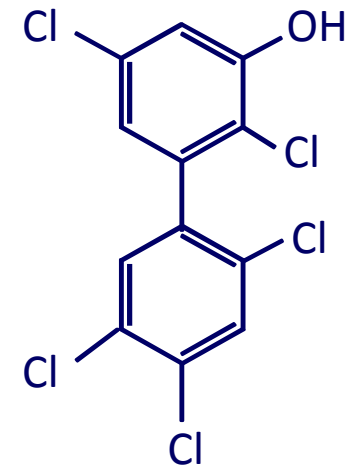


PCB methyl sulfones

## Hydroxylated PCBs





# ***Persistent organic pollutants: History, lessons learned and the way ahead***

**Åke Bergman**

Executive director of SWETOX\*

Professor emeritus at Stockholm University

Guest professor at Tongji University, Shanghai, China

\* Swetox a Swedish academic center for research, education and societal interactions on all aspects on chemicals, health and environment – CHEN

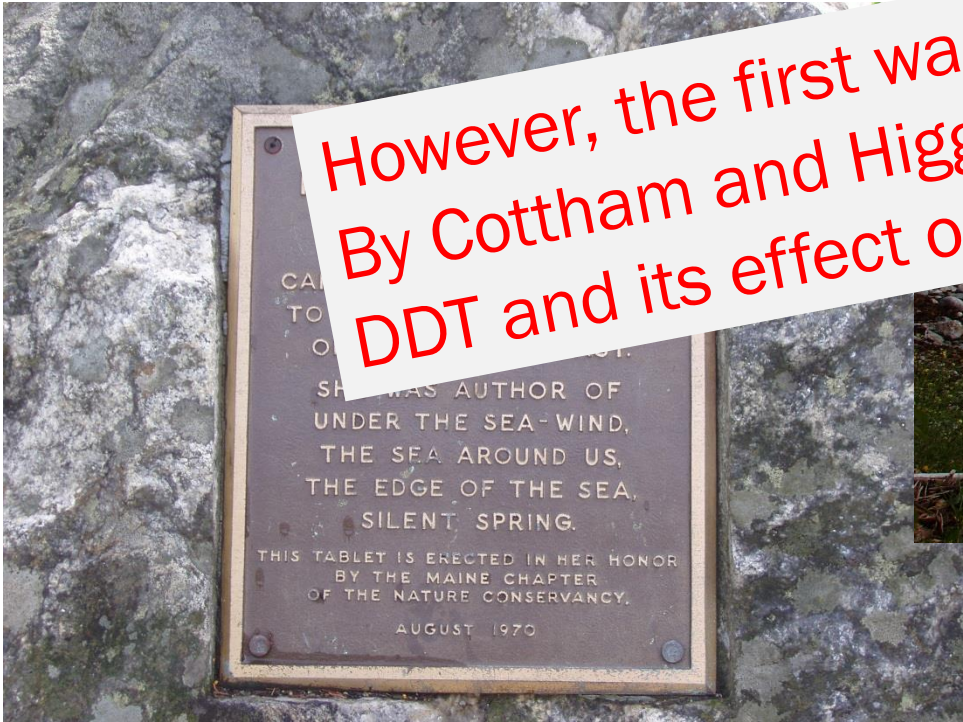


# Outline

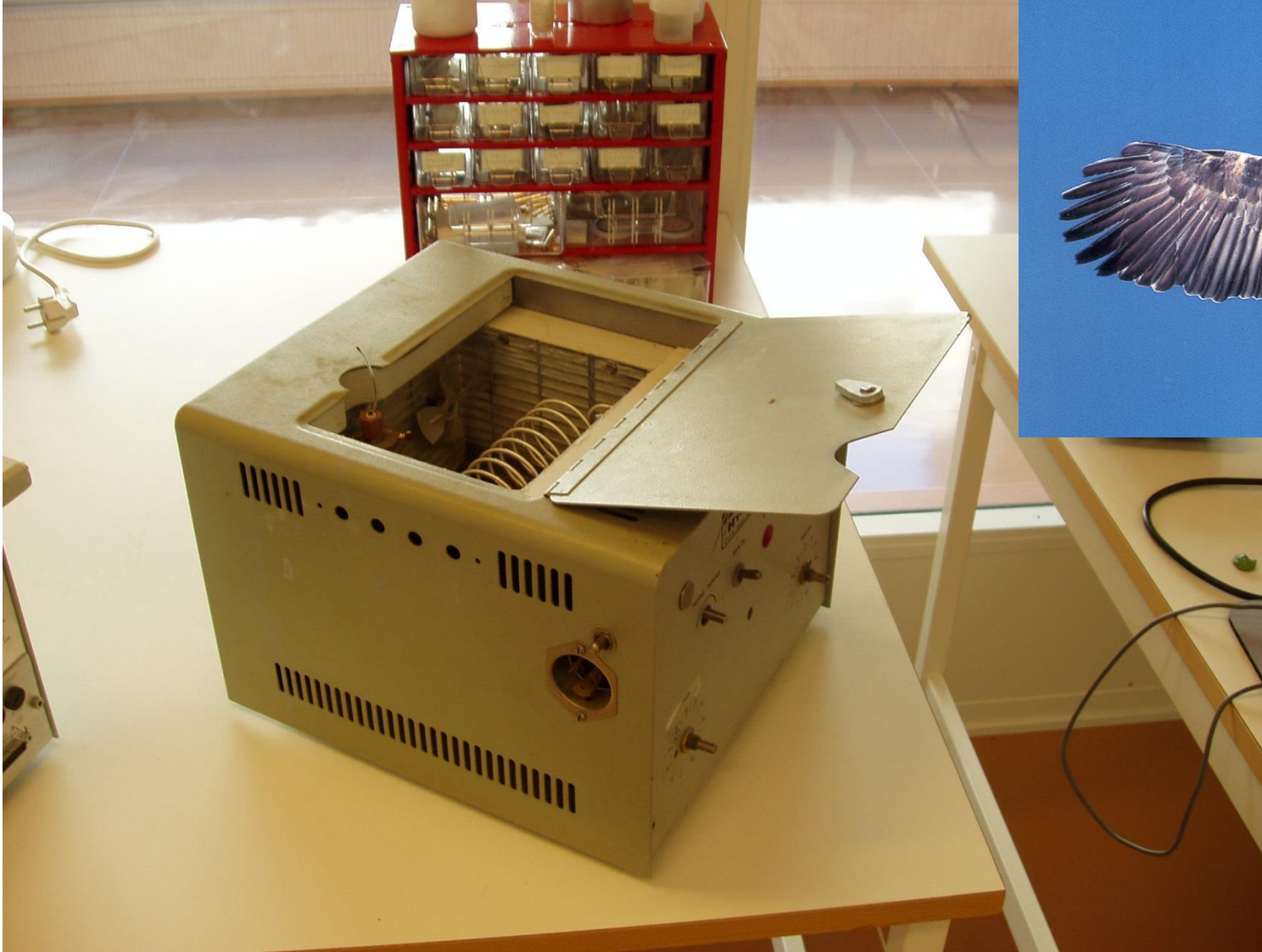
- A look in the rearview mirror
  - PCBs & DDTs, again
  - Methylsulfonyl-PCBs and methylsulfonyl-DDE
  - Hydroxy-PCBs and Halogenated phenols
- A complex world of anthropogenic chemicals
  - EDCs
  - Chlorinated paraffins (CPs)
  - Semi-persistent Chemicals
- The way forward

# Persistent Organic Pollutants – POPs in a historic perspective

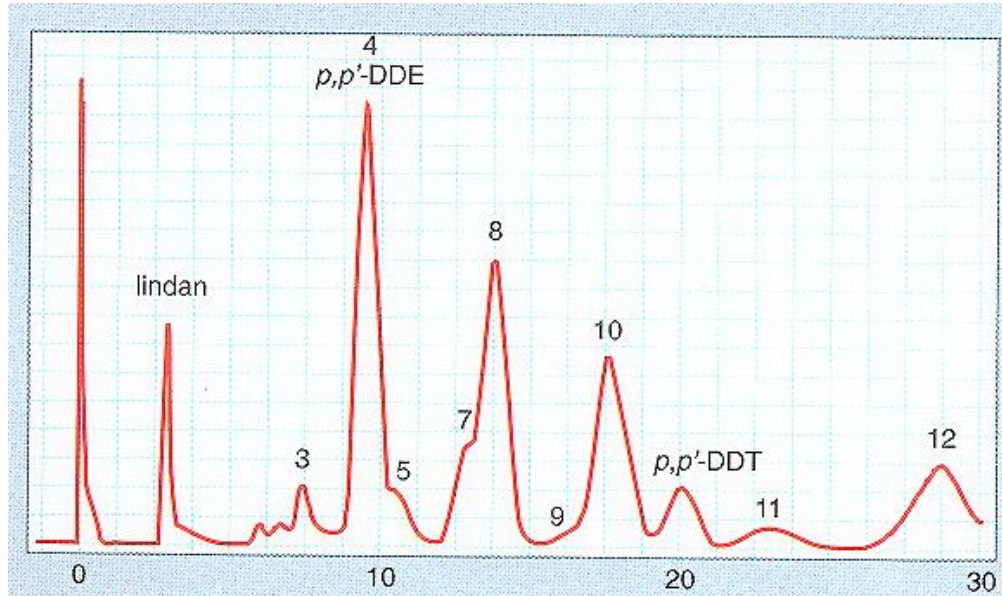
However, the first warning came 16 years earlier - 1946  
By Cottham and Higgings (J. Econ. Entomol. Vol. 39, p 44-52)  
DDT and its effect on fish and wildlife



