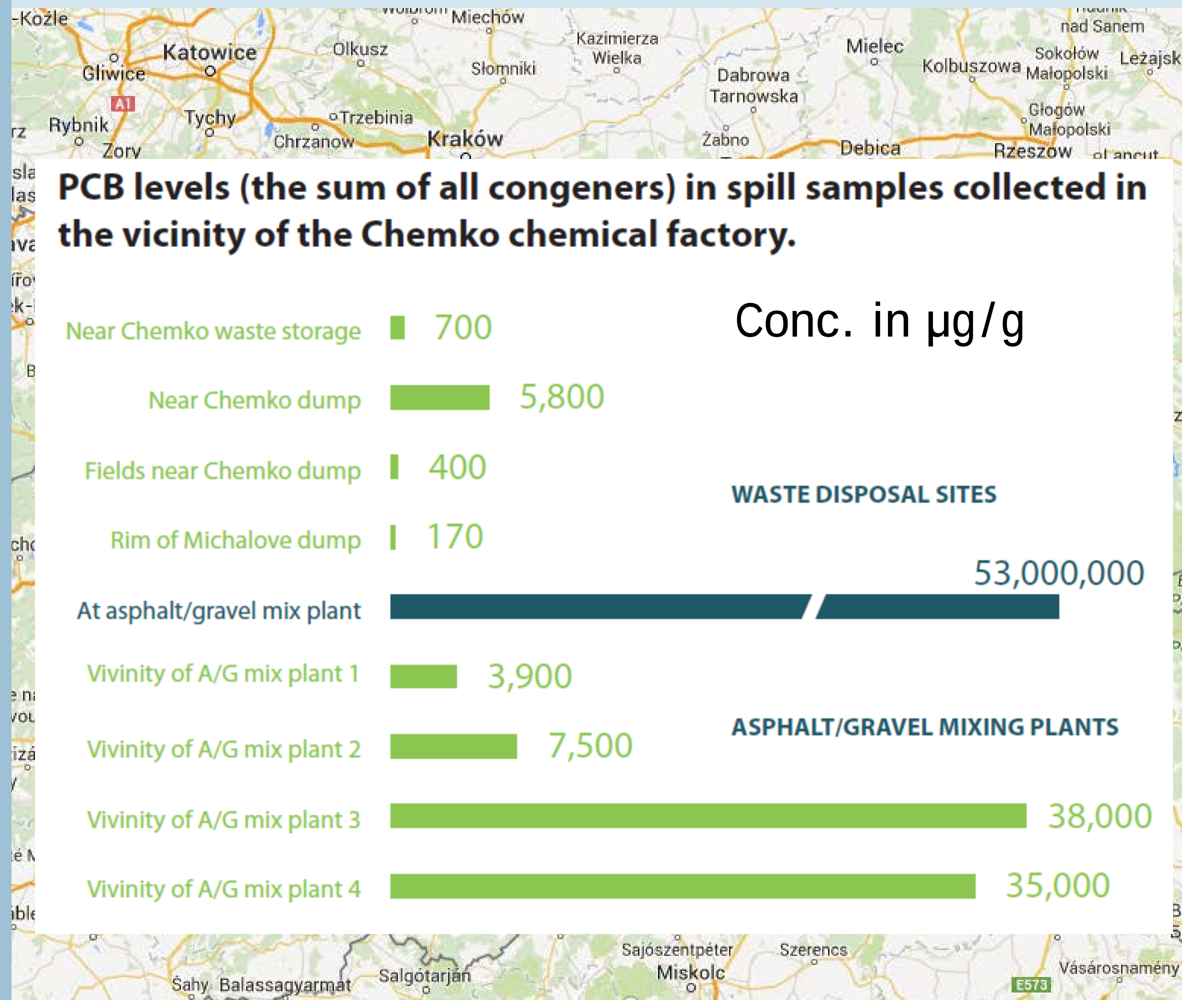
The Slovak Republic, a part of former Czechoslovakia, belonged to the eight world's largest producers of PCB commercial mixtures. More than 21,000 tonnes of PCBs were produced by Chemko Strážske under the brand names Delor, Hydelor, and Delotherm from 1959 to 1984, and broadly utilized in former Czechoslovakia for production of capacitors, paints, and varnishes. About 46% of the produced PCB was exported mainly to former East Germany. The rest (11,613 tonnes) was used in the territory of former Czechoslovakia.

PCB manufactured by Chemko Strážske plant from 1959 to 1984

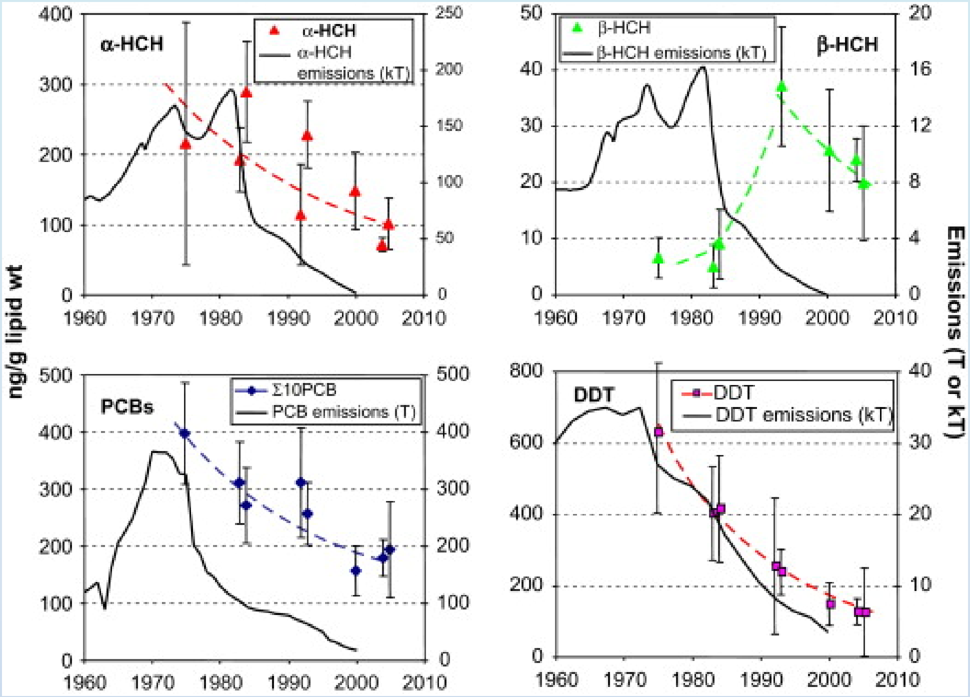


It is now prohibited to use PCBs in open systems. However, PCBs are still used in power capacitors. Such capacitors can contain from 1.4 to 20 kg of PCBs. Transformers and heat exchangers have already been refilled with non-PCB containing fluids. Because PCBs were also used as a paint additive (their content was up to 21%), old paint coatings might still contain PCBs.

Strážske, Slovakia



Typical soil levels in Brno: 0.1-14 ng/g



Temporal trends of α- and β-HCH, ∑ 10 PCBs and ∑DDT in ringed seal blubber from Lancaster Sound in the Canadian Arctic archipelago.

Rainer Lohmann , Knut Breivik , Jordi Dachs , Derek Muir

Global fate of POPs: Current and future research directions

Environmental Pollution, Volume 150, Issue 1, 2007, 150 - 165

Any questions about PCBs?

Dioxins and furans

Dioxins in the news…

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7 January 2011 Last updated at 08:22 GMT

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Dioxin animal feed scare shuts German farms

More than 4,700 German farms have been closed after
were found t
a poisonous

Officials insist
risk to human
precaution.

Most of the a
Germany's Lo

Meanwhile, th
farms affecte
destined for h

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…ties | development

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

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

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Deadly dioxin used on Yushchenko

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

Yushchenko's disfigurement could take two years to heal

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

Mr Yushchenko, who faces PM Viktor 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.

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

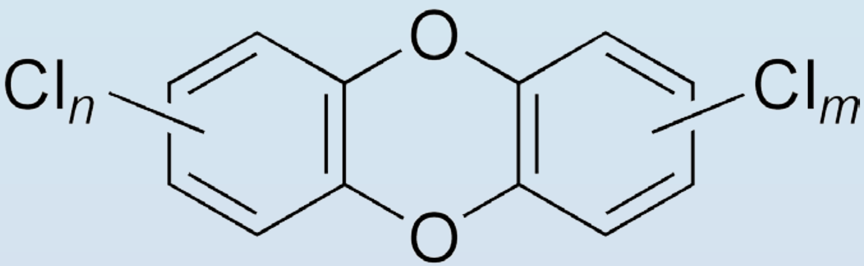
ANALYSIS AND FEATURES

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

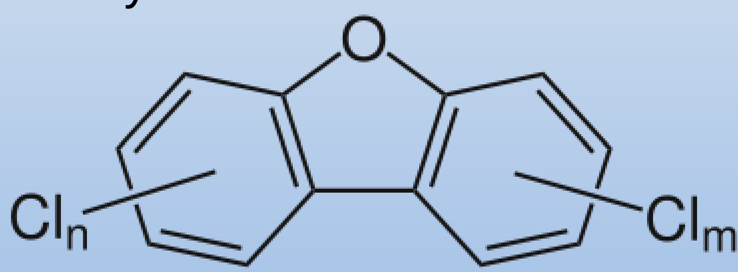
- Cynicism clouds dreams
- Revolution supporters in distress
- Ukraine's heroes turn into foes
- Warm US welcome
- Mending fences with Russia

Dioxins and furans

Polychlorinated dibenzodioxins



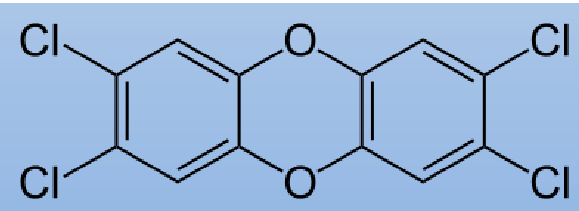
Polychlorinated dibenzofurans



The International Programme on Chemical Safety (IPCS)

