Primary Sources of Selected POPs

Regional and Global Scale Inventories

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Outline

- ✓ Motivation

  Why do we need emission inventories?

- ✓ Current status, selected POPs in general

  What data are available at regional and global scale?

- ✓ Industrial chemicals

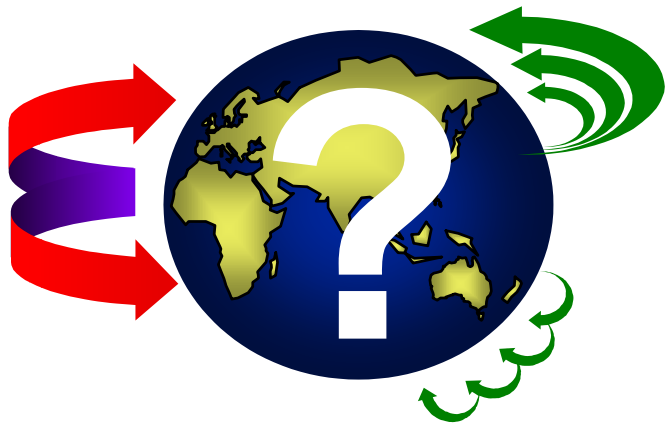
  Can we learn anything from PCBs that may be valid for other industrial chemicals?

- ✓ Outlook

  Some general issues concerning regional and global sources and emissions of POPs

Why do we need emission data?

- ✓ Source-receptor relationships
- ✓ Documentation between states
- ✓ Emission reduction strategies



Wania and Mackay, 1996

If we want to control POPs, knowledge about the sources is essential!

Current status

From the literature...

”*Surprisingly little is known about the amounts of POPs produced and discharged globally.*”

Wania and Mackay, 1996

”*Emission inventories for POPs are restricted to relatively few compounds, are generally uncertain and lack spatial and temporal resolution.*”

UN-ECE, 1994; Vallack et al. 1998

”*Much research remains to be done in developing and refining our understanding and quantification of POP sources.*”

Jones and de Voogt, 1999

Simplified source classification

Controllable PRIMARY sources (anthropogenic)

Accidentally formed (PCDD/Fs, PAHs)

PCBs

Deliberately produced

Industrial (PCBs, PBDEs..)

Pesticides (HCHs, DDT.....)

Other

Miscellaneous (HCB)

Non-Controllable

Secondary re-emissions

"True" natural

Methodolgies used to estimate sources and emissions of POPs in the literature have been different for various key source categories