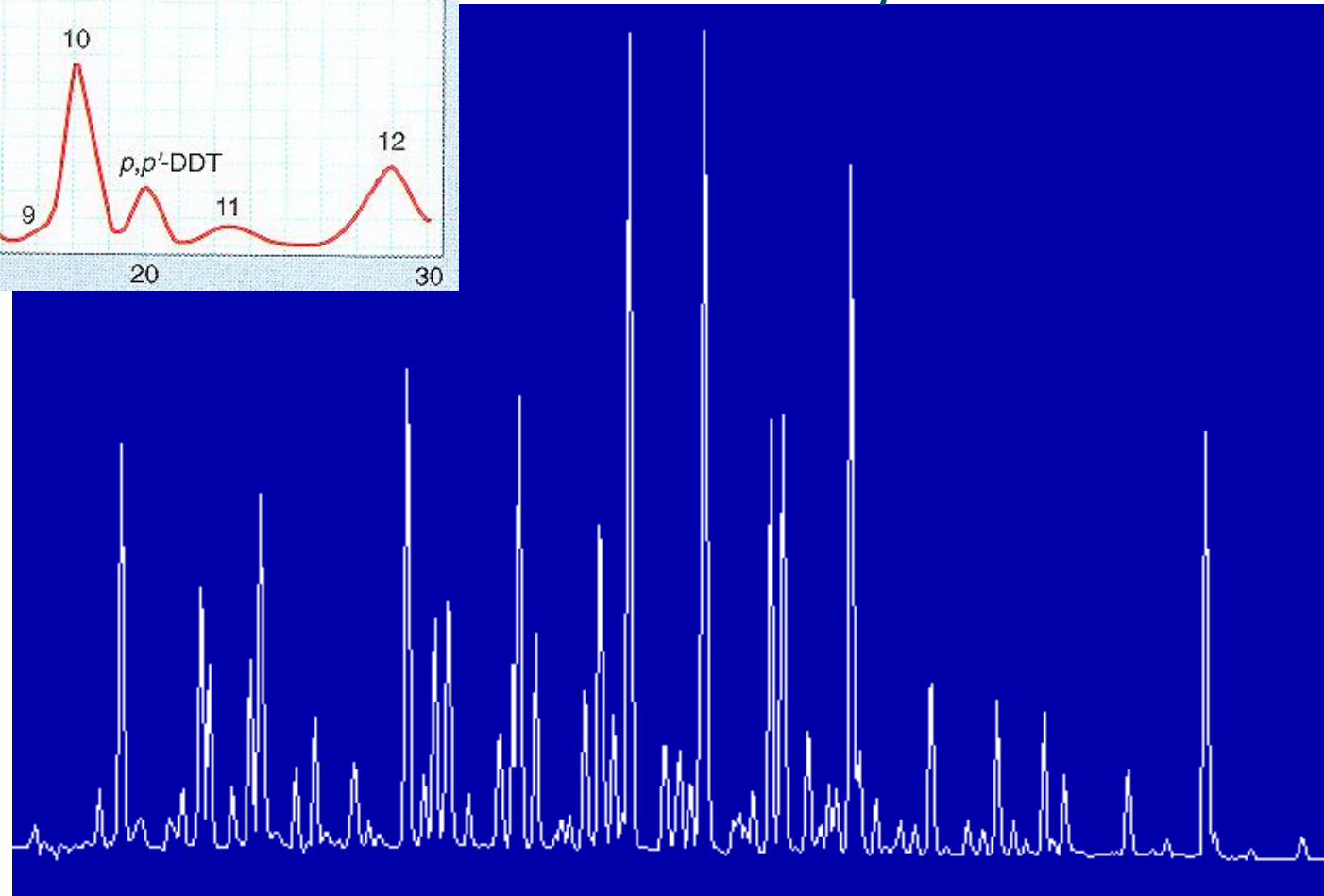
# The instrument used by Sören Jensen 50 years ago



# PCB as analysed in the past (mid to late 1960's)



and nowadays



# Accidents and Intoxications: A base for action

HCB

## Hexachlorobenzene episode in Turkey.

[Gocmen A.](#) et al in Biomed Environ Sci. 2 (1989) 36-43

<sup>1</sup>

### Abstract

During the period 1955-1959, approximately 4000 people in southeast Anatolia developed porphyria due to the ingestion of hexachlorobenzene (HCB), a fungicide added to wheat seedlings. These HCB exposures subsequently led to the development of bullae on sun-exposed areas, hyperpigmentation, hypertrichosis, and porphyrinuria.

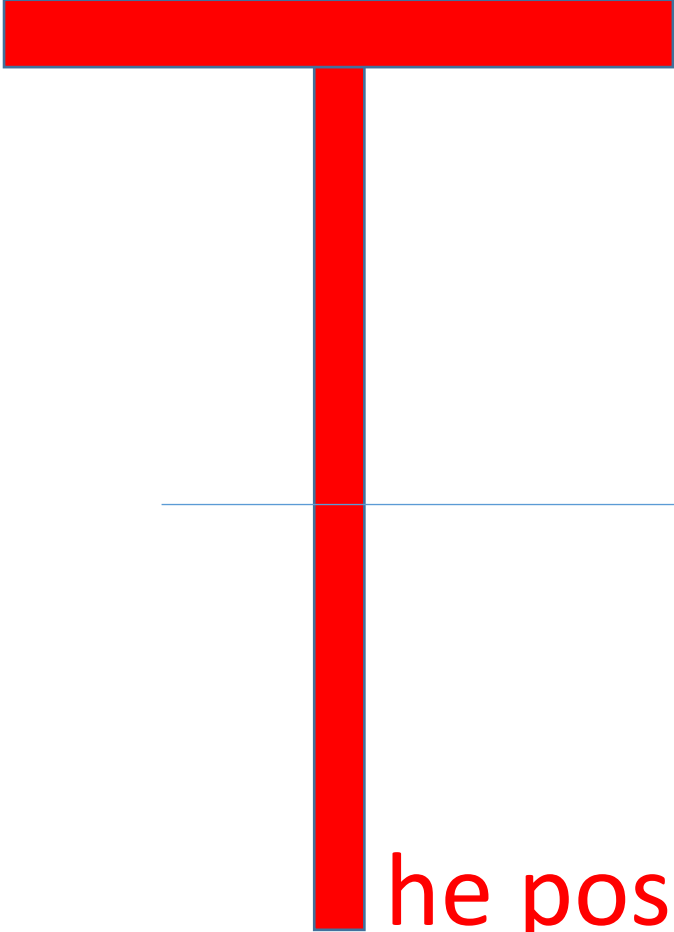
PBB



2,4,7,8-TCDD  
Seveso



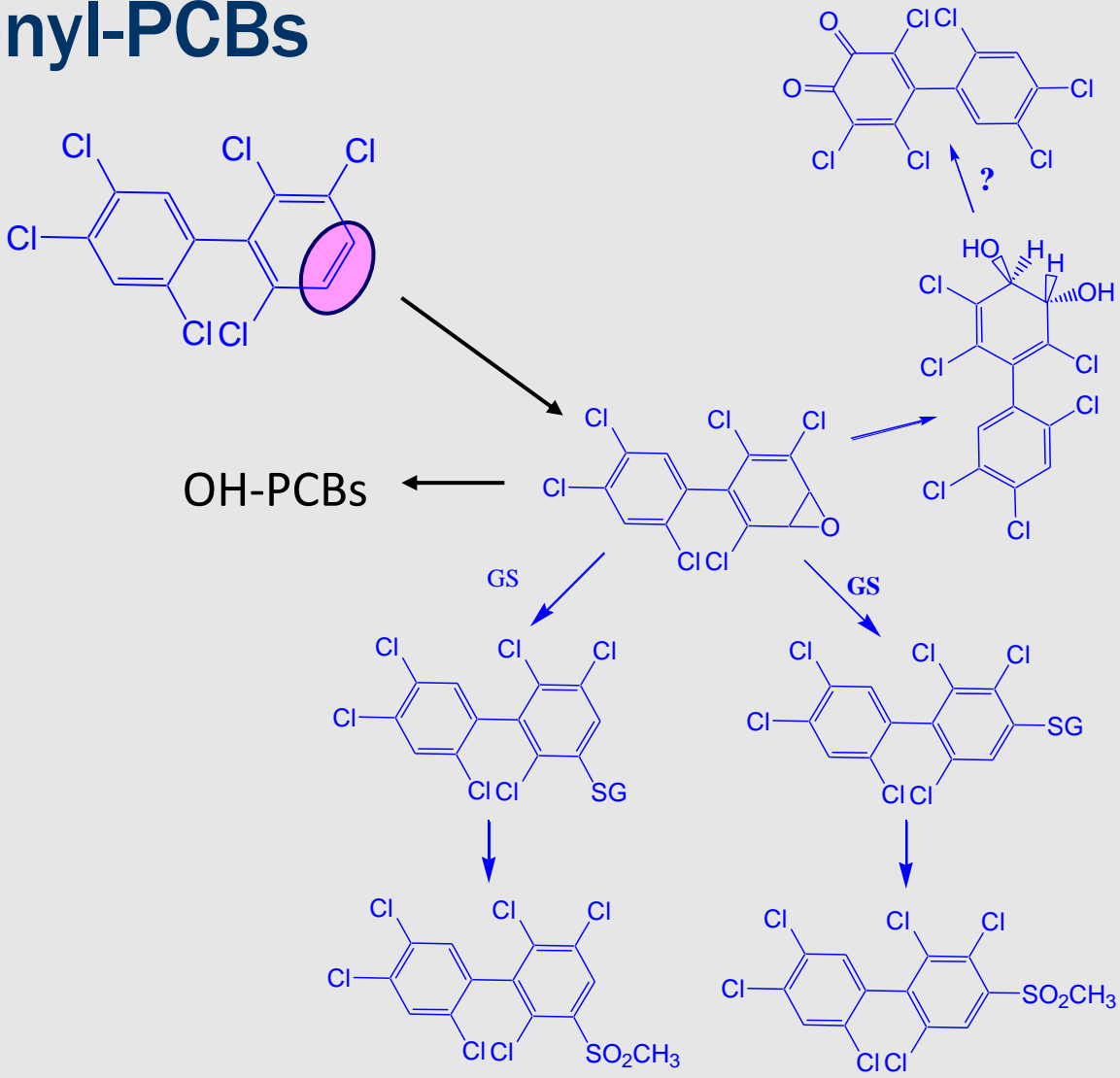




he possibility and responsibility!