WHO UNEP

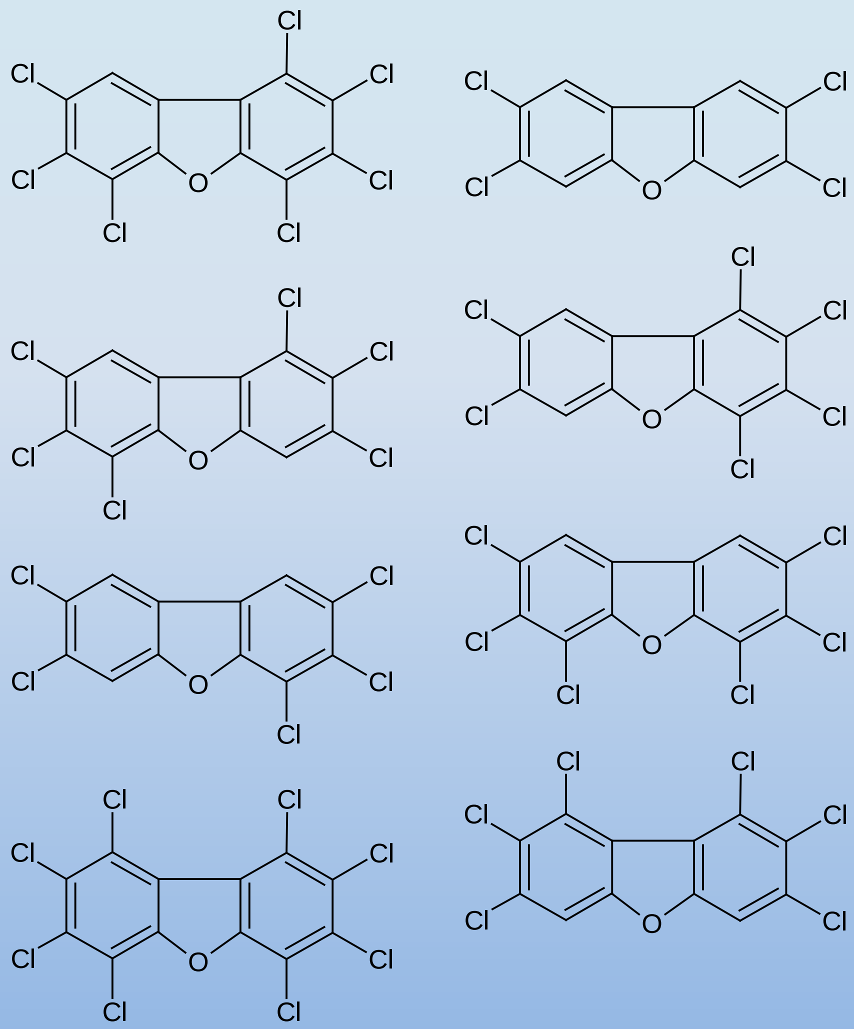
Compound	WHO 1998 TEF	WHO 2005 TEF*
chlorinated dibenzo-p-dioxins		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	**0.0003**
chlorinated dibenzofurans		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	**0.03**
2,3,4,7,8-PeCDF	0.5	**0.3**
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	**0.0003**



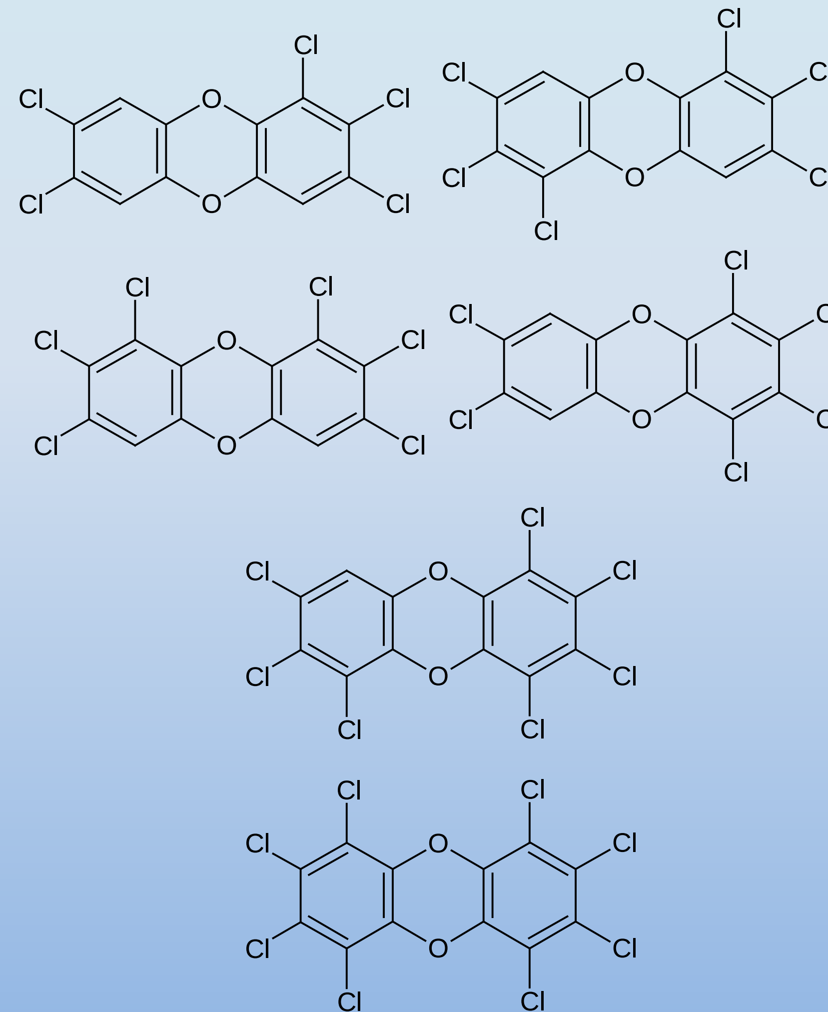
2,3,7,8-TCDD

Chemical Structures

Furans



Dioxins



Physical-chemical properties

Dioxins and Furans	Molar Mass	Vapour Pressure (Pa)	logKoa	Particle Fraction
2378-TCDF	306	0.0017	9.9	0.09
12378-PeCDF	340	0.00024	11.4	0.76
23478-PeCDF	340	0.00019	11.5	0.80
123478-HxCDF	375	0.000071	12.0	0.92
123678-HxCDF	375	0.000069	12.0	0.92
234678-HxCDF	375	0.000055	12.1	0.94
123789-HxCDF	375	0.000040	12.2	0.95
1234678-HpCDF	409	0.000055	12.1	0.93
1234789-HpCDF	409	0.0000079	12.3	0.96
OCDF	444	0.0000013	12.8	0.99
2378-TCDD	322	0.0020	10.0	0.11
12378-PeCDD	356	0.00018	10.4	0.25
123478-HxCDD	391	0.00088	12.2	0.95
123678-HxCDD	391	0.000052	12.2	0.95
123789-HxCDD	391	0.000045	12.3	0.96
1234678-HpCDD	425	0.00077	11.5	0.81
OCDD	460	0.0000014	13.0	0.99

Beyer et al. 2002, Paasivirta et al. 1999, Harner et al. 2000

Chemicals divided according to partitioning properties

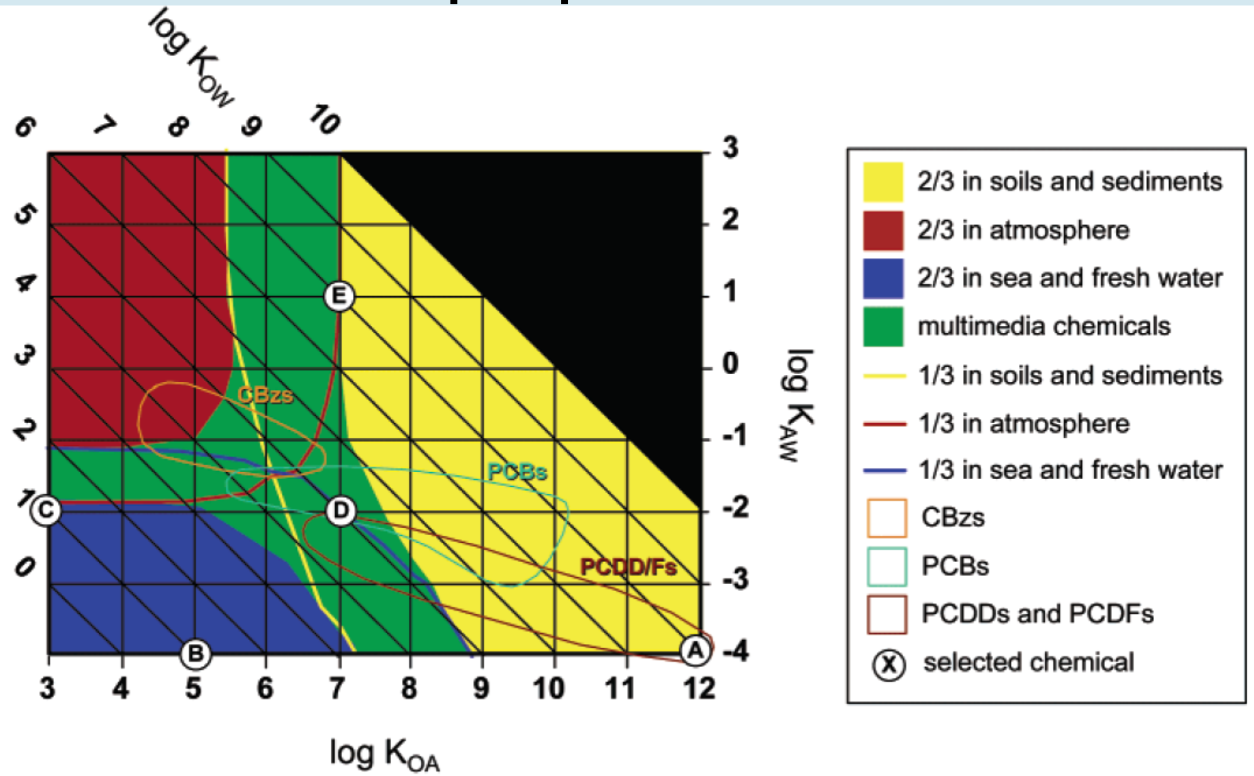


FIGURE 3. Primary environmental compartments for hypothetical chemicals defined by their partitioning properties log K_{AW}, log K_{OA}, and log K_{OW}. The distribution between media was calculated with the Globo-POP model assuming 10 years of steady emissions of perfectly persistent chemicals into air, water, and soil (1/3 each) using a zonal emission distribution matching that of the human population. Chemicals with a log $K_{OW} > 10$ are unlikely to exist. The white circles locate the five chemicals used in the sensitivity analysis within that chemical space. Closed curves indicate the partitioning properties of the chlorobenzenes (CBzs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs).