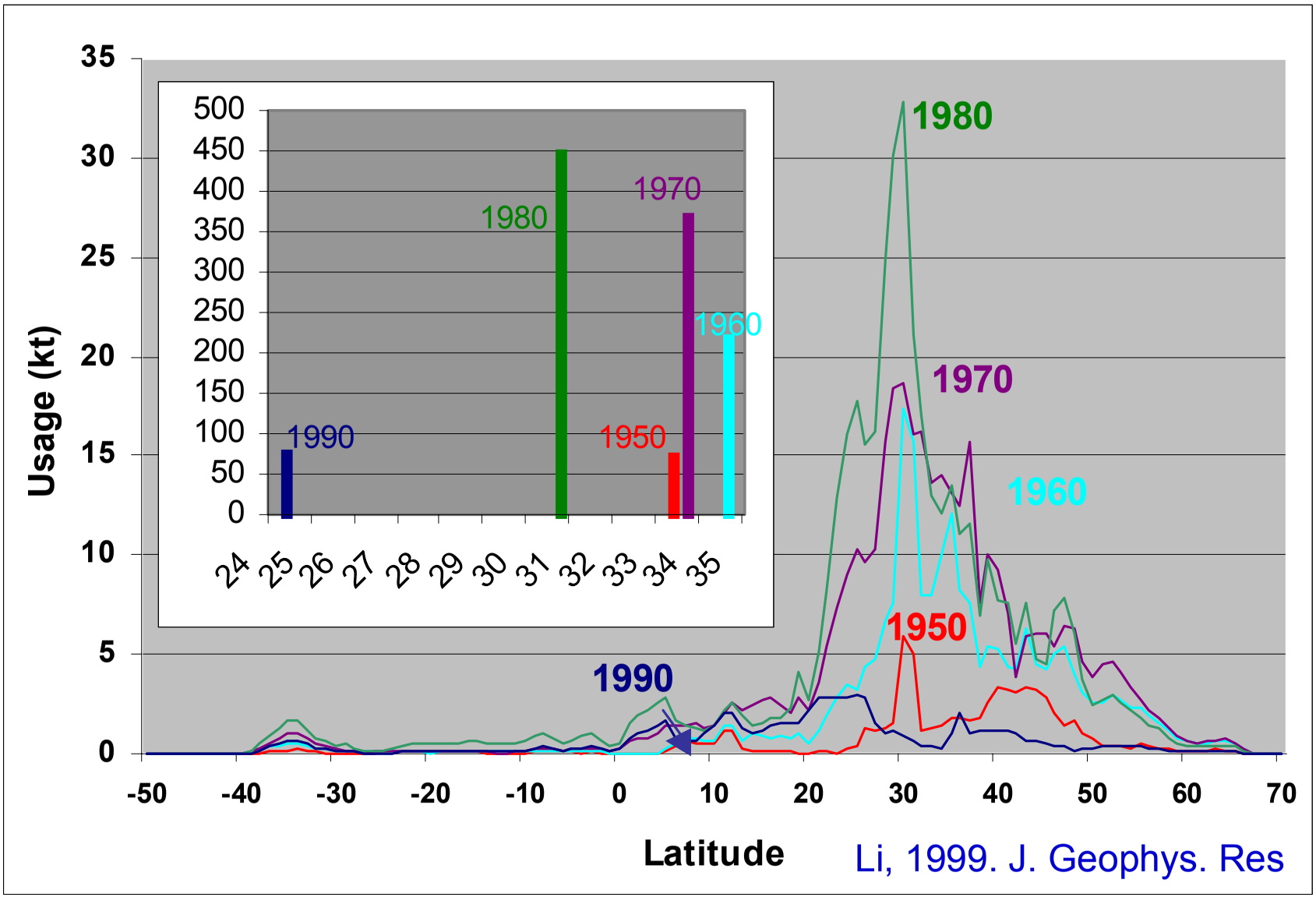
Overview – *selected* inventories

Chemical							Mode of release	Spatial		Temporal Coverage	Reference
DDT	HCB	HCHs	PAHs	PCBs	PCDD/Fs	Other		Coverage	Distr.		
	■						A	G	-	~1995	Bailey, 2001
	■	■	■	■	■	■	A	E	C/G	1990	Berdowski et al. 1997
				■			A	G	C	1930-2000	Breivik et al. 2002
					■		L,W	E	C	~1994	Buckley-Golder et al. 1999
■	■	■	■	■	■	■	A	E/U	C	1980-2000	EMEP (Vestreng&Klein,2002)
		■					A	G	G	1948-2000	Li et al 2000; Li, 2002
						T	A	U	G	1947-2000	Li et al 2001
■							A	G/U	G	1945-2000	Li (in prep)
■	■	■	■		■		A	E	C/G	1970-1995	Pacyna et al (in press)
					■	■	A	U			US-EPA (various)
					■		M	E	C	~1994	Quass and Fermann, 1997

A = Atmospheric, C = By country, E = Europe, G = Global *or* Grid, L = Land, M = Multimedia, T = Total *or* Toxaphene, U = USA, W = Water

Pesticides (Li and coworkers)

Technical HCH vs latitude

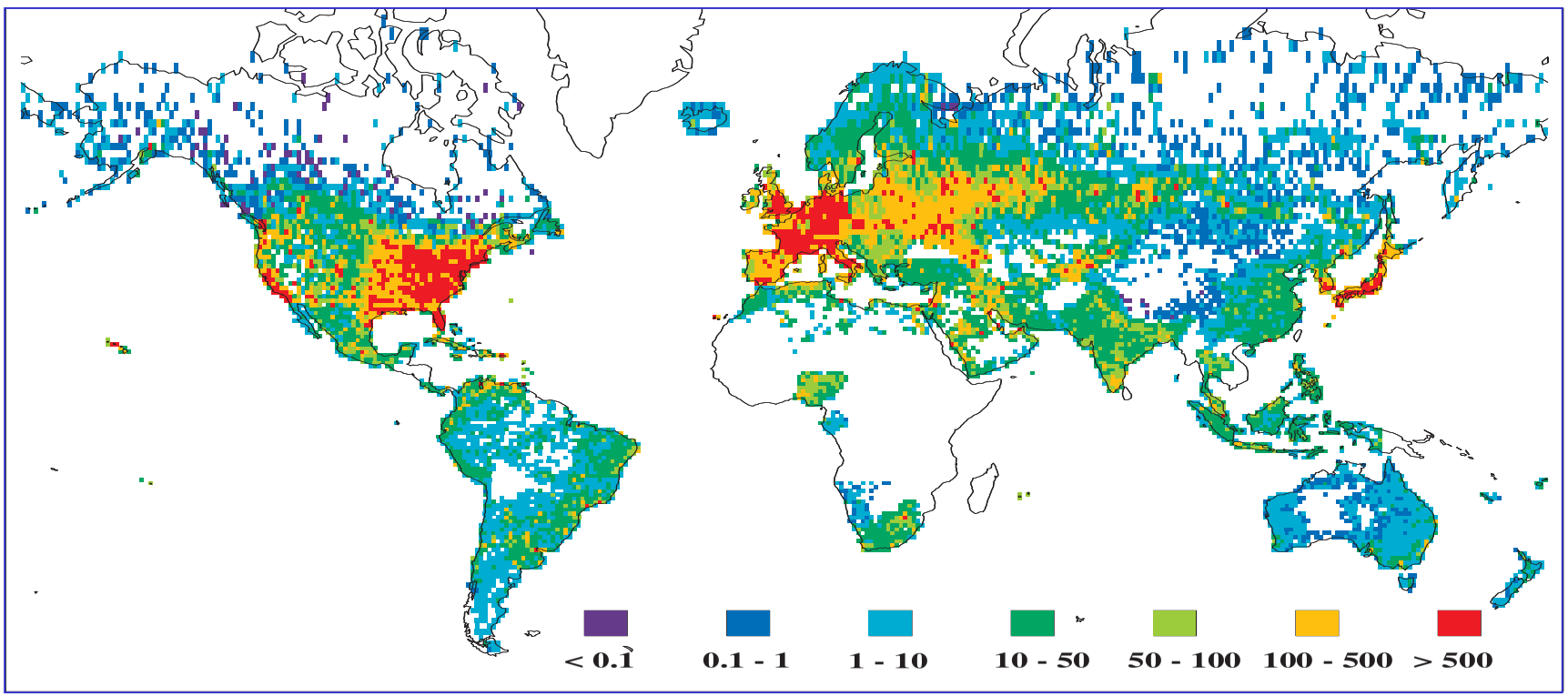


Li, 1999. J. Geophys. Res

Towards a global historical emission inventory for selected PCBs:
A mass balance approach

3-step approach:

Production
↓
Consumption
↓
Emission



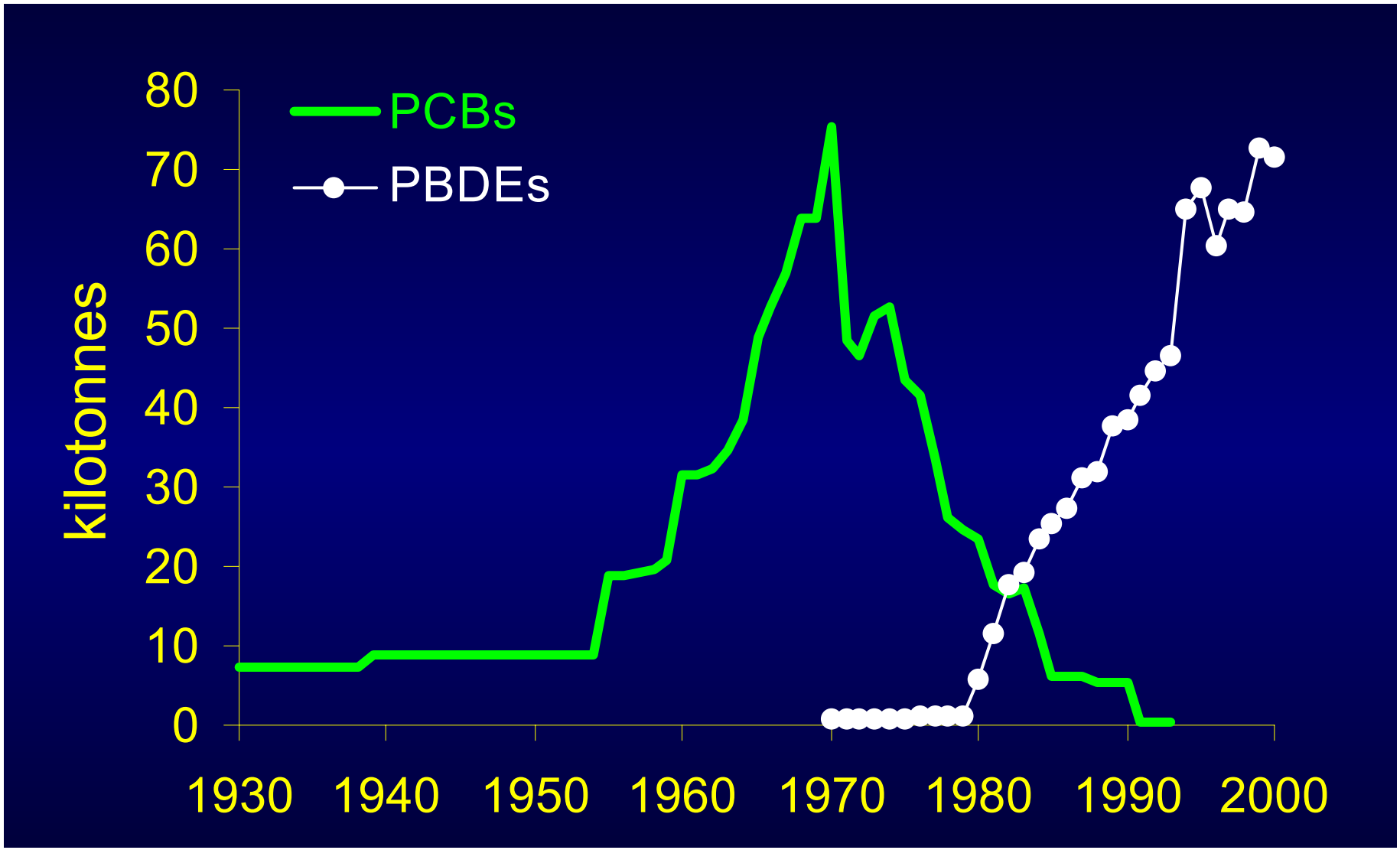
Industrial chemicals: PCBs (vs. PBDEs)

Similarities:

I. High-volume production
II. Produced as chemical mixtures
III. Diverse usage patterns
IV. Processes affecting their emissions?

PCBs (vs. PBDEs)

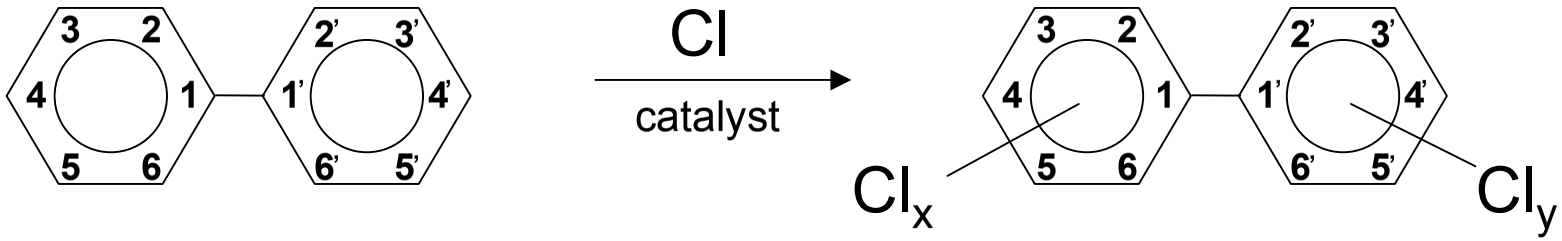
I. Global high volume production



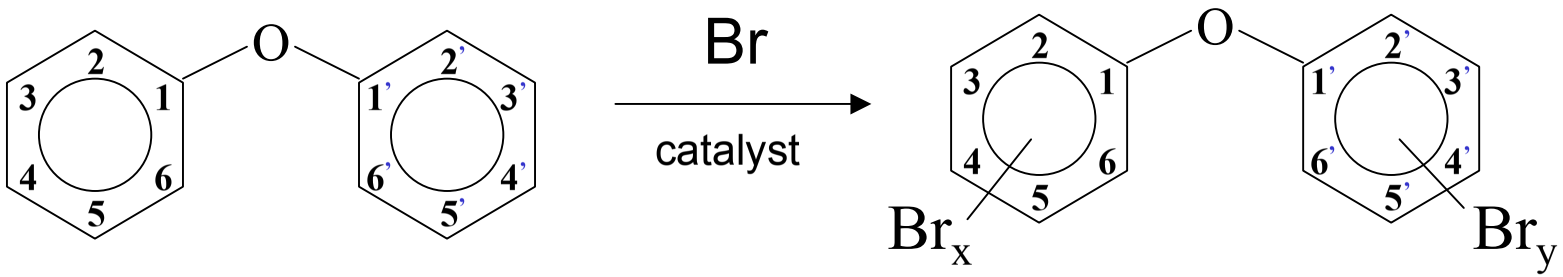
PBDEs: Anna Palm (*Pers. Comm.*) PCBs: Breivik et al (2002)