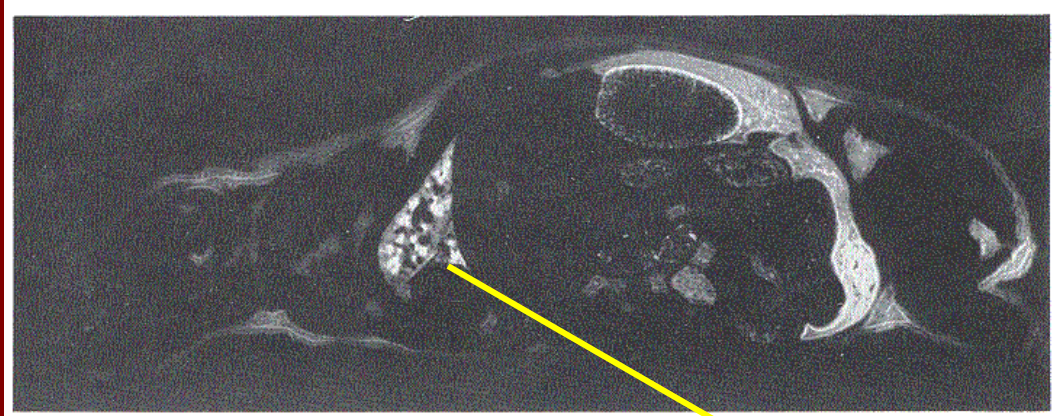
# PCBs form methylsulfonyl-PCBs



MeSO<sub>2</sub>-PCBs



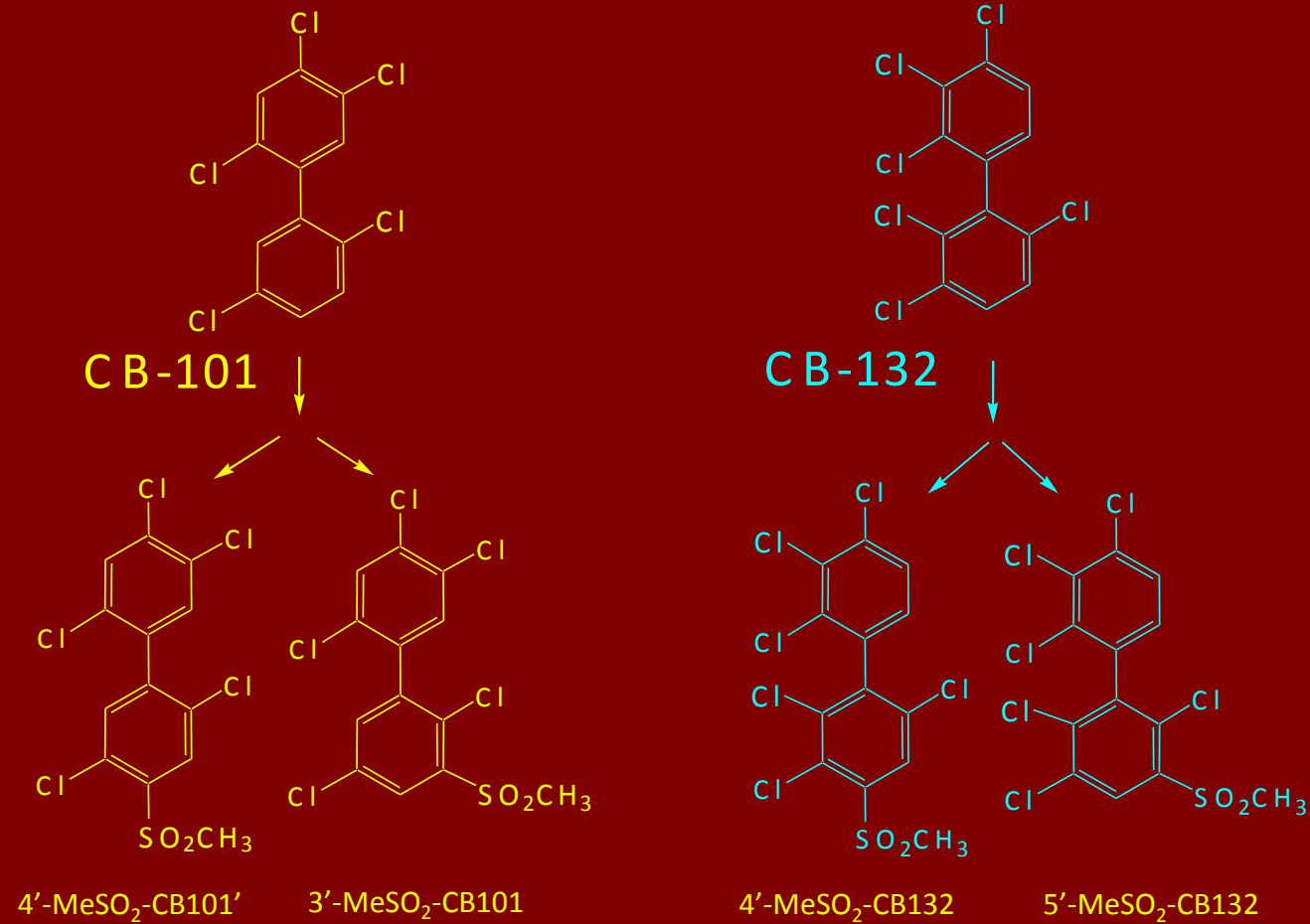
# Lung retention of a PCB methyl sulfone



Brandt & Bergman, *Experientia*, 1976,  
Brandt, thesis 1977



# MeSO<sub>2</sub>-PCBs in humans and the environment



# Route of MeSO<sub>2</sub>-PCB formation

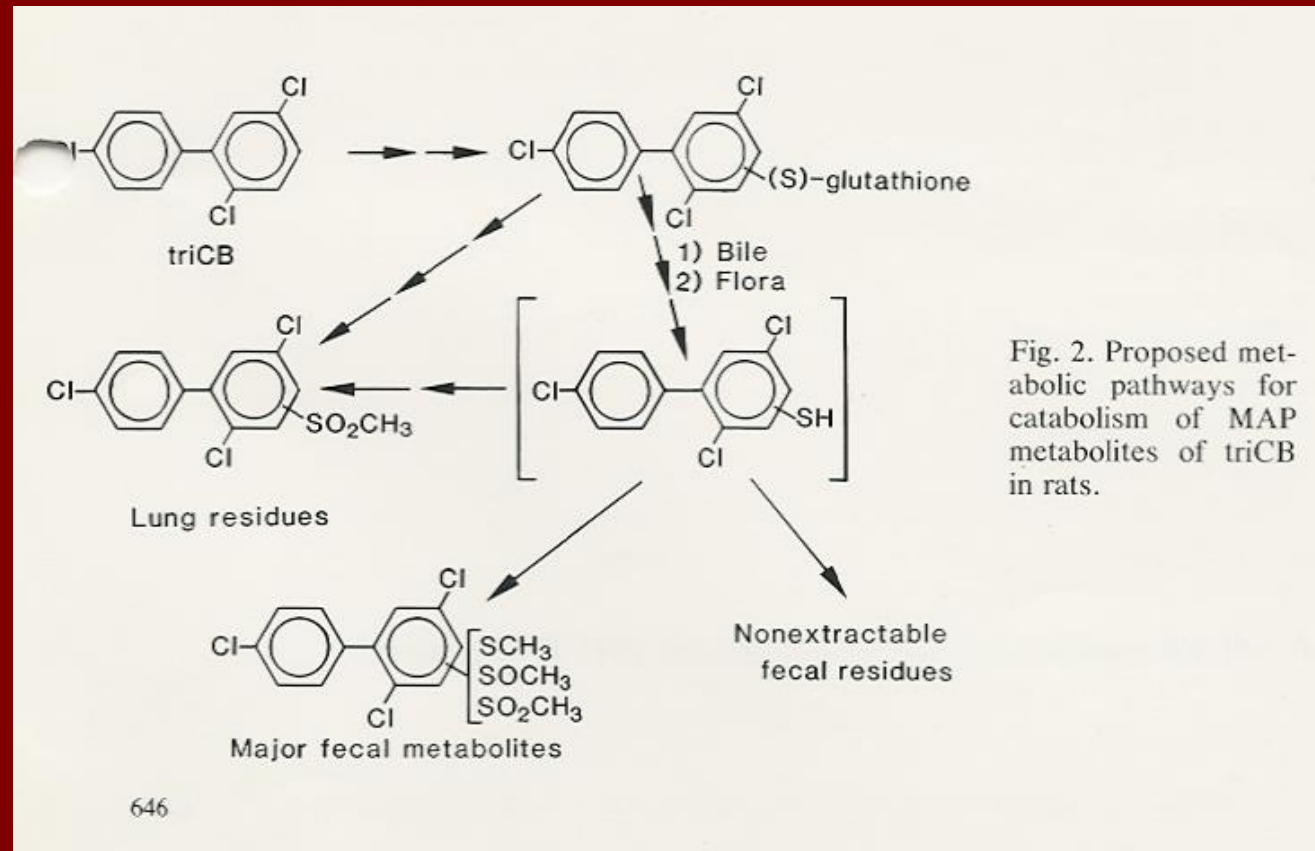
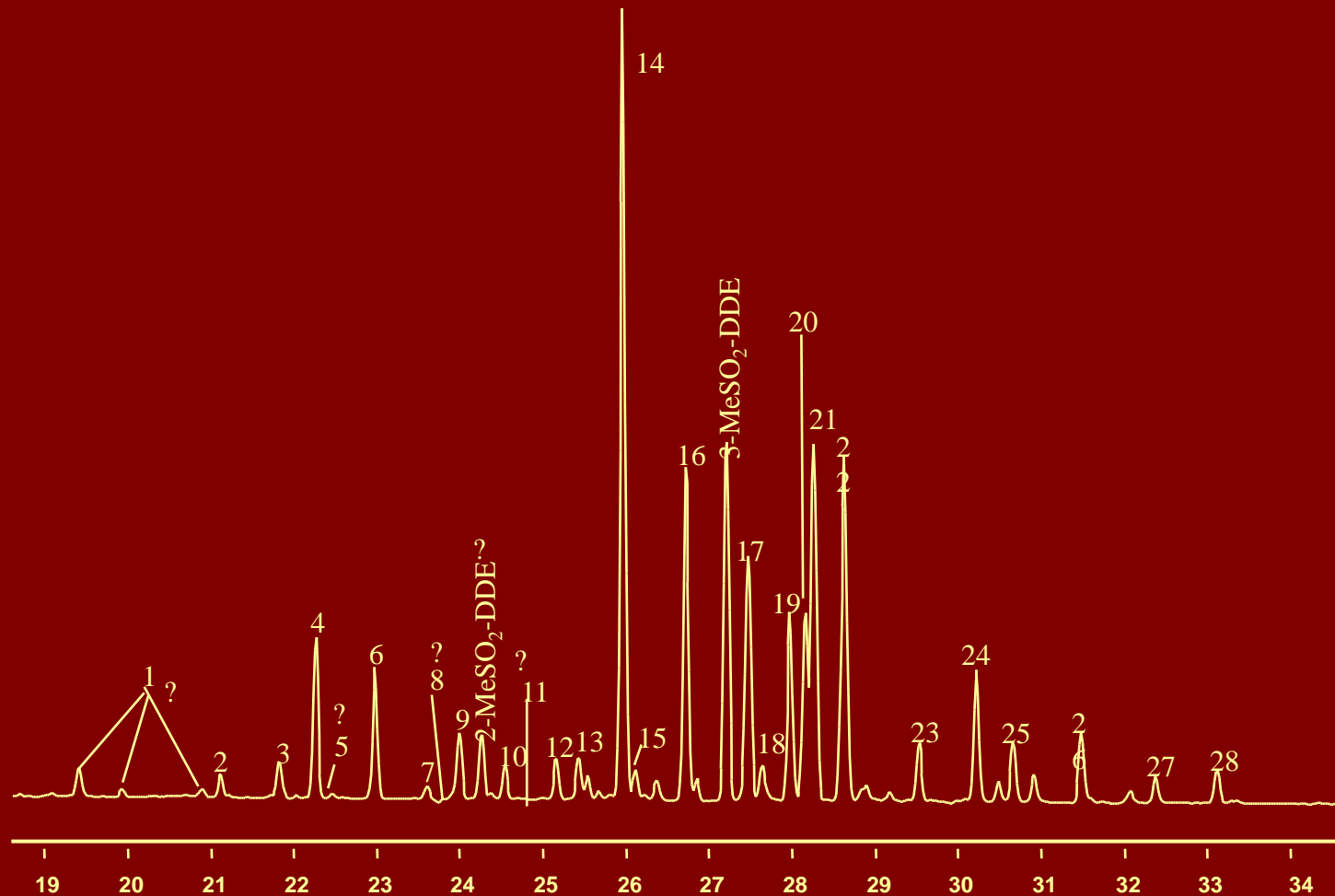