From Wania, 2003, Environmental Science and Technology

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
- Listed under Annex C of Stockholm Convention: "Parties must take measures to reduce the **unintentional releases** of chemicals listed under Annex C with the goal of continuing minimization and, where feasible, ultimate elimination."

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		

Table 1
National PCDD/PCDF inventories for emissions to air (update of references UNEP, 1999; Fiedler, 2003a)

Country/State	g TEQ/a		Reference year	Reference
	Best	Max		
Australia	150	2300	1998	UNEP (1999)
Austria	29		1994	UNEP (1999)
Belgium	661		1995	UNEP (1999)
Switzerland	181		early 1990s	UNEP (1999)
Canada	164		1999	Environment Canada (2001)
Croatia	95.5		ca. 1997	UNEP (1999)
Czech Republic	179		2001	RECETOX (2003)
Denmark	19	170	1998/99	COWI (2001)
Finland	98.3	198	ca. 1997	UNEP (1999)
France	380		2002	CITEPA (2004)
Germany	323		1994	UNEP (1999)
Hong Kong SAR	23	33	1997	Hong Kong (2000)
Hungary	103		1998	UNEP (2000)
Ireland	34.0		2000	Hayes and Marnane (2000)
Japan	372	400	2003	MoE (2004)
The Netherlands	486		1991	UNEP (1999)
New Zealand	14	51	1998	Buckland *et al.* (2000), Dyke *et al.* (2000)
Norway	9.15		ca. 1997	UNEP (1999)
Sweden	22	88	1993	UNEP (1999)
Slovak Republic	616		1996	UNEP (2000)
Taiwan	67.3		2000	Chen (2004)
United Kingdom	560	1099		UNEP (1999)
United States of America	2501	4901	1995	US-EPA (2000)
Global flux	7087	12570		

Fielder et al. Chemosphere , 2007

Temporal trends of PCDD/Fs

What do you think the temporal trends are? Increasing? Decreasing? Any guesses?

Sediment core data from Baltic Sea:

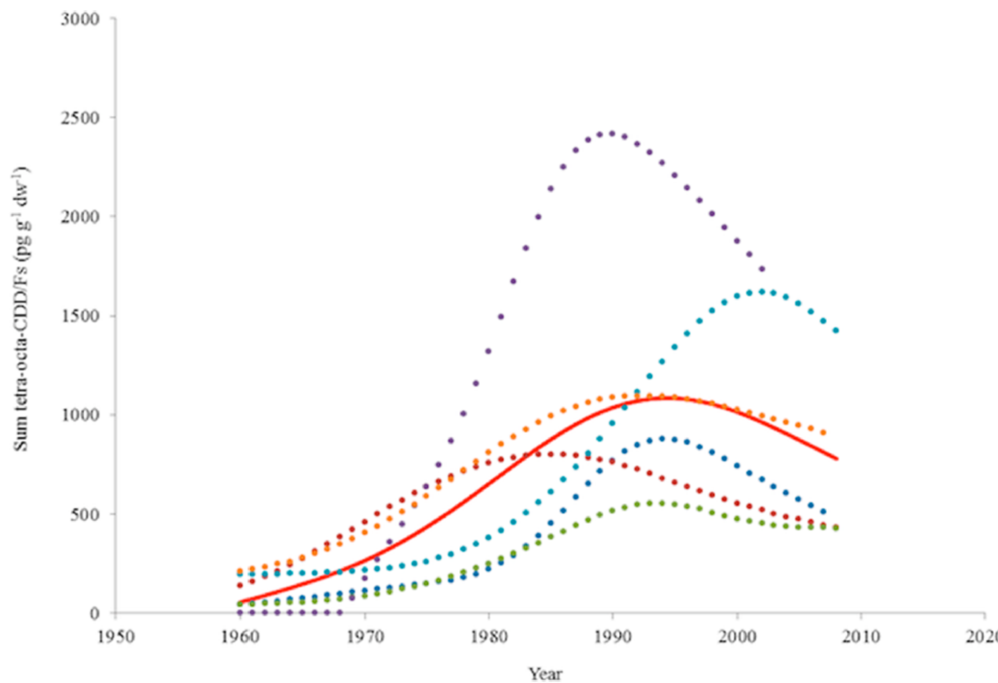


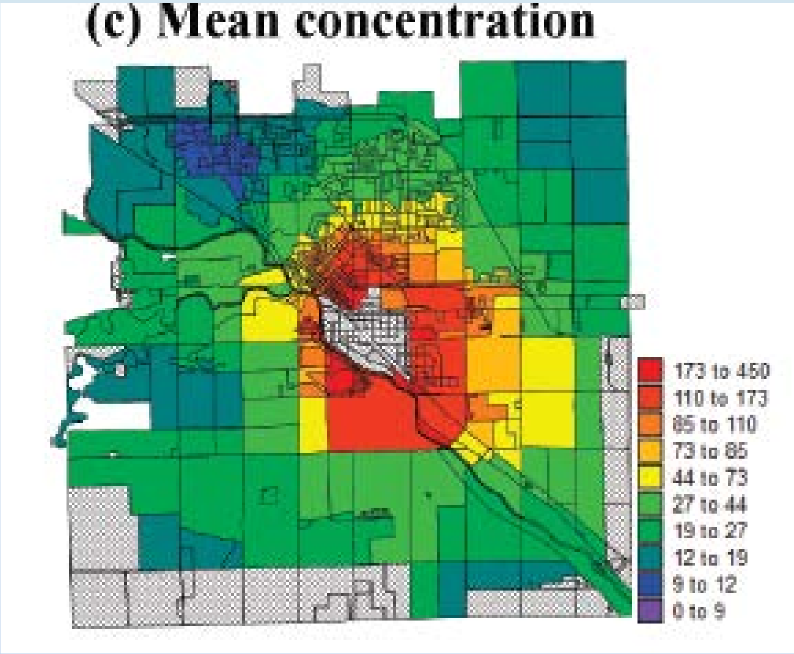
Figure 2. General and individual spline fit curves for the temporal trends of PCDD/Fs in Baltic Sea sediment. Dotted lines: blue, Station O1; red, Station O2; green, Station O3; purple, Station O4; light blue, Station O5; orange, Station O6; red line, Model.

Assefa et al. 2014, Environmental Science & Technology

Spatial patterns of PCDD/Fs

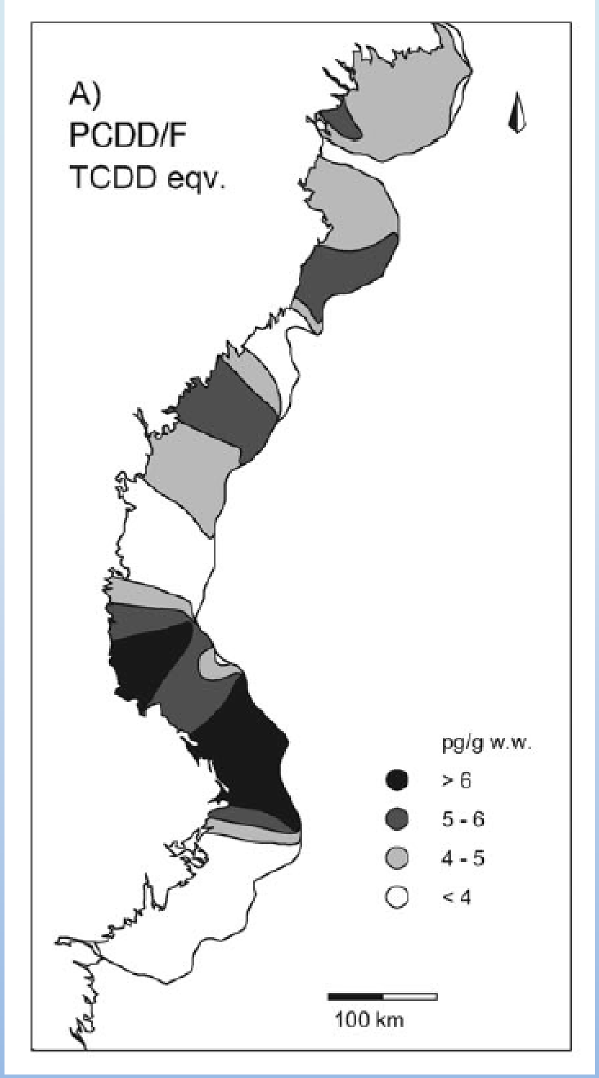
- Higher concentrations closer to sources, in highly developed, industrialized areas
- Concentrations patterns in air, soil, sediment and biota mirror each other
- Trends on a large scale – globally – and small scale - locally