PCBs (vs. PBDEs)

II. Produced as chemical mixtures



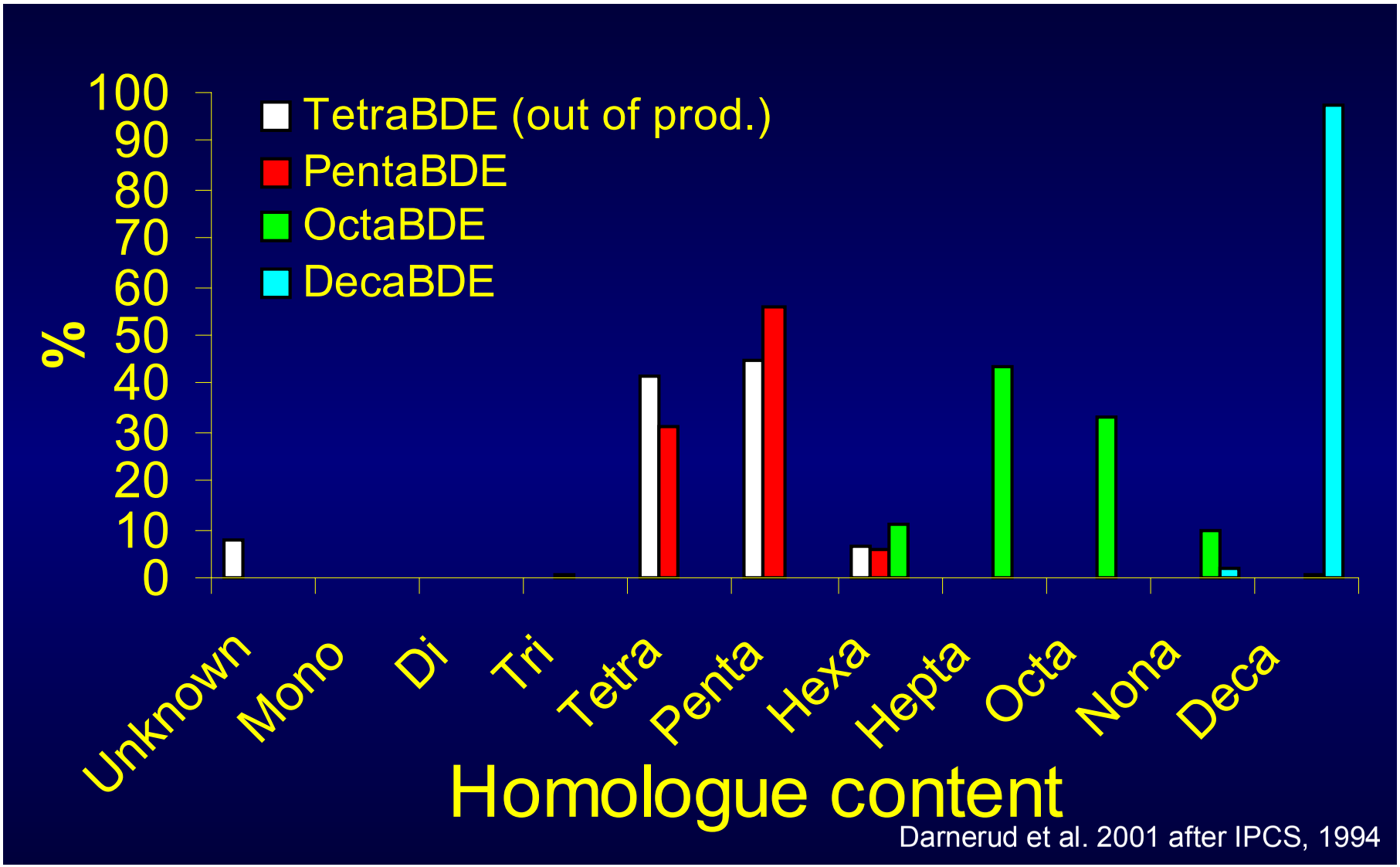
PCBs: Large variety of tehcnical mixtures, 21- 68 % Cl (w/w)



PBDEs: More specific than the PCBs; substitution is likely to occur first in the 4-positions and next in the 2-positions

PCBs (vs. PBDEs)