Fig. 2. Proposed metabolic pathways for catabolism of MAP metabolites of triCB in rats.

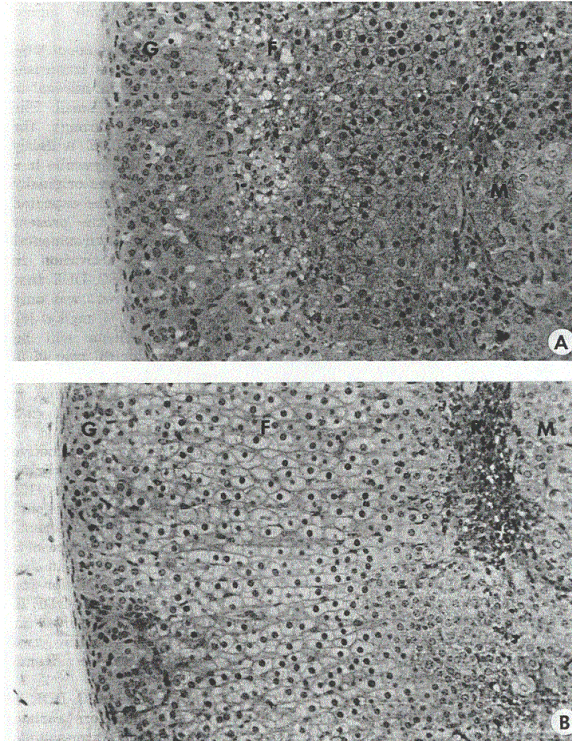
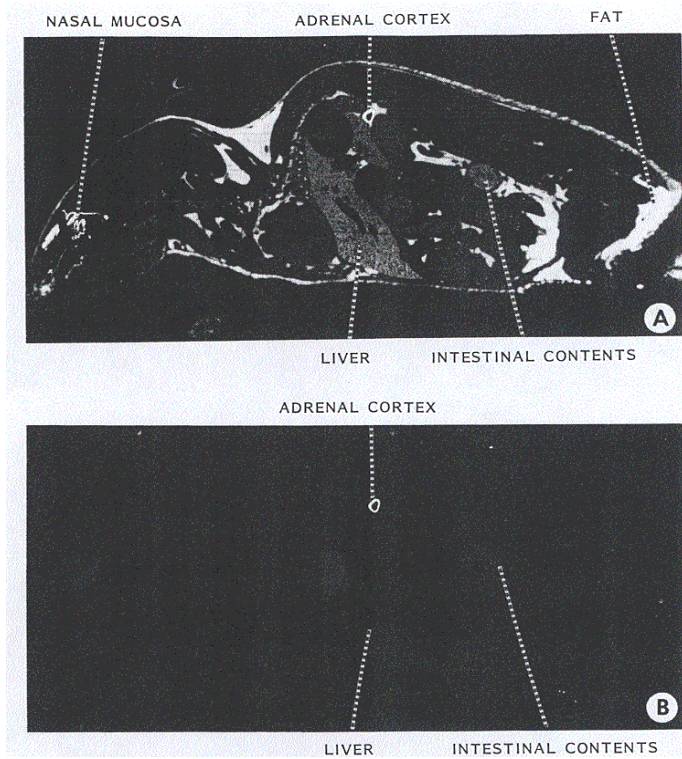
Bakke, Bergman & Larsen, Science 217 (1982) 645



# PCB methyl sulfones in grey seal blubber



# MeSO<sub>2</sub>-DDE in the adrenal cortex



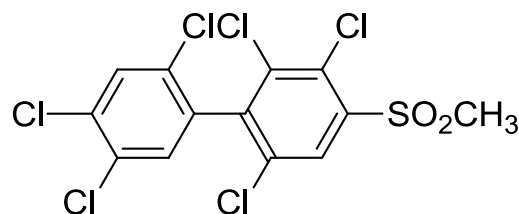
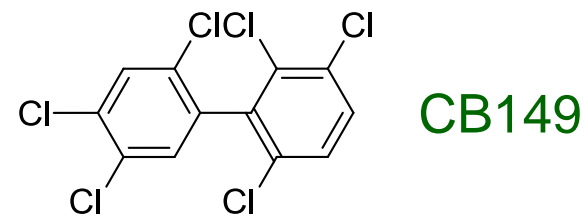
Lund, Bergman & Brandt i Chem.-Biol. Interact. 65 (1988) 25-40.