Local scale – PCDD/Fs in soil around an incinerator



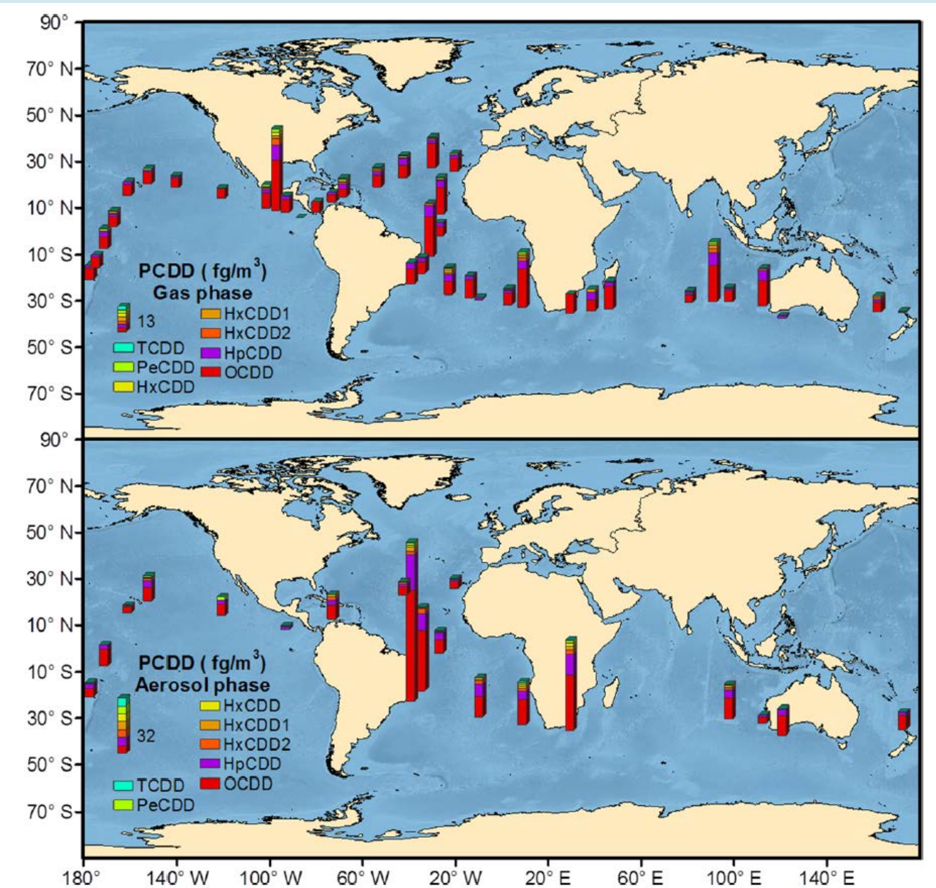
Goovaerts et al. 2008

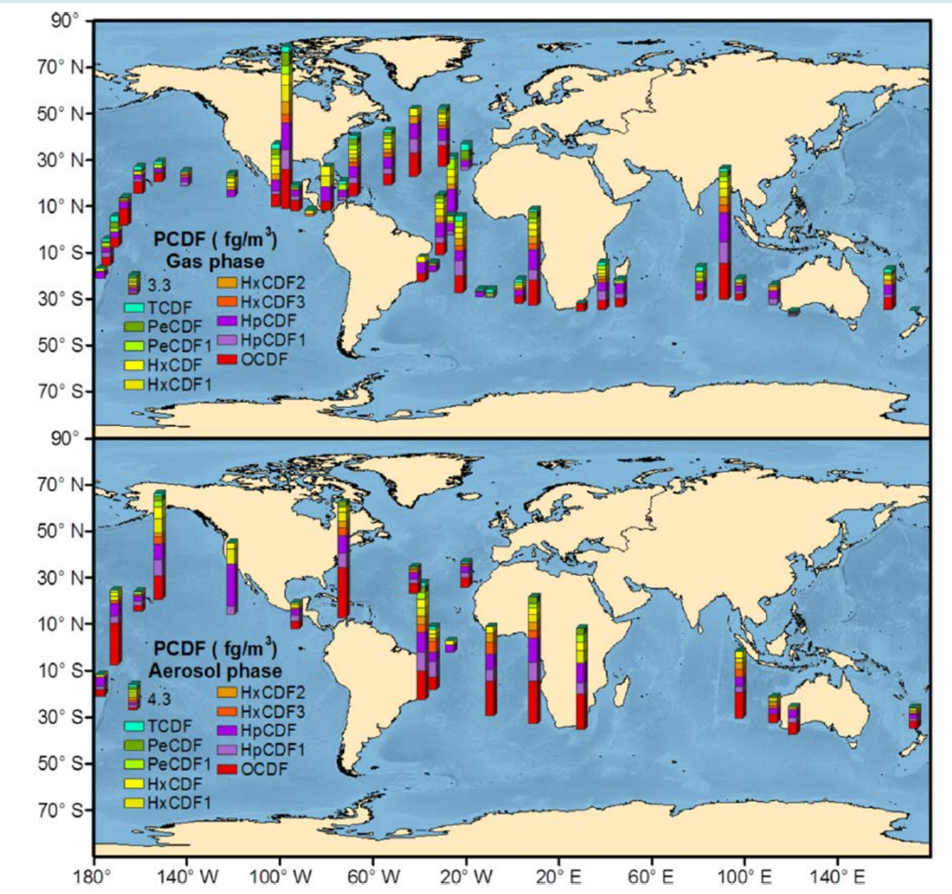
Regional scale – PCDD/Fs in fish from the coast of Sweden



Bignert et al. 2007

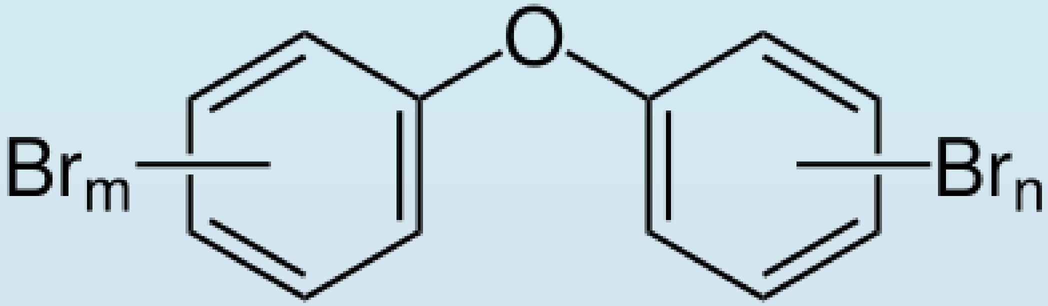
Global scale – PCDD/Fs





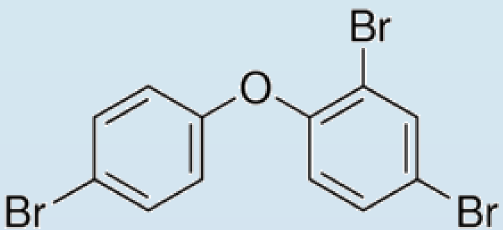
Morales et al. 2014

PBDEs

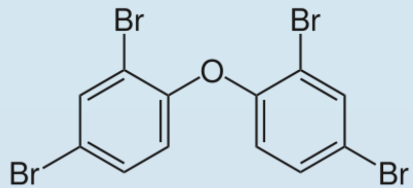


- Polybrominated diphenyl ethers
- Flame retardants
- Classified by either technical mixture or congener group
  - Confusing!! E.g., penta-BDE can refer to either the technical mixture called "Penta" or could refer to a PBDE with 5 bromines
  - Commercial mixtures sometimes distinguished as "c-penta"