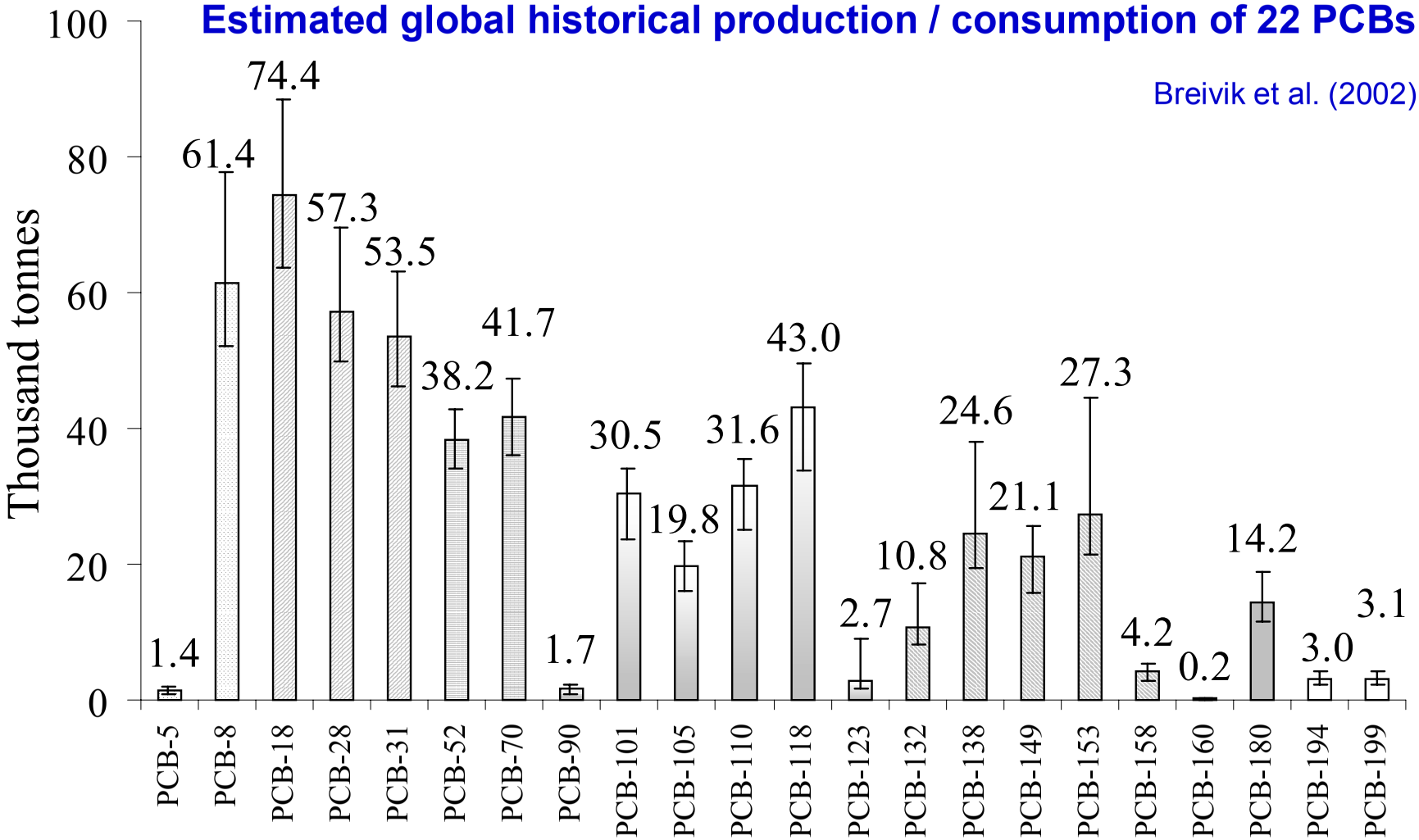
II. Produced as chemical mixtures



Darnerud et al. 2001 after IPCS, 1994

PCBs (vs. PBDEs)

II. Produced as chemical mixtures



PCBs (vs. PBDEs)

III. Diverse usage patterns

PCBs

✓Open usage (*paper, plasticiser,* [...])