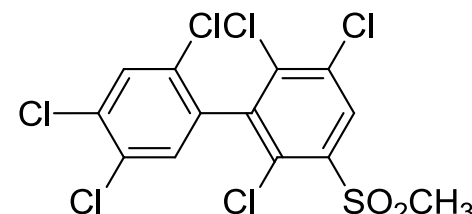
Picture from Anders Bergman

# Chiral PCBs and MeSO<sub>2</sub>-PCBs

- Asymmetric substitution of both rings
- 3 or 4 *ortho* chlorines



4-MeSO<sub>2</sub>-CB149

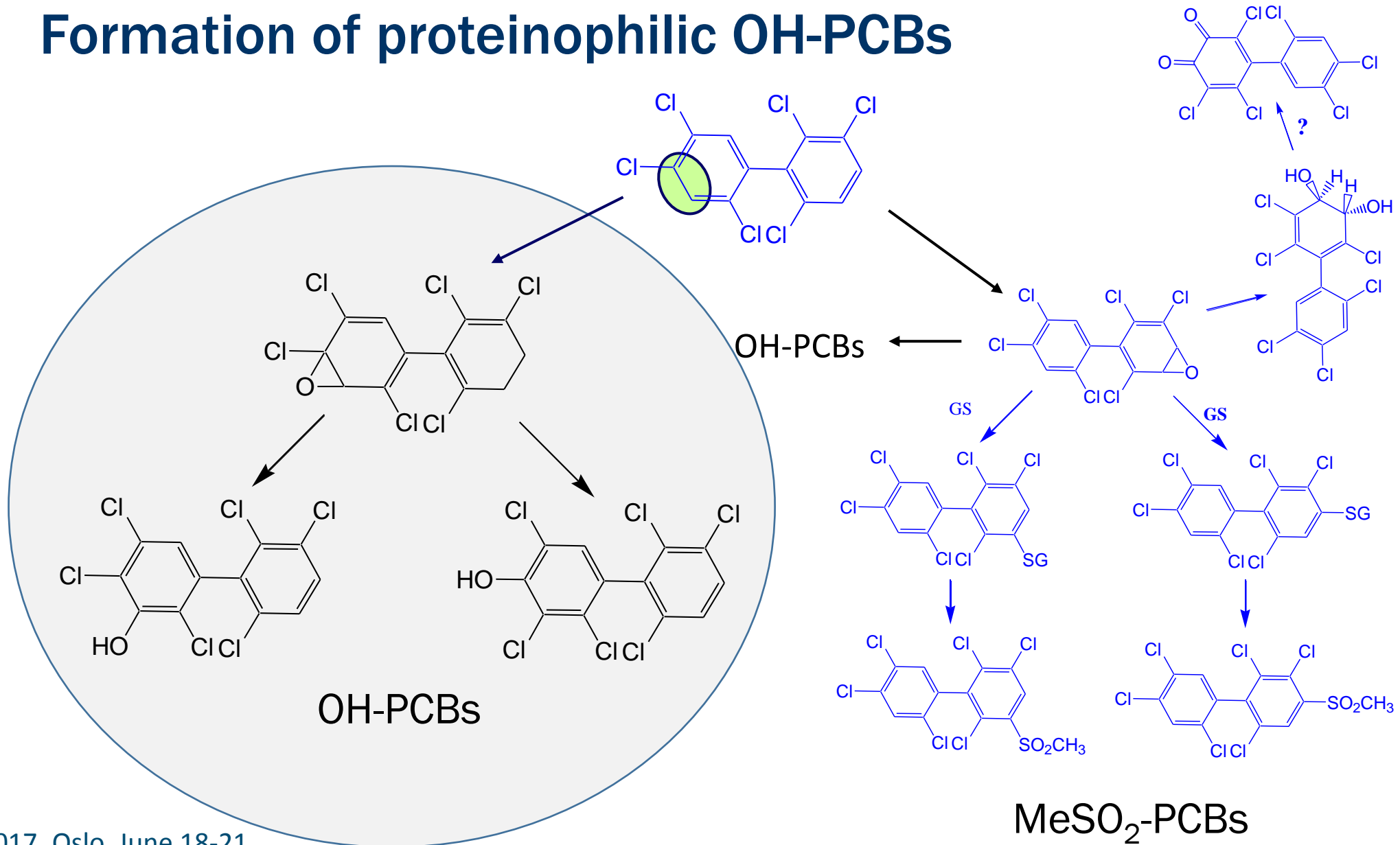


5-MeSO<sub>2</sub>-CB149

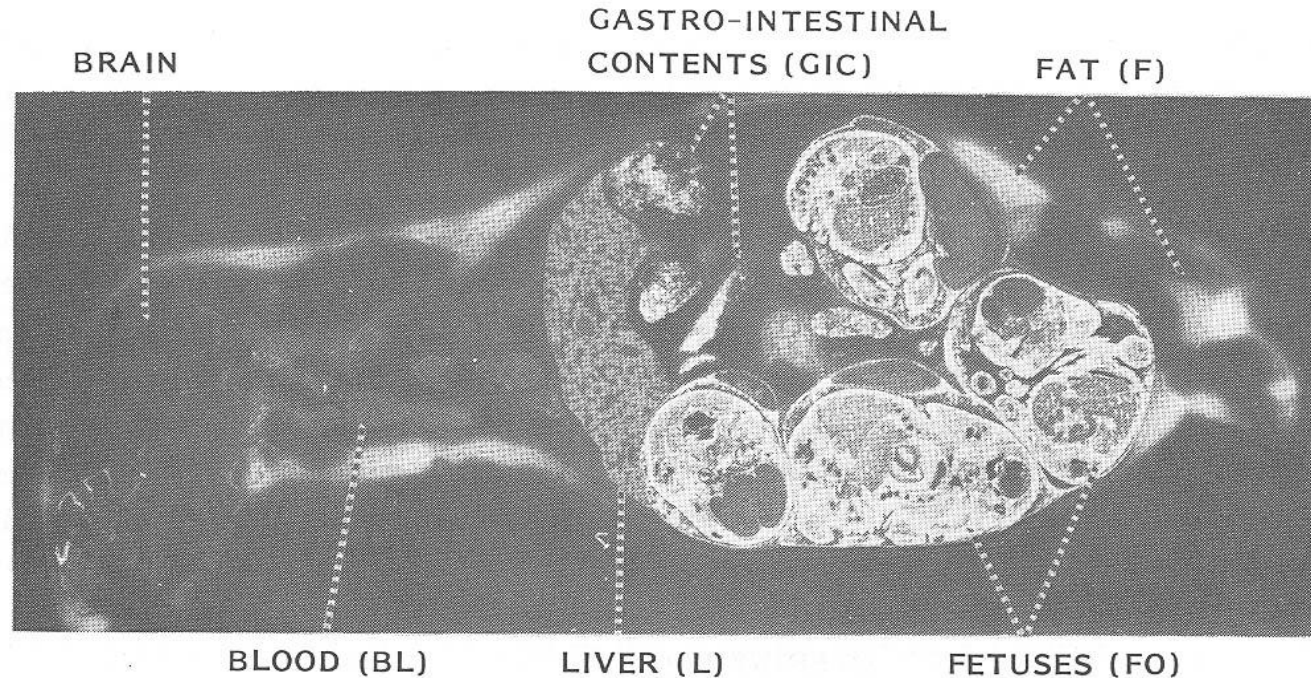
10 chiral MeSO<sub>2</sub>-PCBs detected in wildlife from the Baltic Sea



# Formation of proteinophilic OH-PCBs

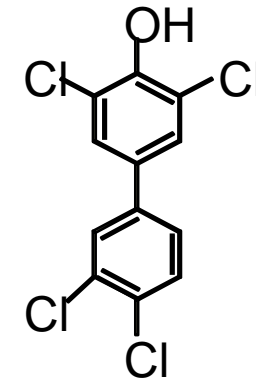


# Autoradiogram of pregnant mouse dosed with radiolabelled 3,3',4,4'-tetrachlorobiphenyl (CB-77)



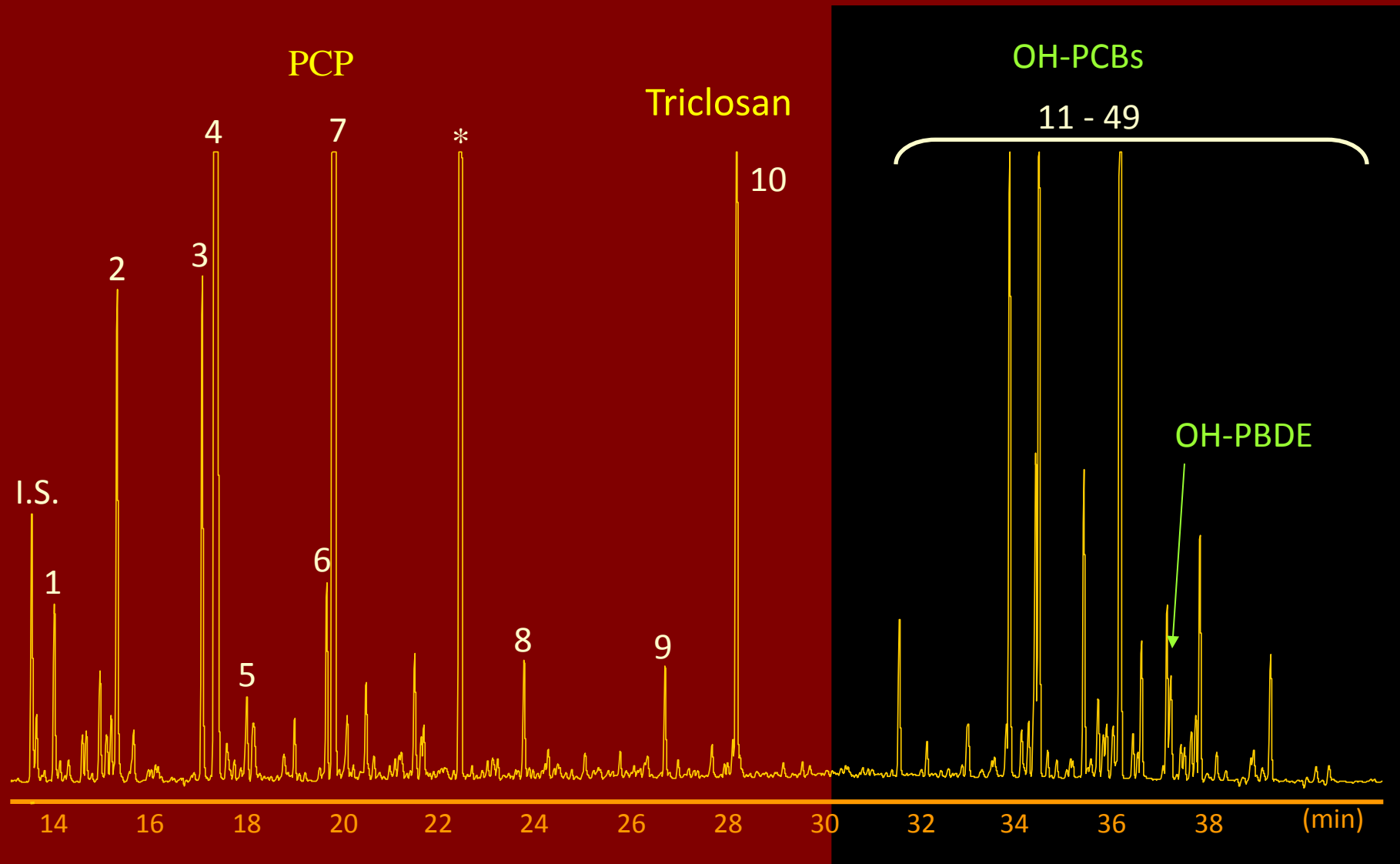
Darnerud et al., Xenobiotica 16 (1986) 295

CB-77 metabolite identified

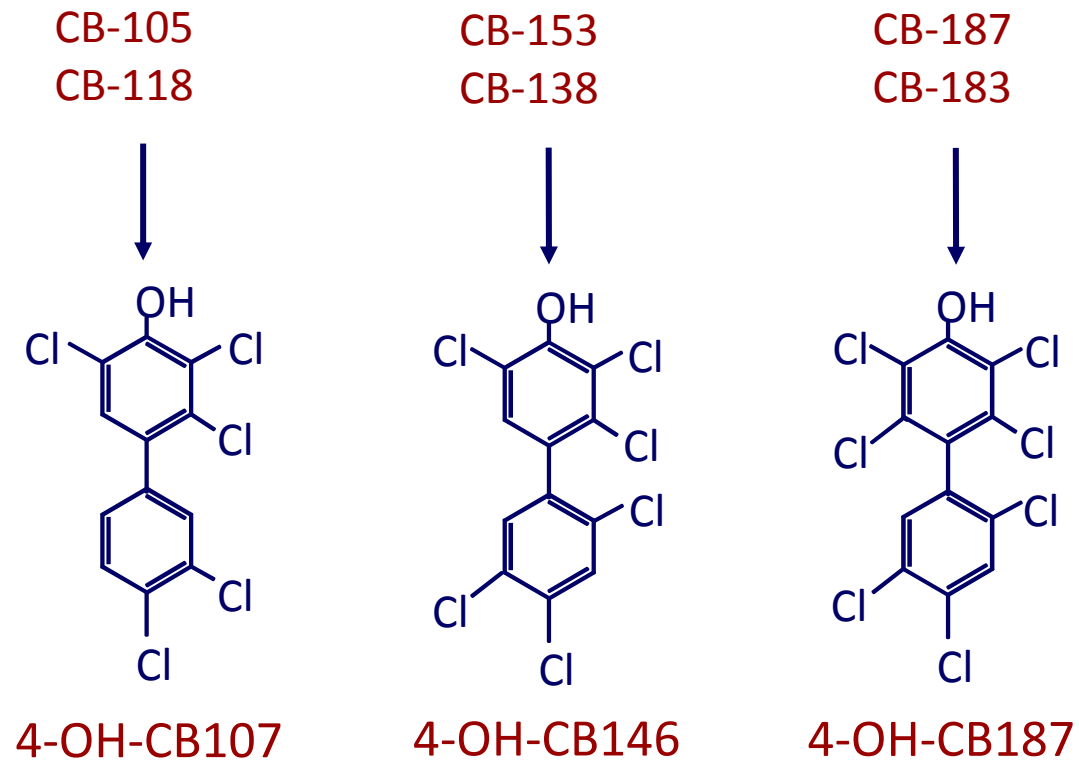


4-OH-CB-79

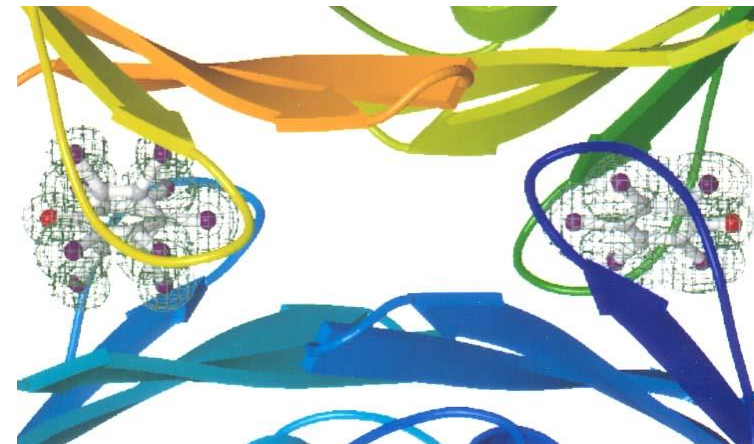
# Halogenated Phenolic Compounds (HPCs) in human blood