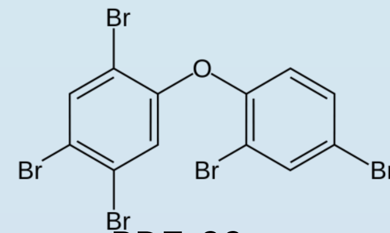
PBDE naming - congeners



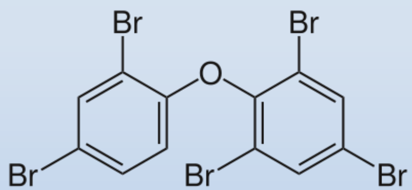
BDE-28
Tribromodiphenyl ether



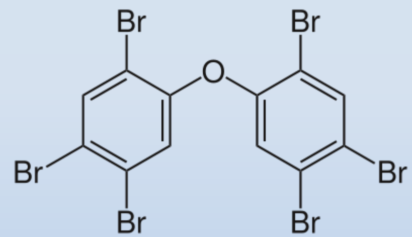
BDE-47
Tetrabromodiphenyl ether



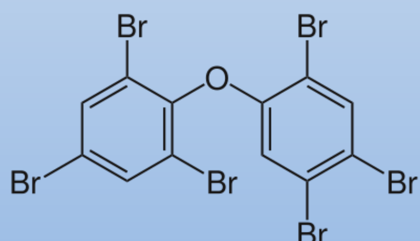
BDE-99
Pentabromodiphenyl ether



BDE-100
Pentabromodiphenyl ether

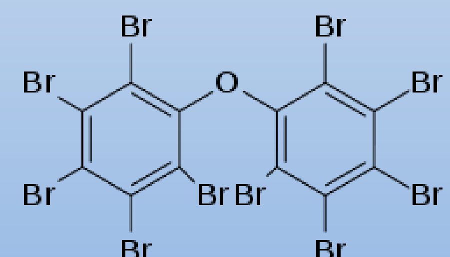


BDE-153
Hexabromodiphenyl ether



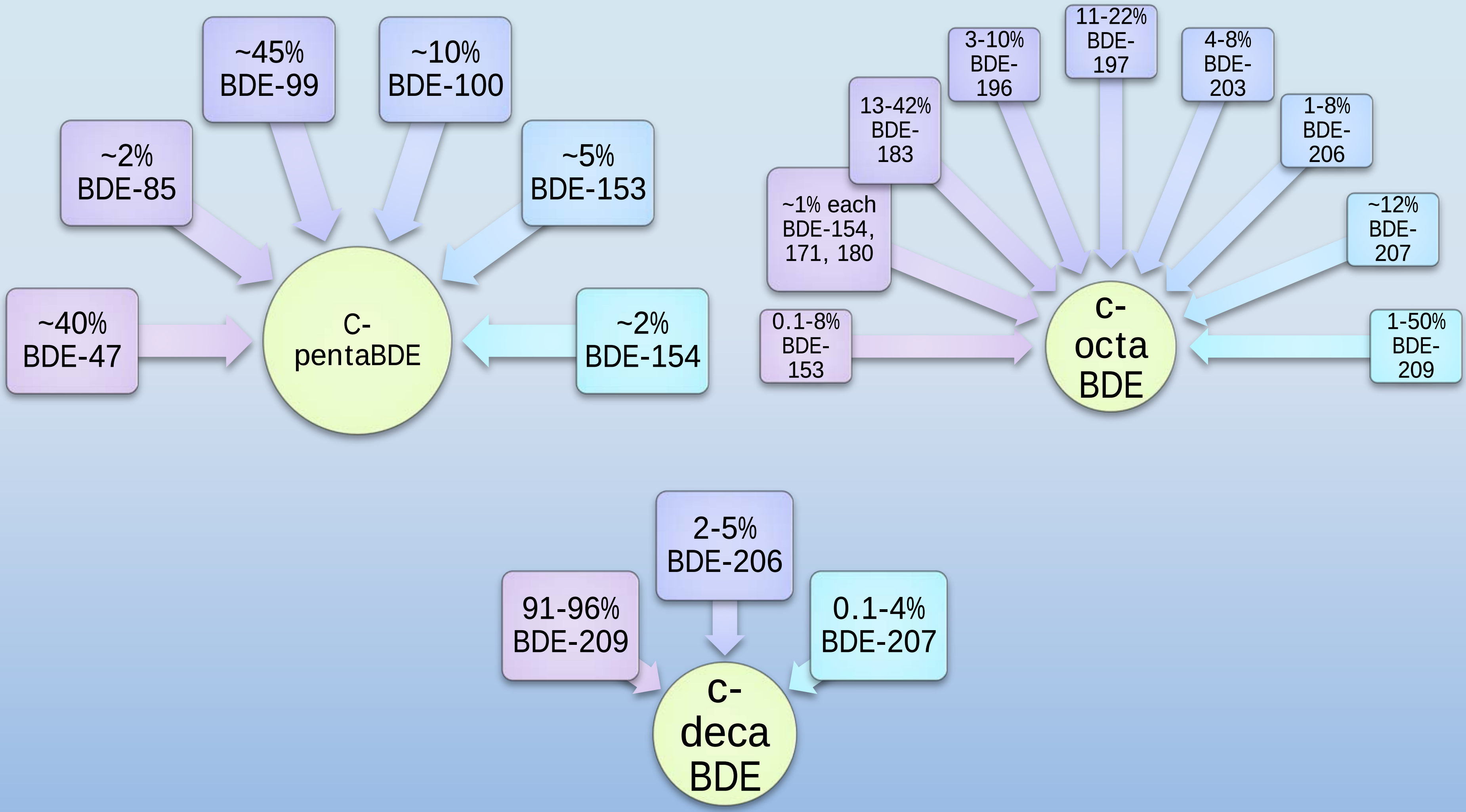
BDE-154
Hexabromodiphenyl ether

BDE-183
Heptabromodiphenyl ether



BDE-209
Decabromodiphenyl ether

PBDE naming – commercial mixtures

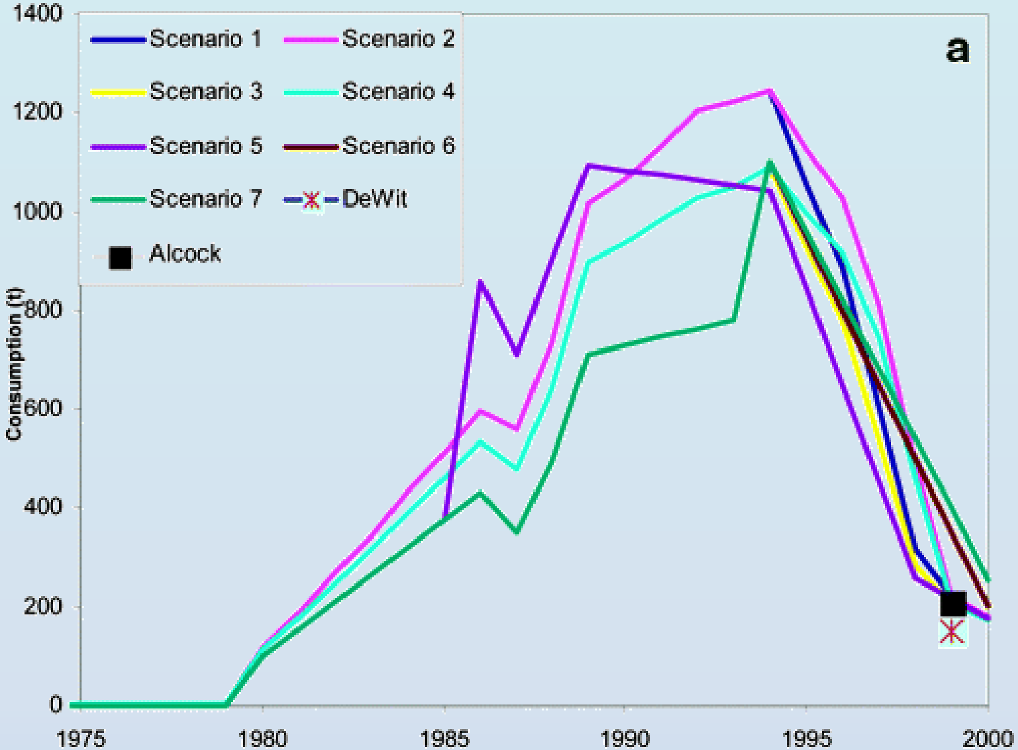


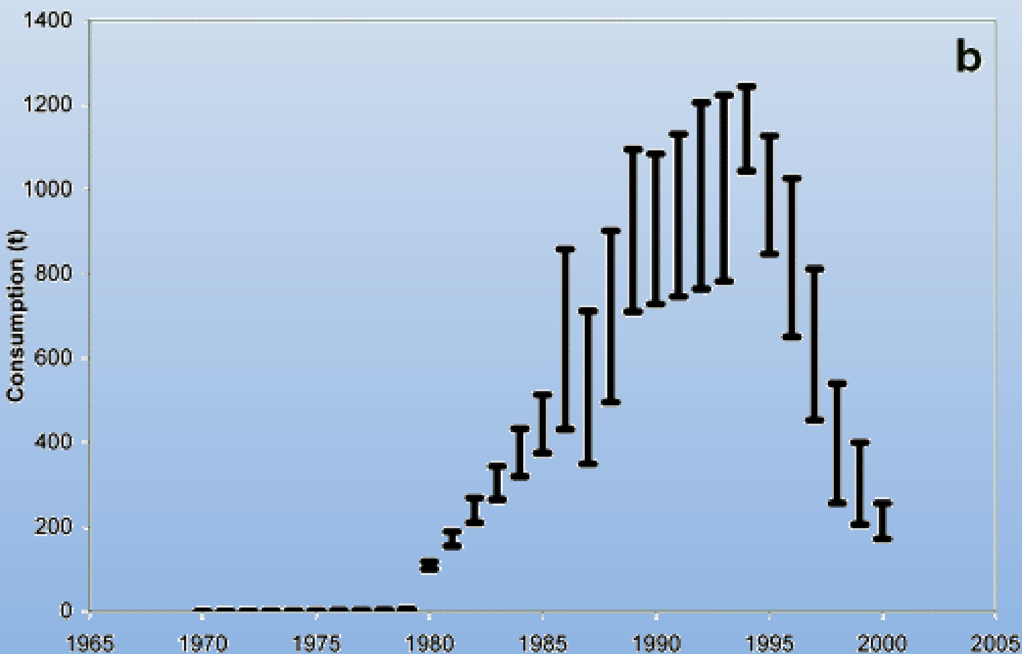
From La Guardia et al. 2006

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

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

Abbasi et al. 2015
Environ Sci Technol

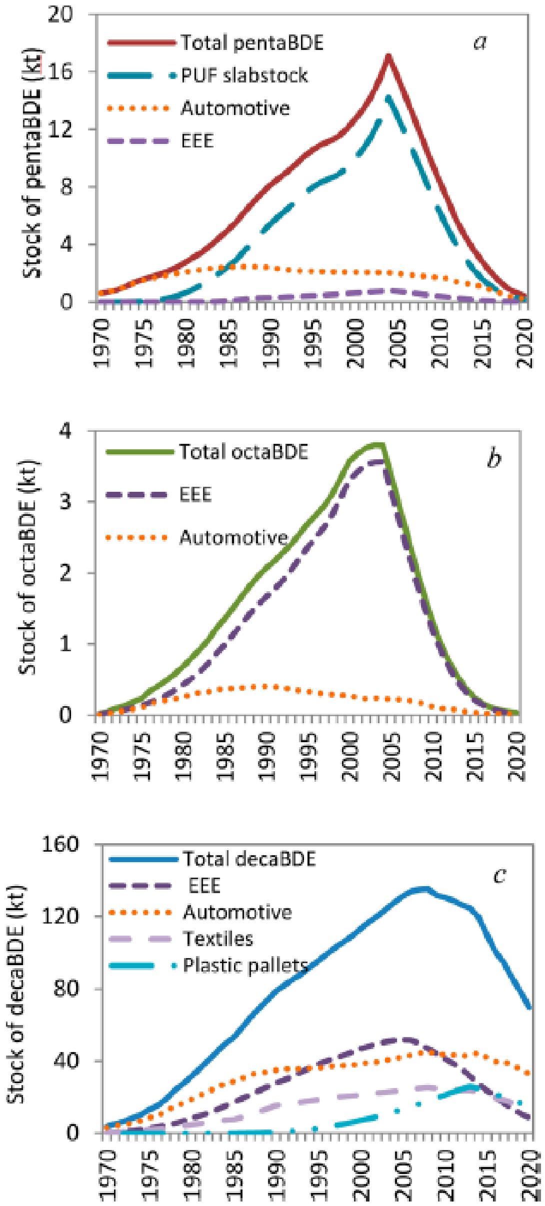


Figure 2. Stock of each PBDE commercial mixture in in-use products in the U.S. and Canada from 1970 to 2020, (a) pentaBDE in EEE, automotive vehicles, and PUF slabstock used in furniture, (b) octaBDE in automotive vehicles and EEE, and (c) decaBDE in plastic pallets, textiles, EEE, and automotive vehicles.