✓Capacitors

✓Transformers

PBDEs

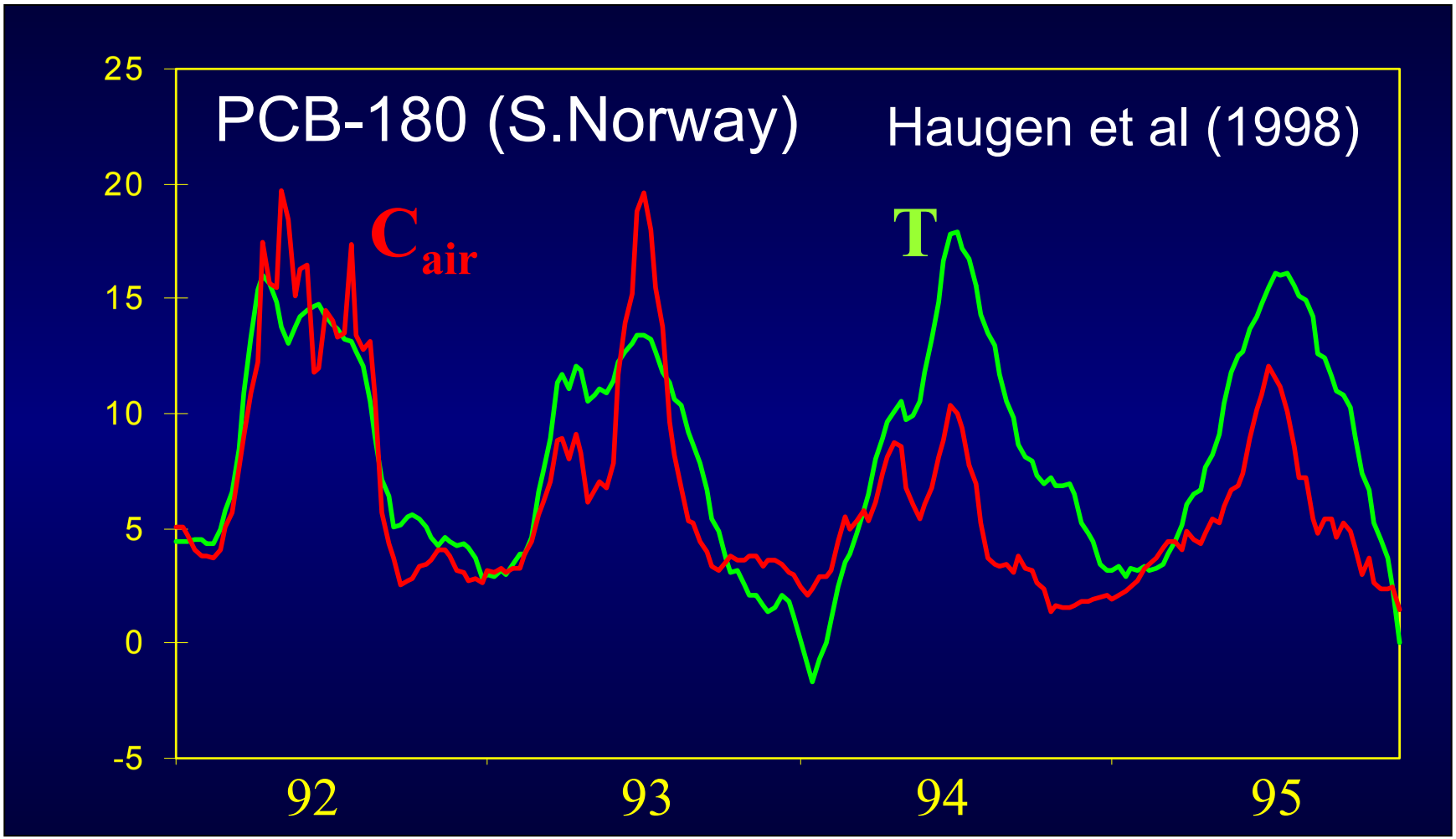
✓Plast materials

✓Textiles

The true emission pattern is anticipated to be equally diverse!

PCBs (vs. PBDEs)

IV. Temperature dependence



Temperature-driven cycles of deposition and evaporation

PCBs (vs. PBDEs)

IV. Temperature dependence (cont.)

✓Evaporation of technical mixtures of PCBs increased by more than an order-of-magnitude when temperature increased from 30 to 60 °C

(Haque et al. 1974, Hutzinger et al. 1974)

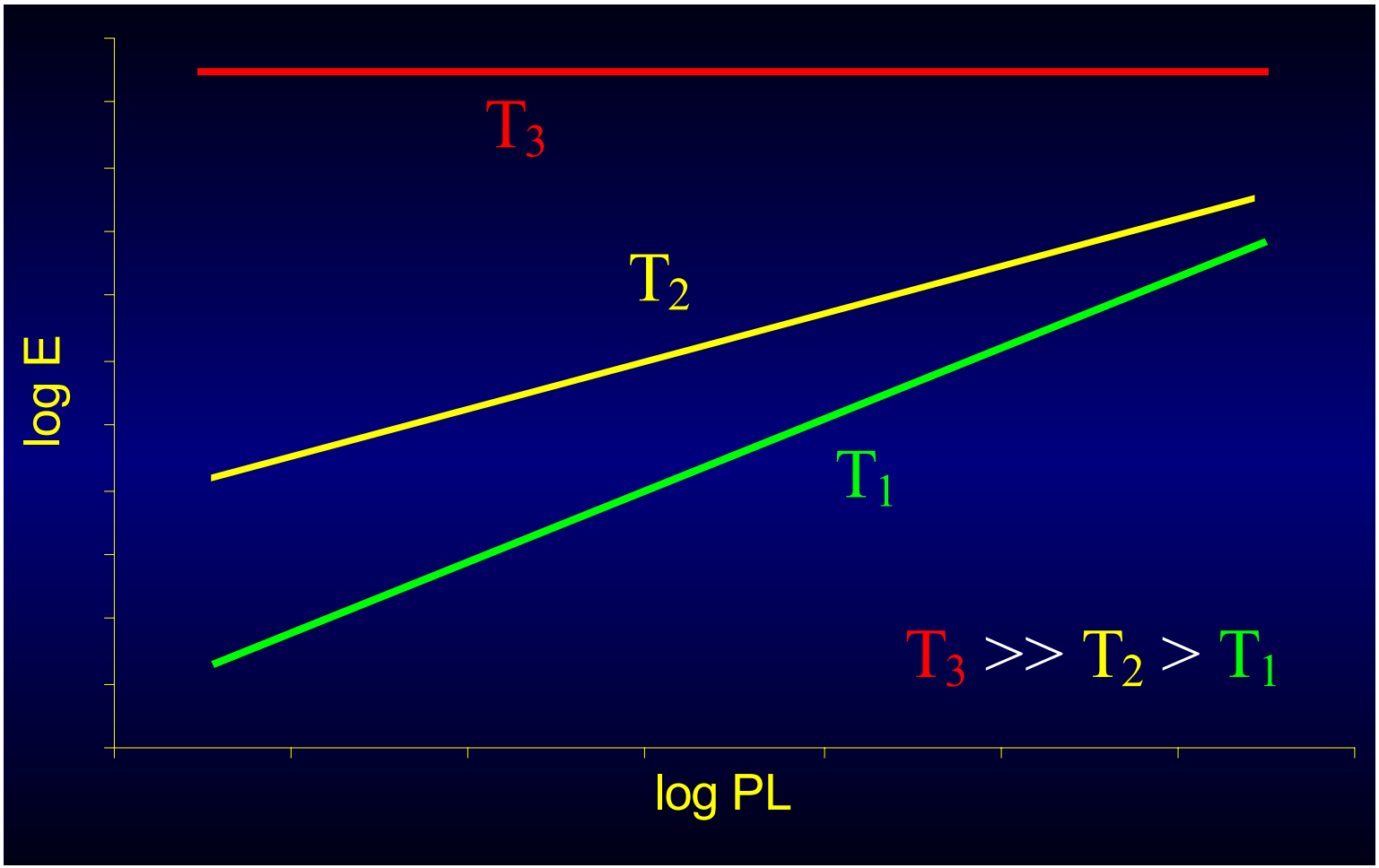
✓Volatilisation decreased by more than two orders of magnitude from Aroclor 1221 (mainly mono- and diCBs) to Aroclor 1260 (mainly hexa- and hepta-CBs) at 100 °C