# Major PCB/OH-PCB metabolites

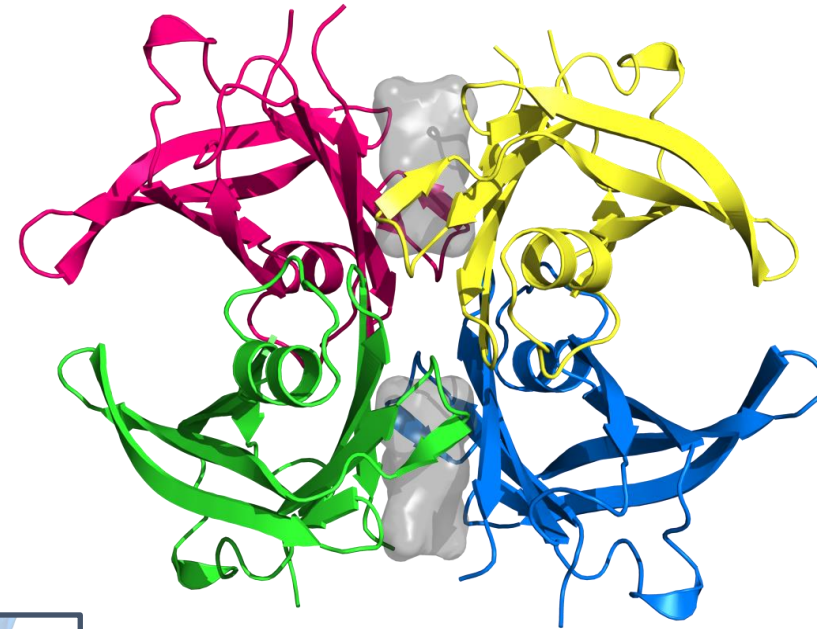
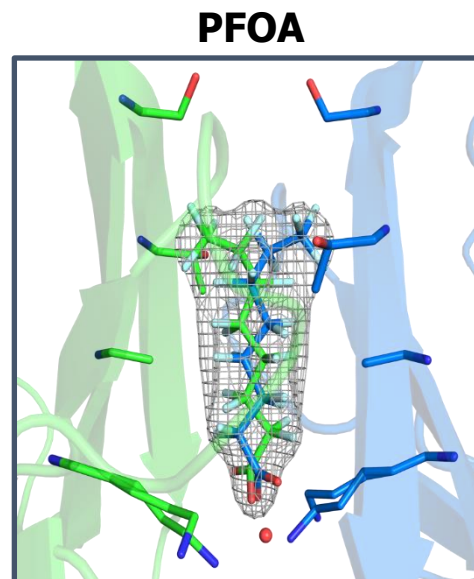
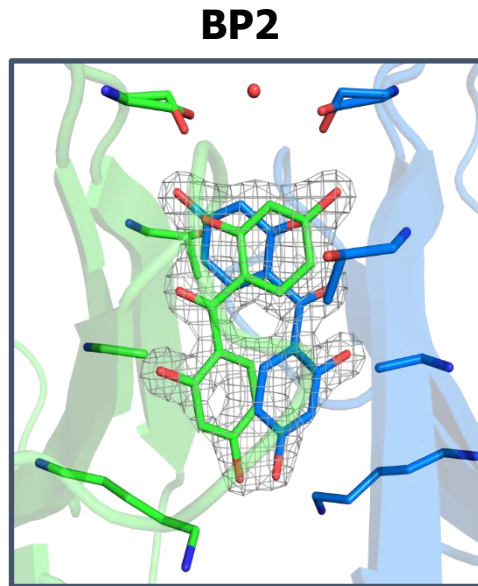


Trantyrethin binding



SWETOX

# Persistent and Proteinophilic



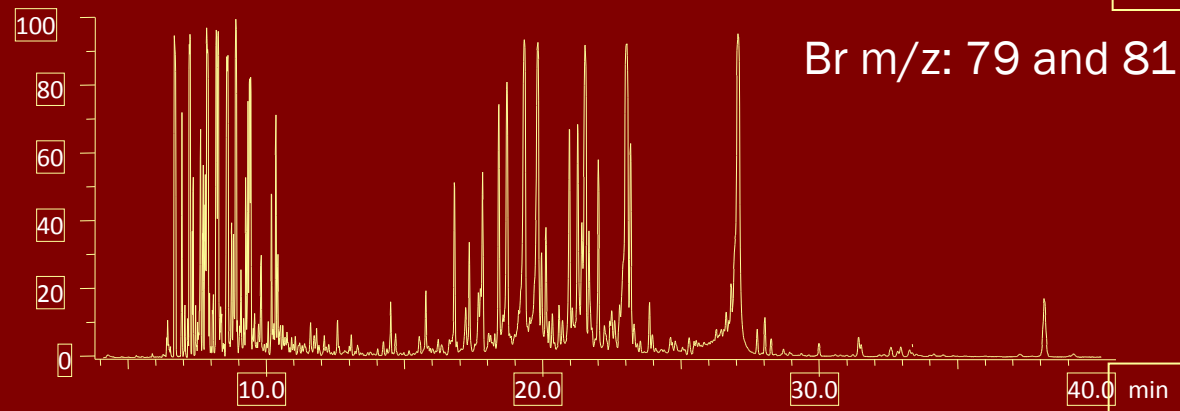
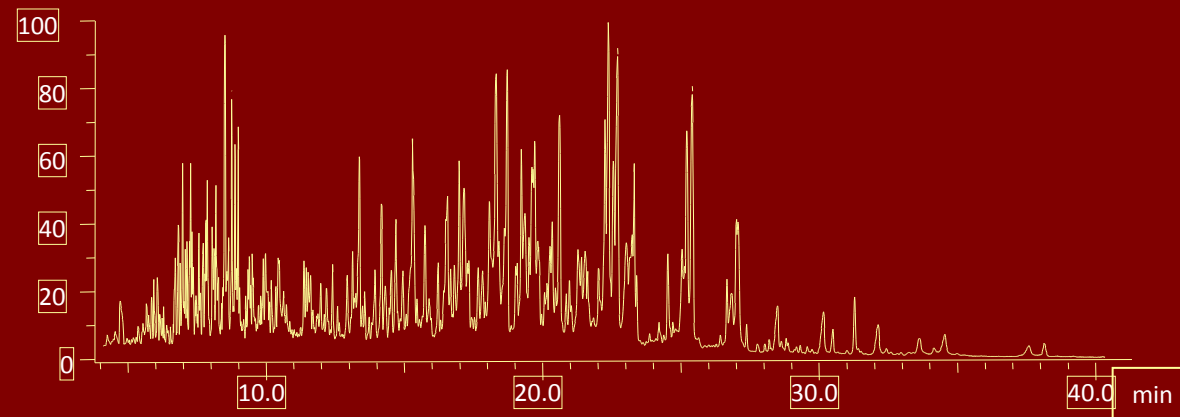
Transthyretin

Zhang, J. et al. ES&T, 50 (2017)  
11984-11993

# PHCs in Baltic Sea salmon blood

RIC in the upper MS chromatogram

ONLY analyzed for Br m/z: 79 and 81 in the lower one



# OH-PBDE toxicity in zebrafish

Transgenic zebrafish embryos are very sensitive to 6-OH-BDE47  
at 24 hours post fertilization



Van Boxtel et al., ES&T 42 (2008) 1773



# Strength of evidence

- Effects can be explained by endocrine mode of actions (mechanisms)
- **The identification of chemicals with endocrine disrupting properties linked to disease outcomes in laboratory studies**
- **Observations of endocrine-related effects in wildlife populations**
- The rate of incidence of many endocrine-related diseases or disorders in humans