Global distributions of PCBs and PBDEs

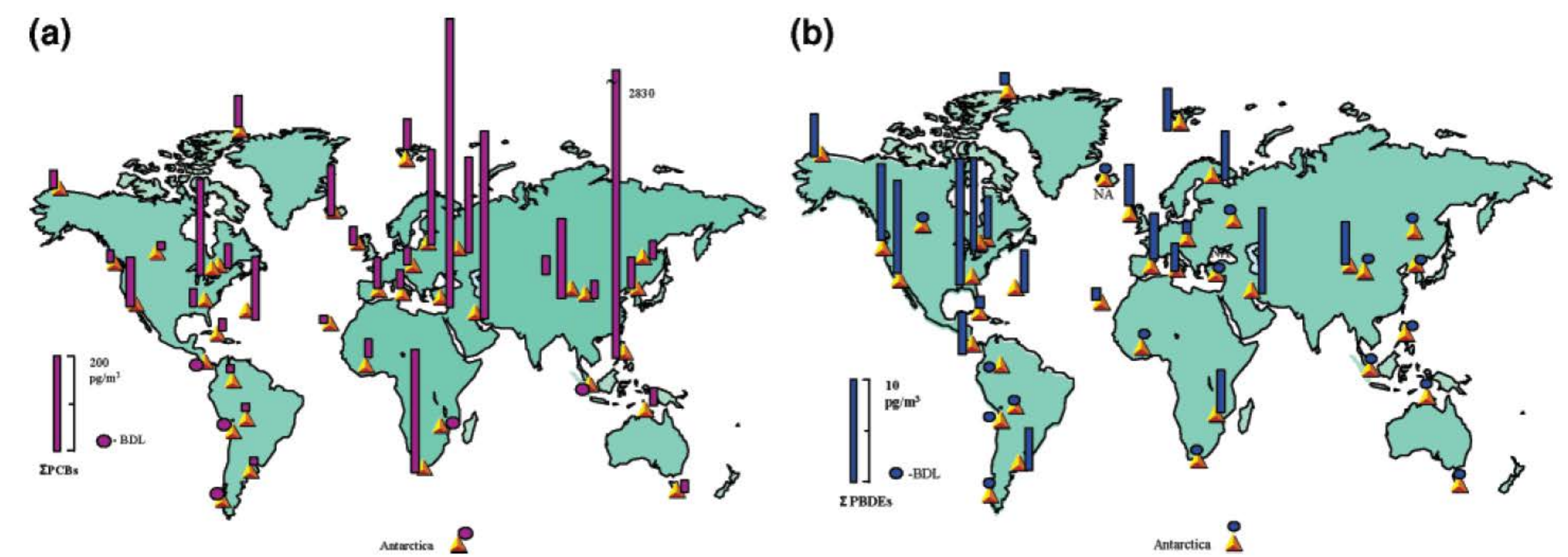
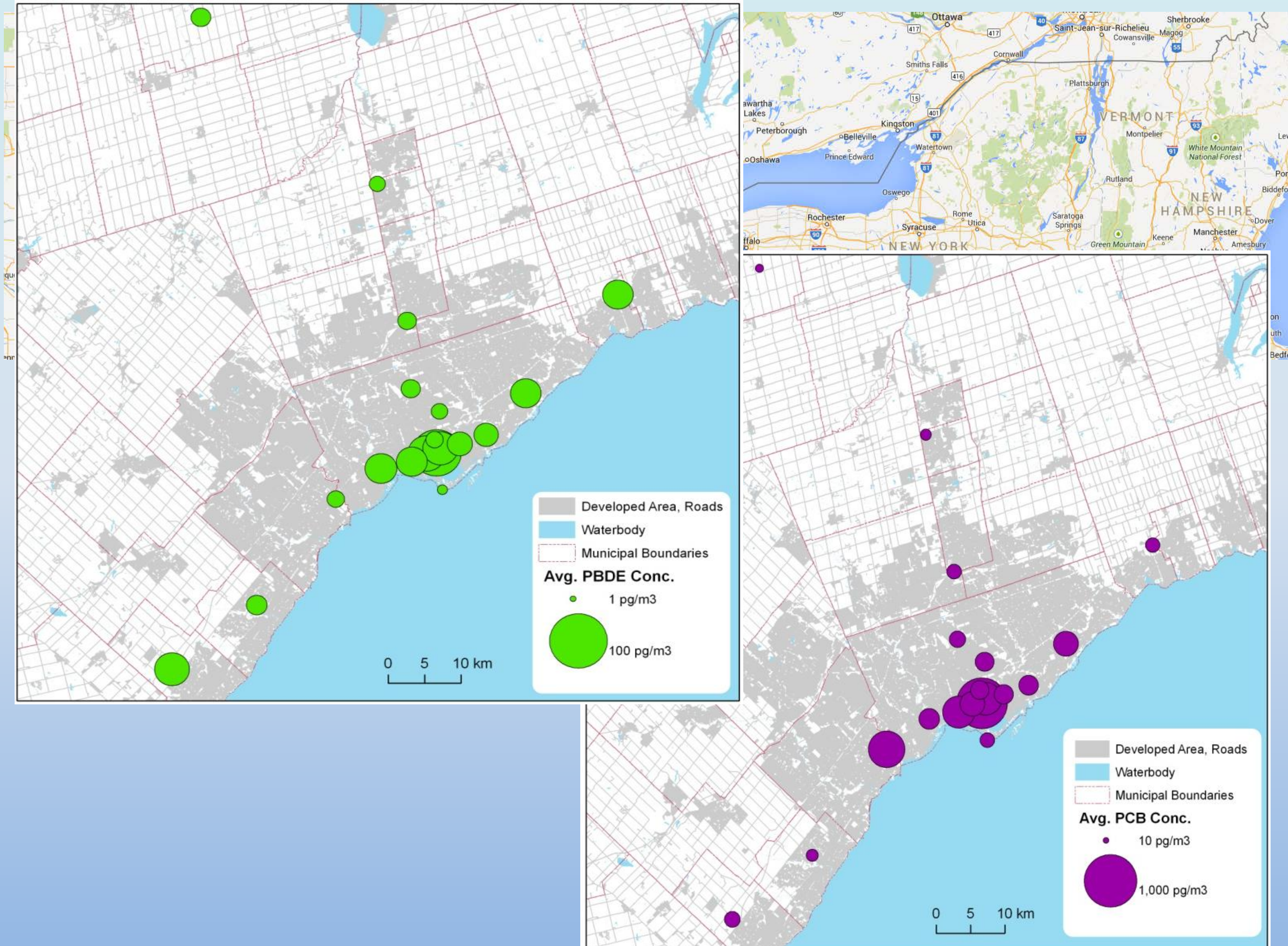


FIGURE 4. Air concentrations (pg/m^3) of (a) PCBs and (b) PBDEs between December 2004 and March 2005 at GAPS sites. See Table S1 for BDL values.

From Pozo et al. 2006


Developed Area, Roads
Waterbody
Municipal Boundaries
Avg. PBDE Conc.
1 pg/m3
100 pg/m3
0 5 10 km
Ottawa
Saint-Jean-sur-Richelieu
Cowansville
Sherbrooke
Magog
Cornwall
Smiths Falls
Plattsburgh
Kingston
Peterborough
Belleville
Watertown
VERMONT
Montpelier
White Mountain National Forest
Oshawa
Prince Edward
Oswego
Rutland
NEW HAMPSHIRE
Rochester
Syracuse
Rome
Utica
Saratoga Springs
Keene
Manchester
Dover
Biddeford
Amesbury
Green Mountain
NEW YORK
Developed Area, Roads
Waterbody
Municipal Boundaries
Avg. PCB Conc.
10 pg/m3
1,000 pg/m3
0 5 10 km

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.