(Hutzinger et al. 1974; Sawhney, 1986)

✓Considerable empirical support for a profound influence of temperature on atmospheric emission strength and emission congener patterns from primary sources of PCBs

PCBs (vs. PBDEs)

IV. Temperature dependence (cont.)



”Hypothetical” relationship between relative atmospheric emission strength due to evaporation, log E, and vapour pressure, log P_L

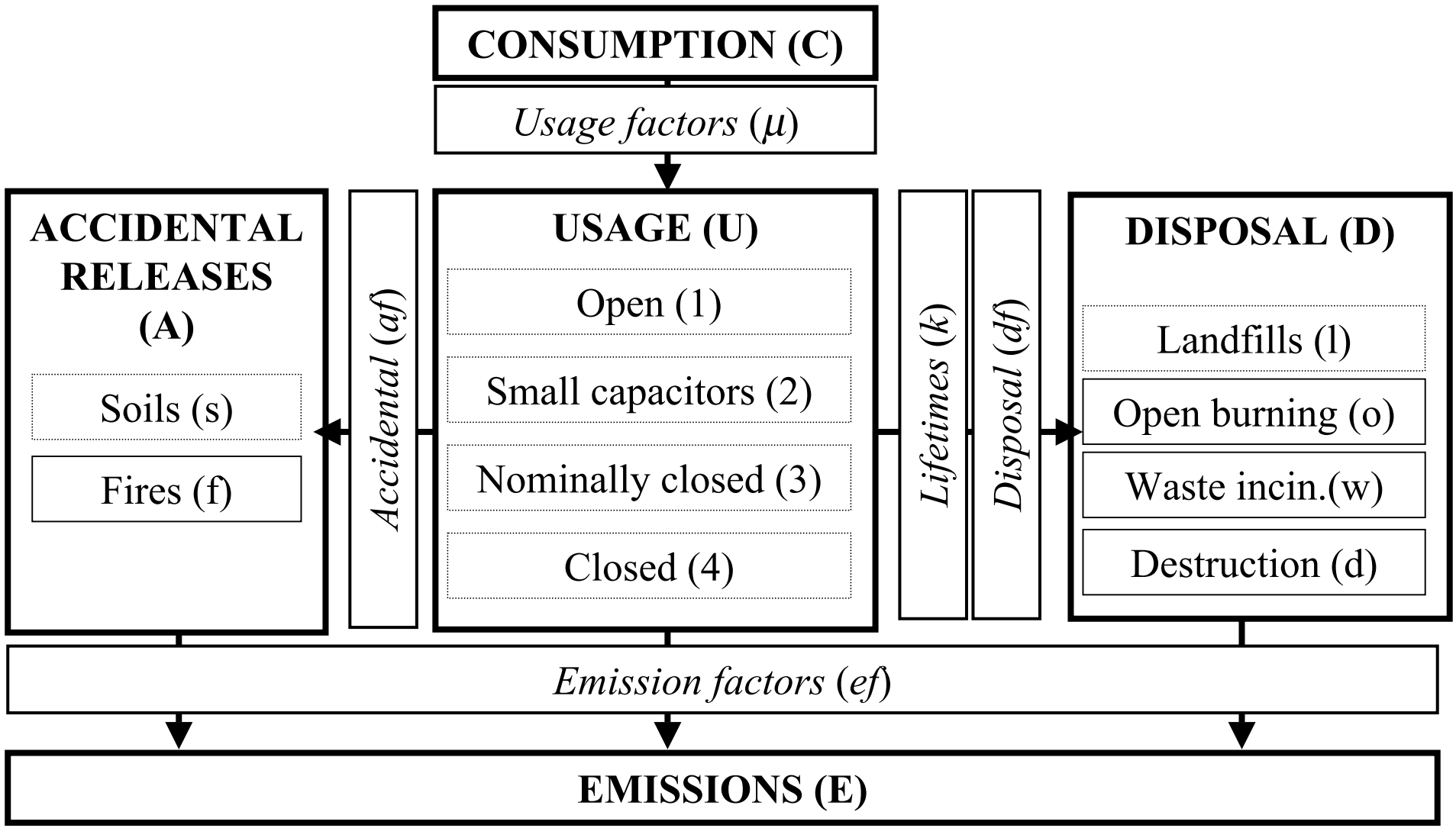
PCBs (vs. PBDEs)