*From UNEP/WHO 2013 Report on EDCs*



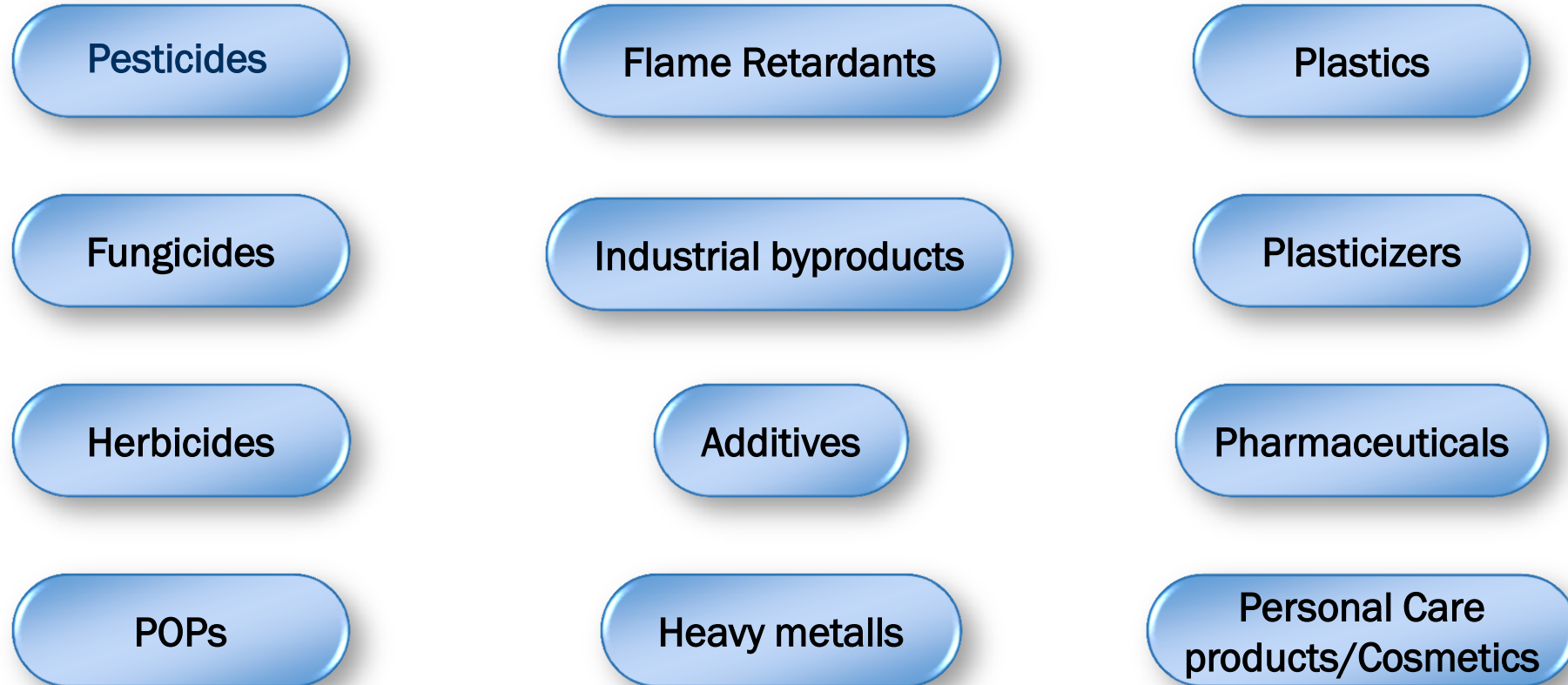
# A complex world of anthropogenic chemicals

1. Active Pharmaceutical Ingredients (APIs); Drugs incl. tobacco
2. Currently Used Pesticides (CUPs)
3. Chemicals in Materials and Goods (CMGs) (monomers, additives, etc.)
4. Cosmetics and Personal Care Products (CPCPs)
5. Additives and Contaminants in Food & Water
6. Transformation products (biogenic and abiotic reactions)

**The way forward**



# 1392 Potential EDCs\*



\* TEDX List of Potential Endocrine Disruptors, accessed June 17, 2017

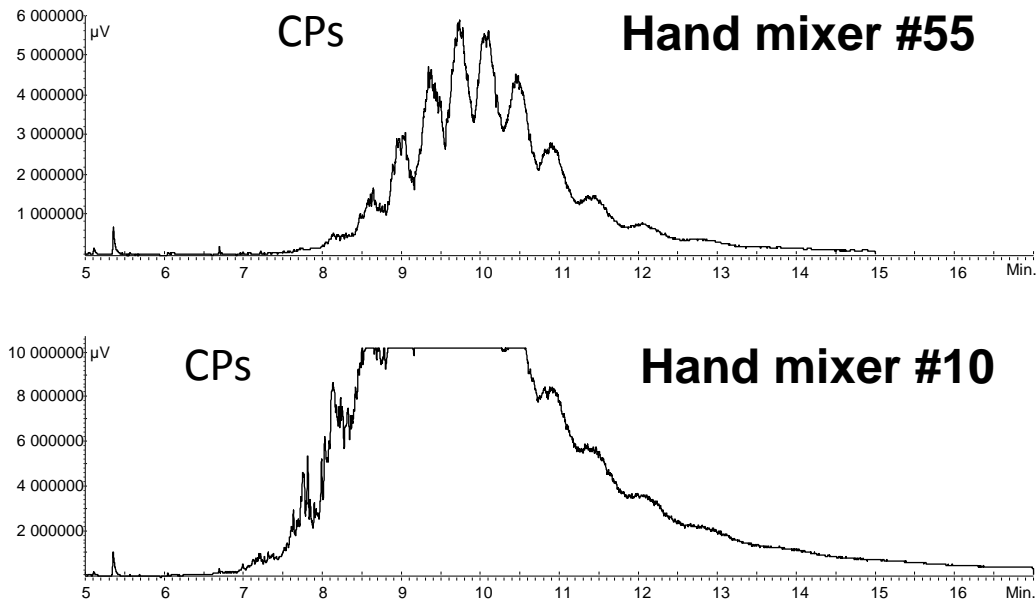
<http://endocrinedisruption.org/interactive-tools/tedx-list-of-potential-endocrine-disruptors/search-the-tedx-list>



# Anthropogenic chemicals have many sources

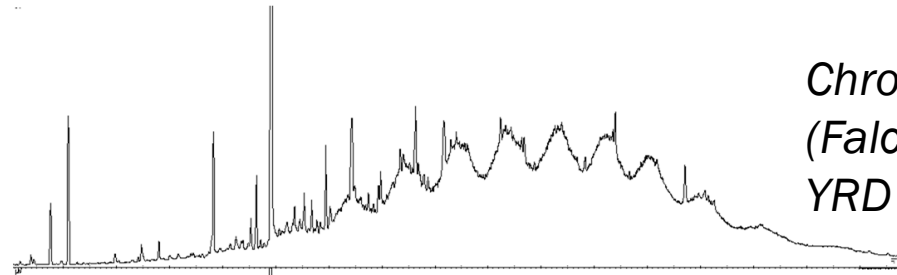


# Unexpected findings of CPs coming from hand mixers

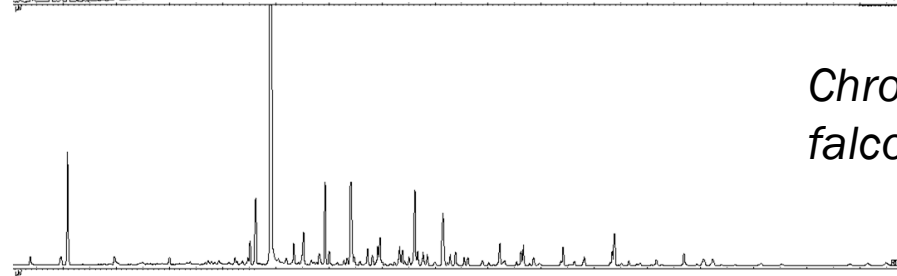


Strid et al., Reports to KemI and NFA, Oct., 2014

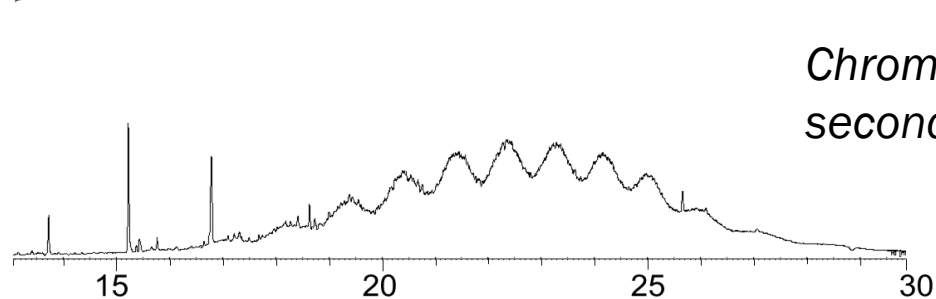
# The chlorinated paraffins (CPs)



*Chromatogram of a Peregrine falcon (Falco peregrinus) sample from the YRD area close to Shanghai*



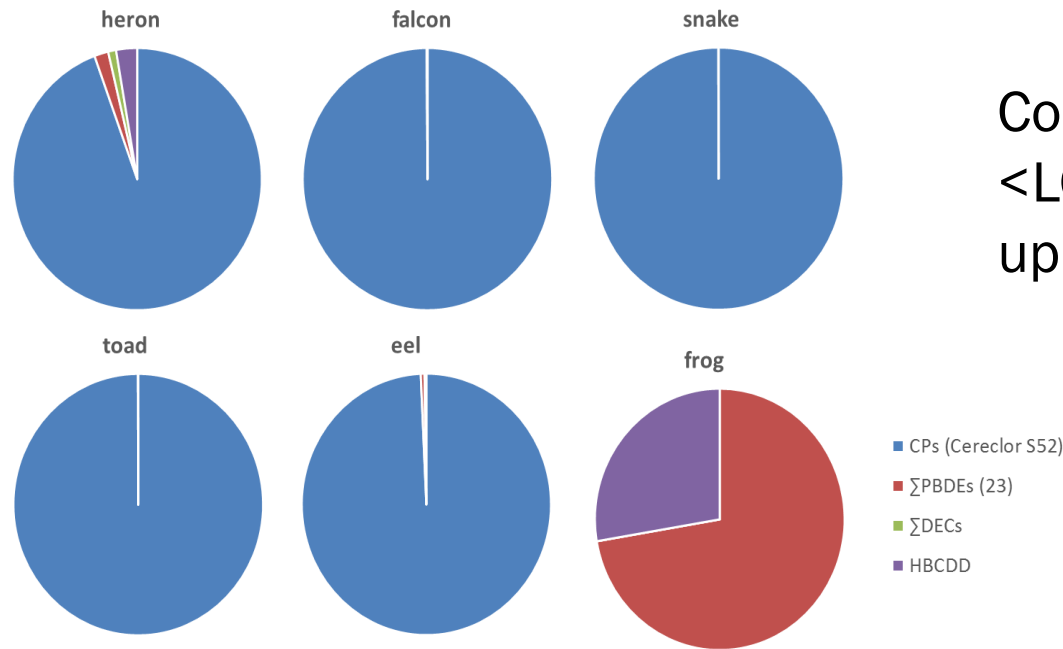
*Chromatogram of the Peregrine falcon first fraction after clean up*



*Chromatogram of the Peregrine falcon second fraction after clean up*

Zhou et al., Science of the Total Environment 554-555 (2016) 320-328

# Significant chlorinated paraffin contamination in wildlife sampled close to the mouth of Yangtze river



Concentration range:  
<LOQ – 340000 ng/g l.w.. i.e.  
up to 340 µg/g!