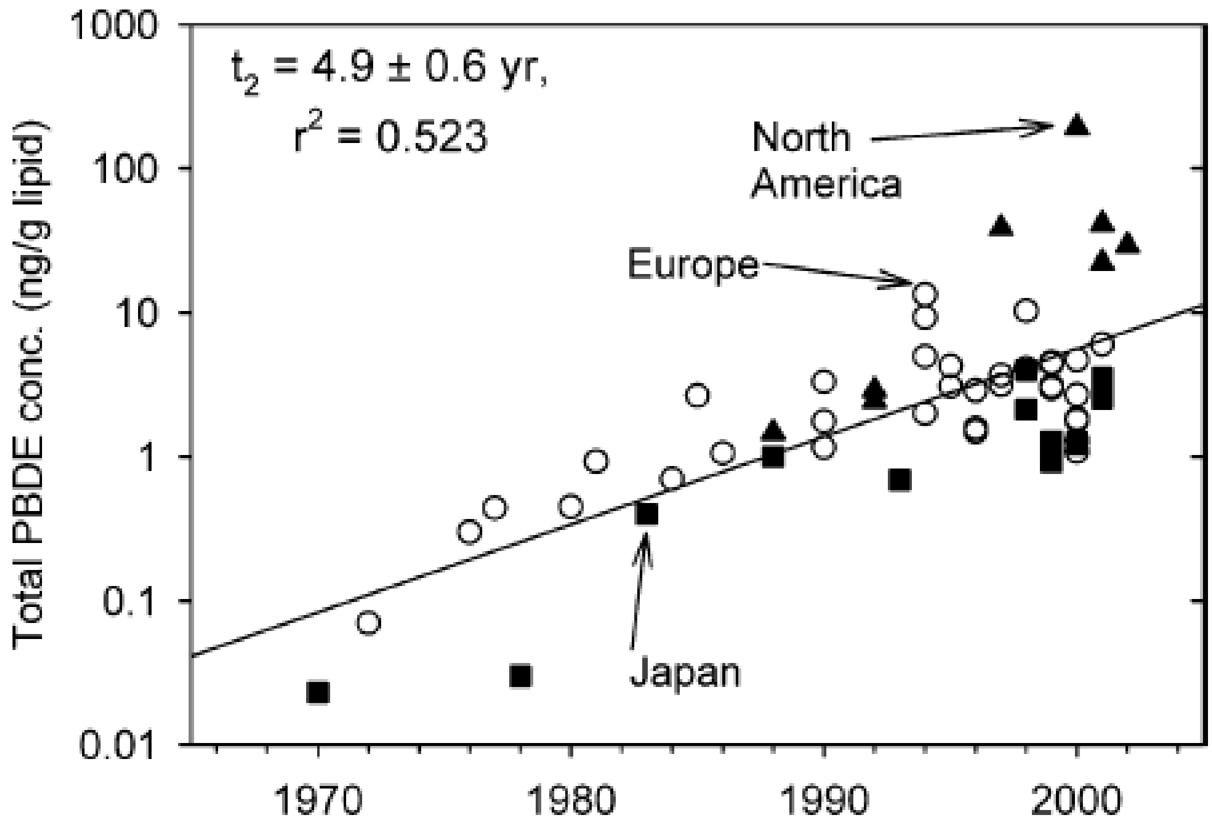
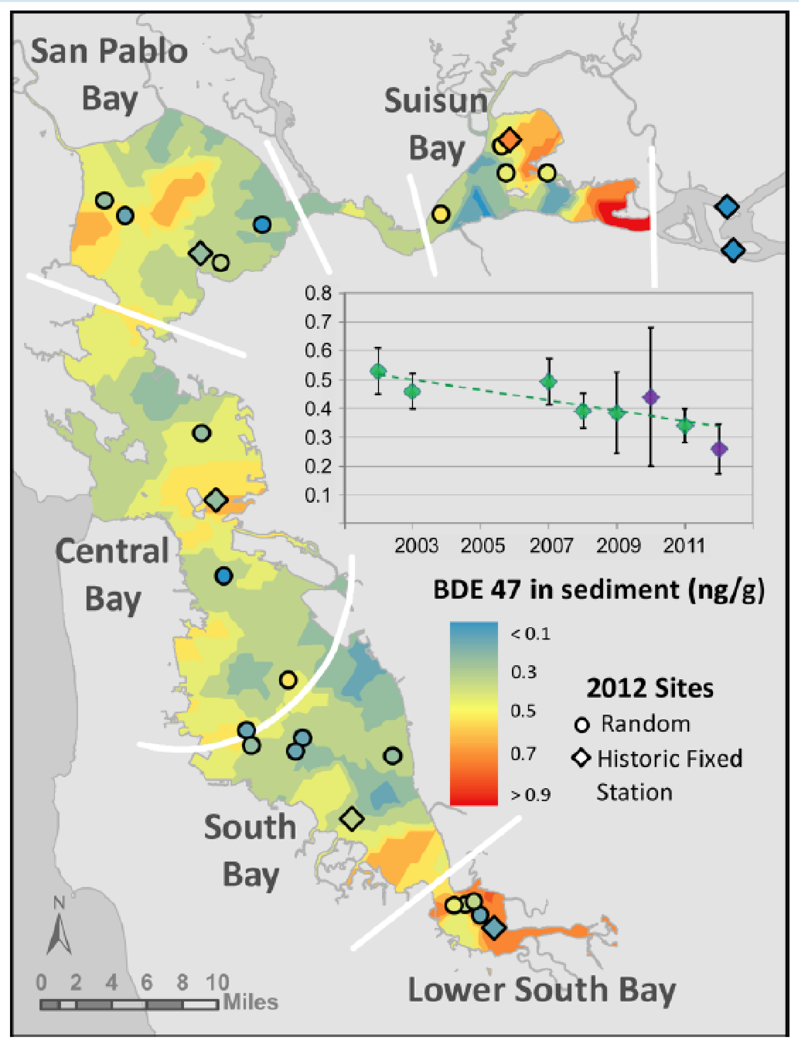


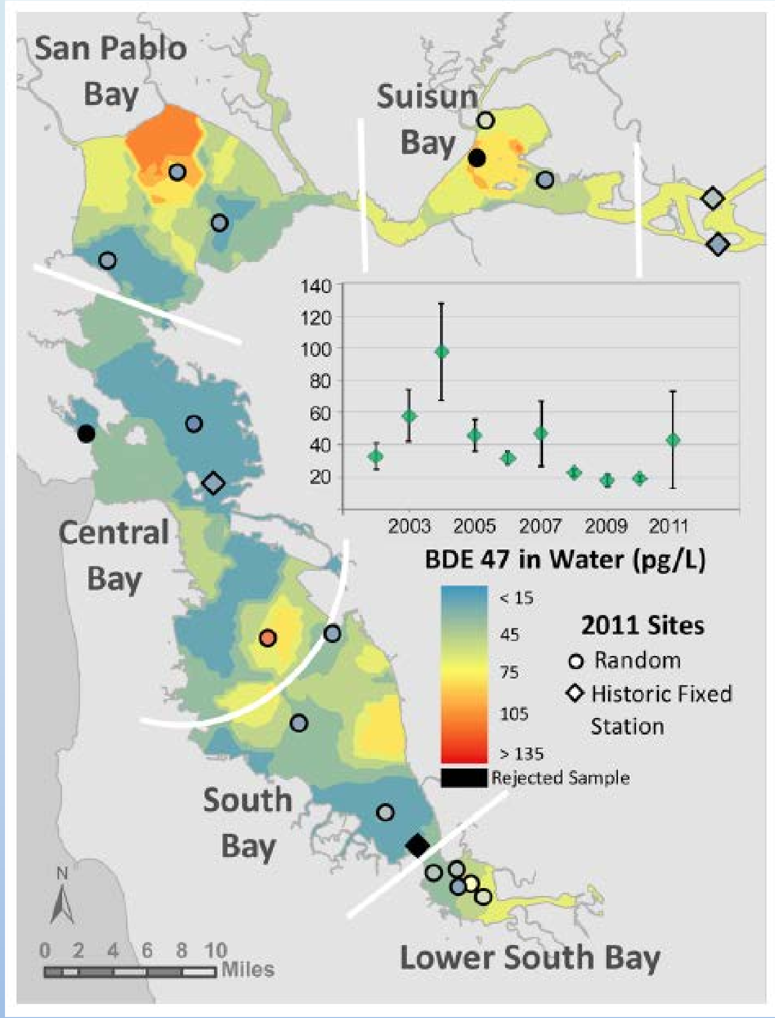
FIGURE 1. Total PBDE concentrations (∑PBDE) in human blood, milk, and tissue (in ng/g lipid) shown as a function of the year in which the samples were taken; see Table 2. The three symbol types indicate the location from which the samples were collected. The overall regression is shown.

Hites 2004 Environmental Science & Technology

Temporal trends of PBDEs

San Francisco Bay sediment and water:





Sutton et al. 2014, Environmental Science & Technology

Where are we in the temporal trend of PBDE exposure?

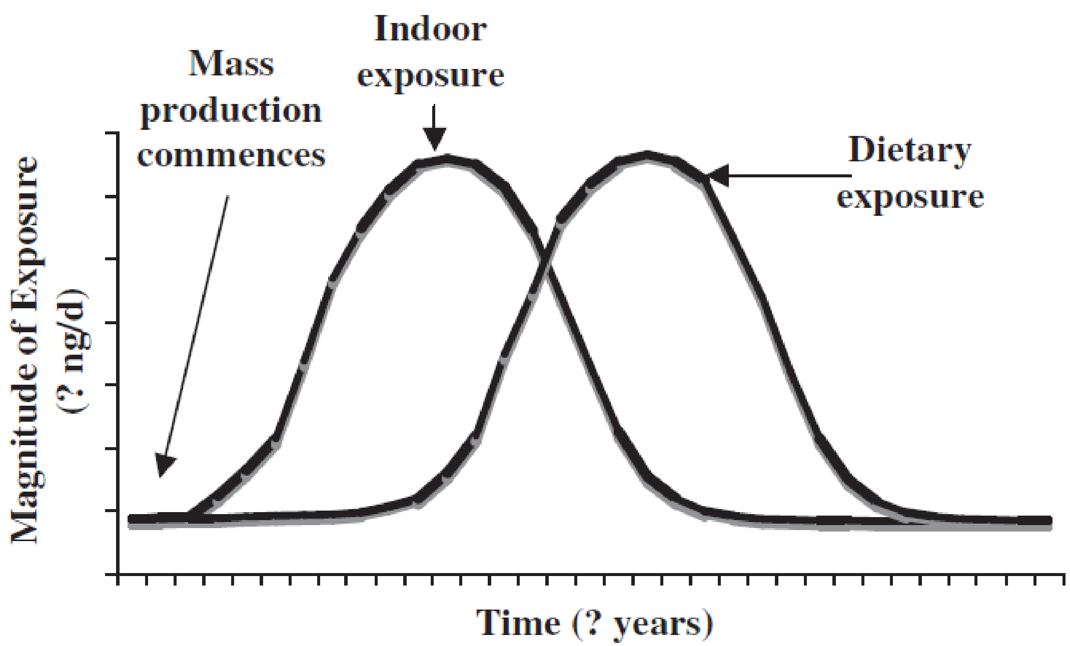
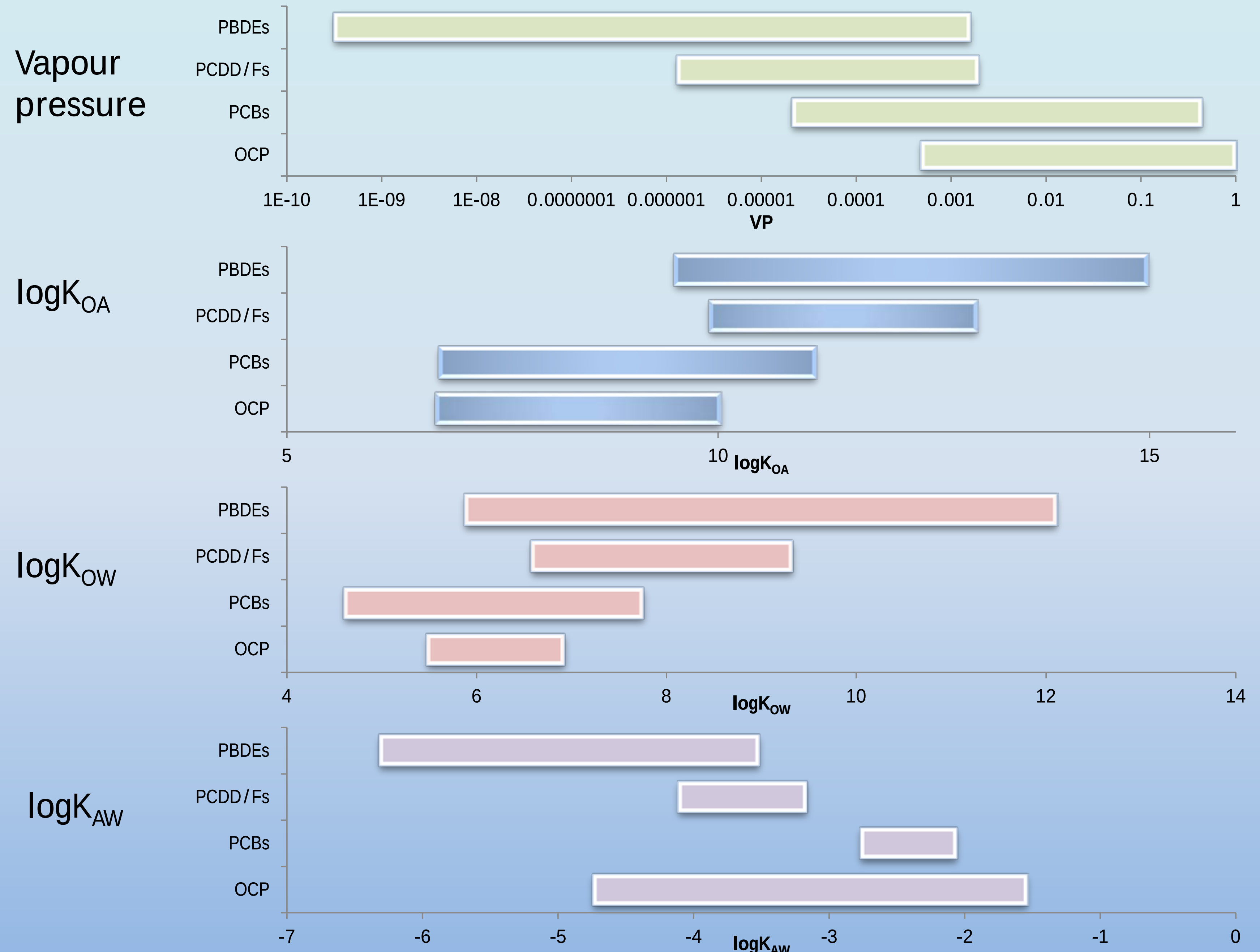