IV. Temperature dependence (cont.)

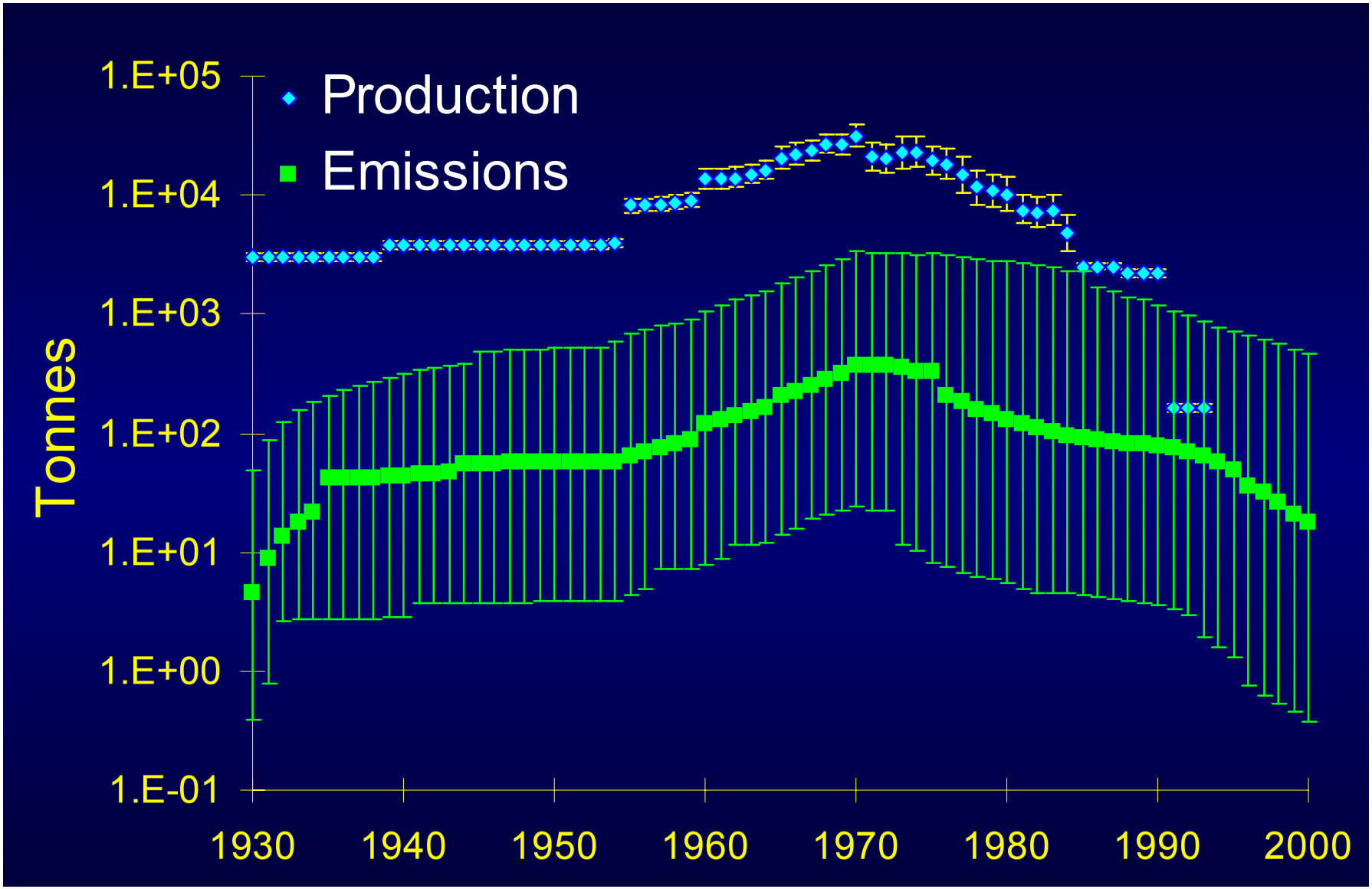
- ✓ May contribute to the interpretation of measured air concentrations:
  - *Air concentration fluctuations that correlate with temperature fluctuations do not necessarily indicate the importance of secondary (re-)emissions*
  - *Unusually high levels of heavy PCB congeners in an air sample <u>may</u> indicate the presence of a high temperature source*
- ✓ The suggested relationship could apply for other industrial chemicals as well (e.g. PBDEs, PBBs)
- ✓ Would further indicate that PCBs and related industrial waste are better stored in a cold place

PCBs (from consumption to emissions)

Development and application of a dynamic mass balance model

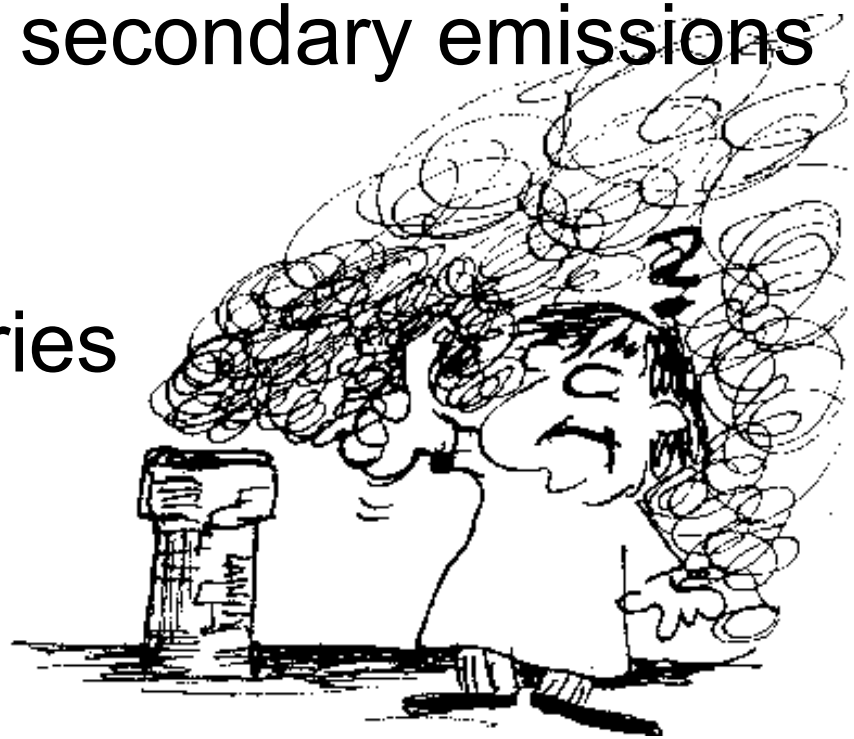


Global Production vs Emissions (ΣPCB_{22})



Outlook and discussion

- ✓ Empirical support / more data!
- ✓ Primary sources vs secondary emissions
- ✓ Natural emissions
- ✓ Multimedia inventories



Acknowledgements

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