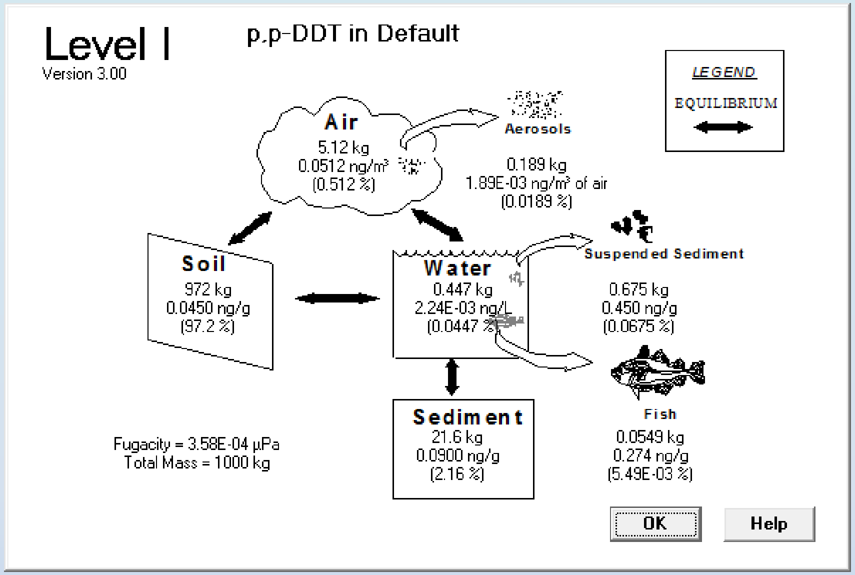
Fig. 1. Hypothetical time course in the relative magnitude of human exposure to PCBs and PBDEs due to (a) indoor exposure, and (b) dietary exposure. Note that the exact and relative magnitude of exposures and time frame of trends are illustrative.

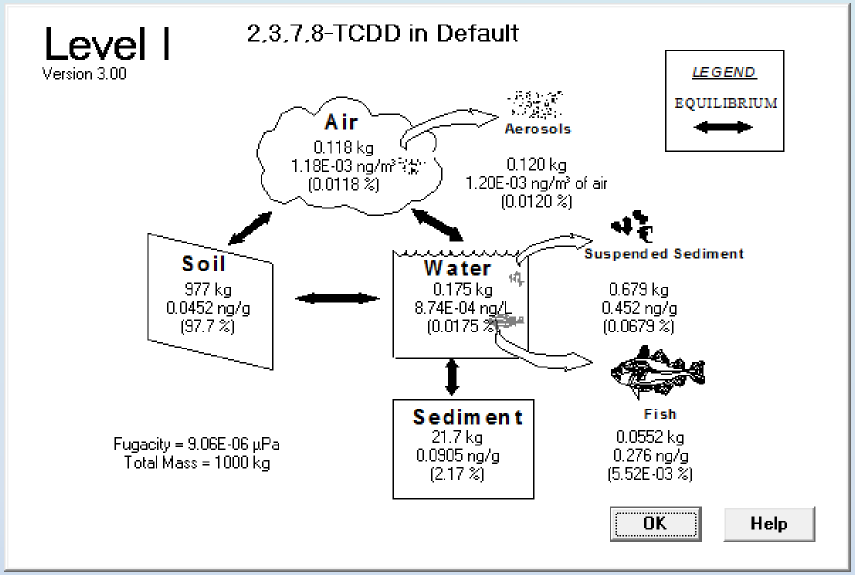
Harrad and Diamond, 2006

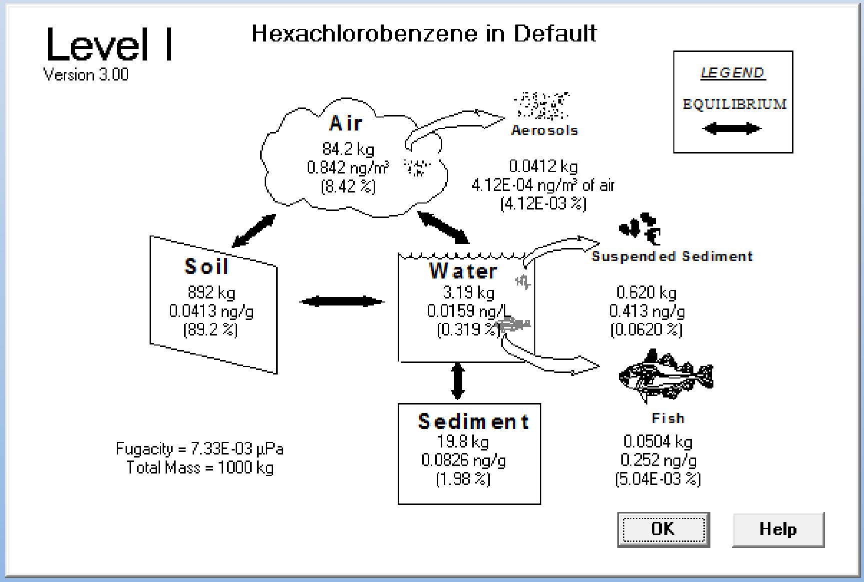


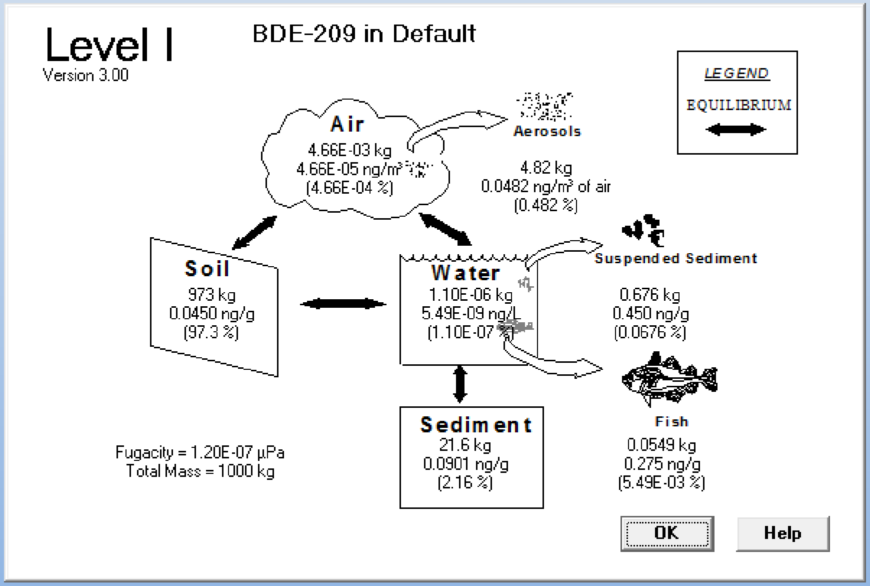
Vapour pressure
PBDEs
PCDD/Fs
PCBs
OCP
1E-10
1E-09
1E-08
0.0000001
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
VP
logK$_{OA}$
PBDEs
PCDD/Fs
PCBs
OCP
5
10
15
logK$_{OA}$
logK$_{OW}$
PBDEs
PCDD/Fs
PCBs
OCP
4
6
8
10
12
14
logK$_{OW}$
logK$_{AW}$
PBDEs
PCDD/Fs
PCBs
OCP
-7
-6
-5
-4
-3
-2
-1
0
logK$_{AW}$

Using phys-chem props, interpret how a different chemical would behave relative to DDT









NEXT WEEK:

"EMERGING" COMPOUNDS -

OCPs, PCBs, PCDD/Fs and PBDEs are now all regulated – lots of compounds are not. How do we identify which compounds we should be concerned about? What are those compounds? Where do we find them? What levels are they at in the environment? What about human exposure?