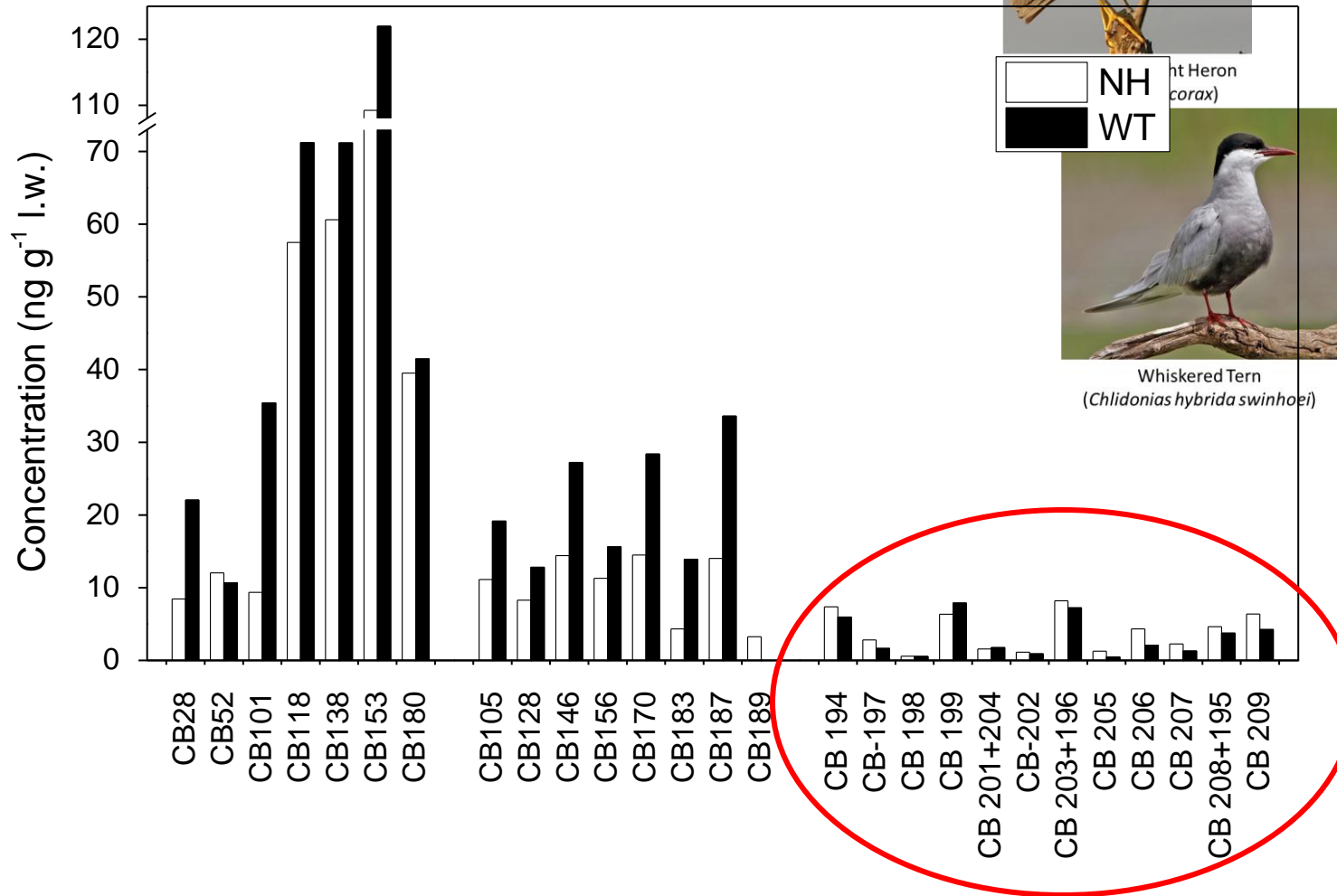


Zhou et al., Science of the Total Environment 554–555 (2016) 320–328

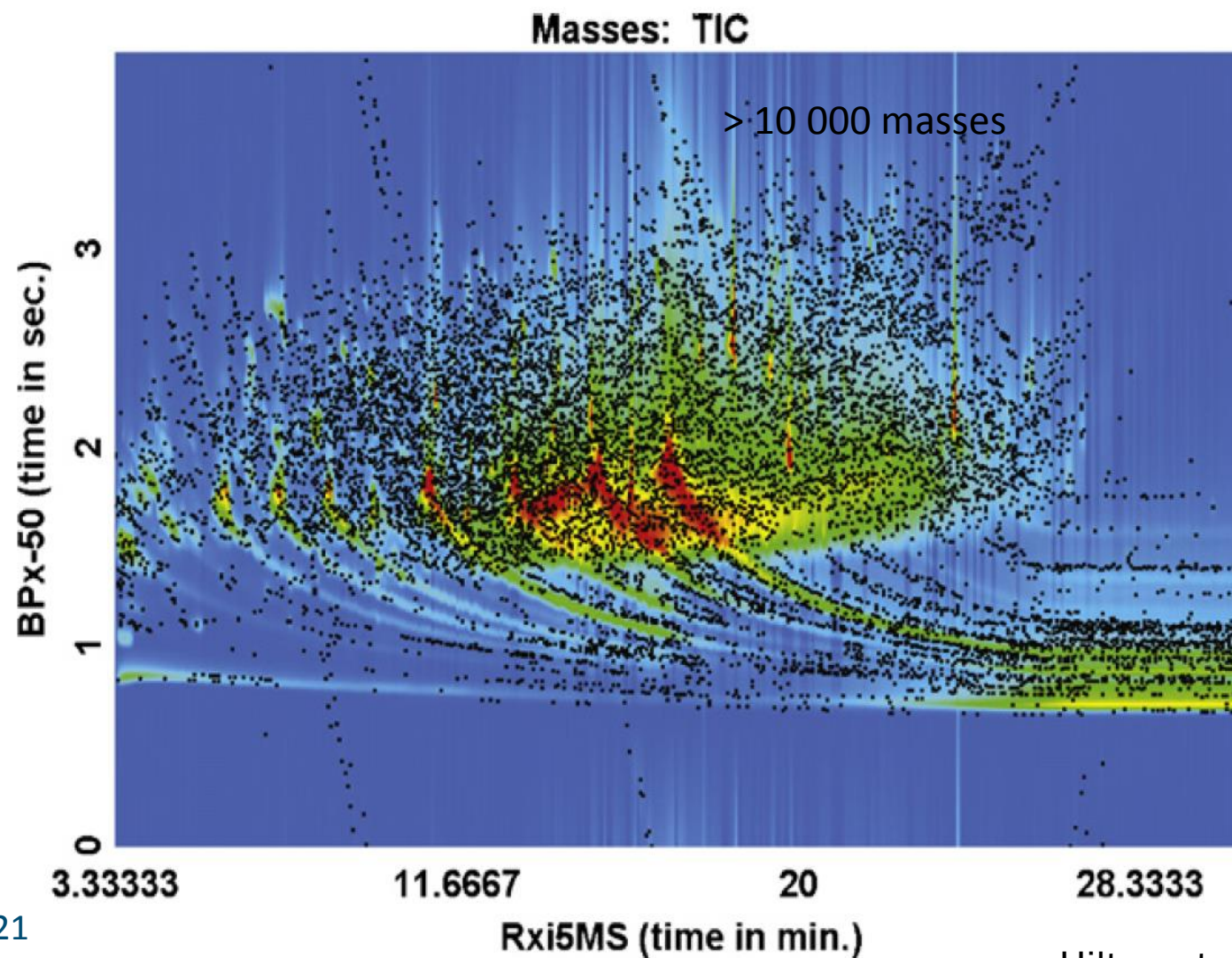
<http://www.chemstrres.com/>



# Highly chlorinated biphenyls



# Background: Chemicals in dust





# Chemicals in Swedish dust

From the Swedish Misse project  
<http://www.aces.su.se/misse/>

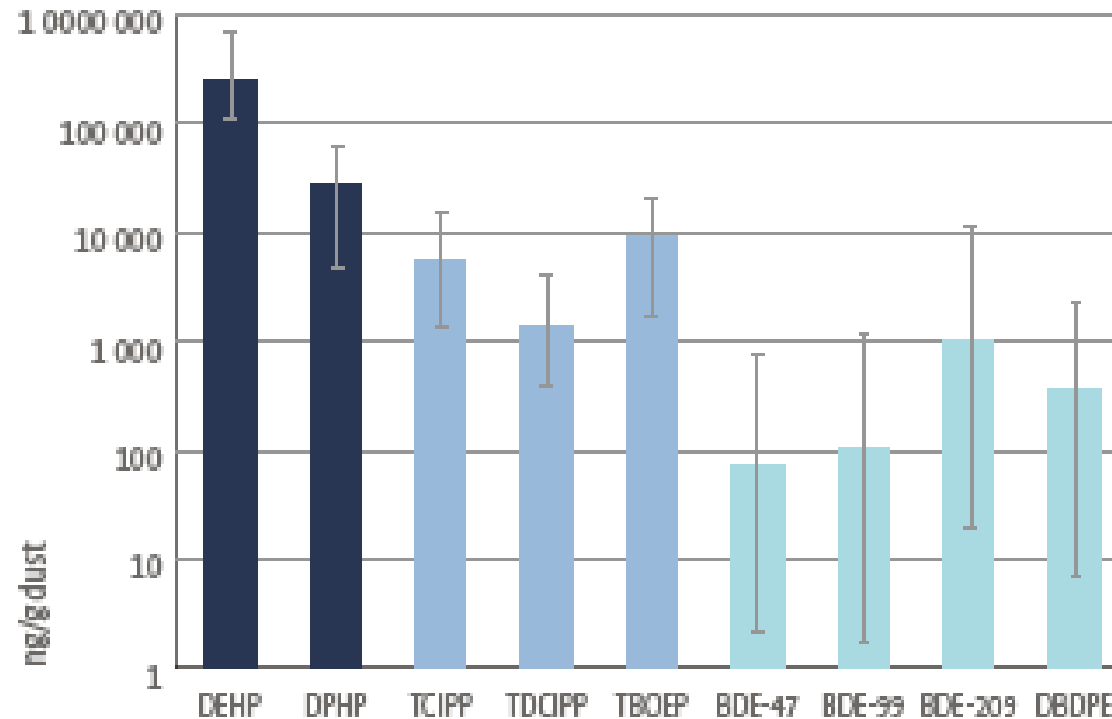


Figure 3.10.1. Average concentration (ng/g dust, error bars max/min) of phthalate esters (DEHP and DPHP), PFRs (TCIPP, TDCIPP and TBOEP) and BFRs (BDE-47, BDE-99, BDE209 and DBDPE) analyzed in Swedish household dust (n=17).

# Organo-phosphate esters in Swedish dust

From the Swedish Misse project  
<http://www.aces.su.se/misse/>

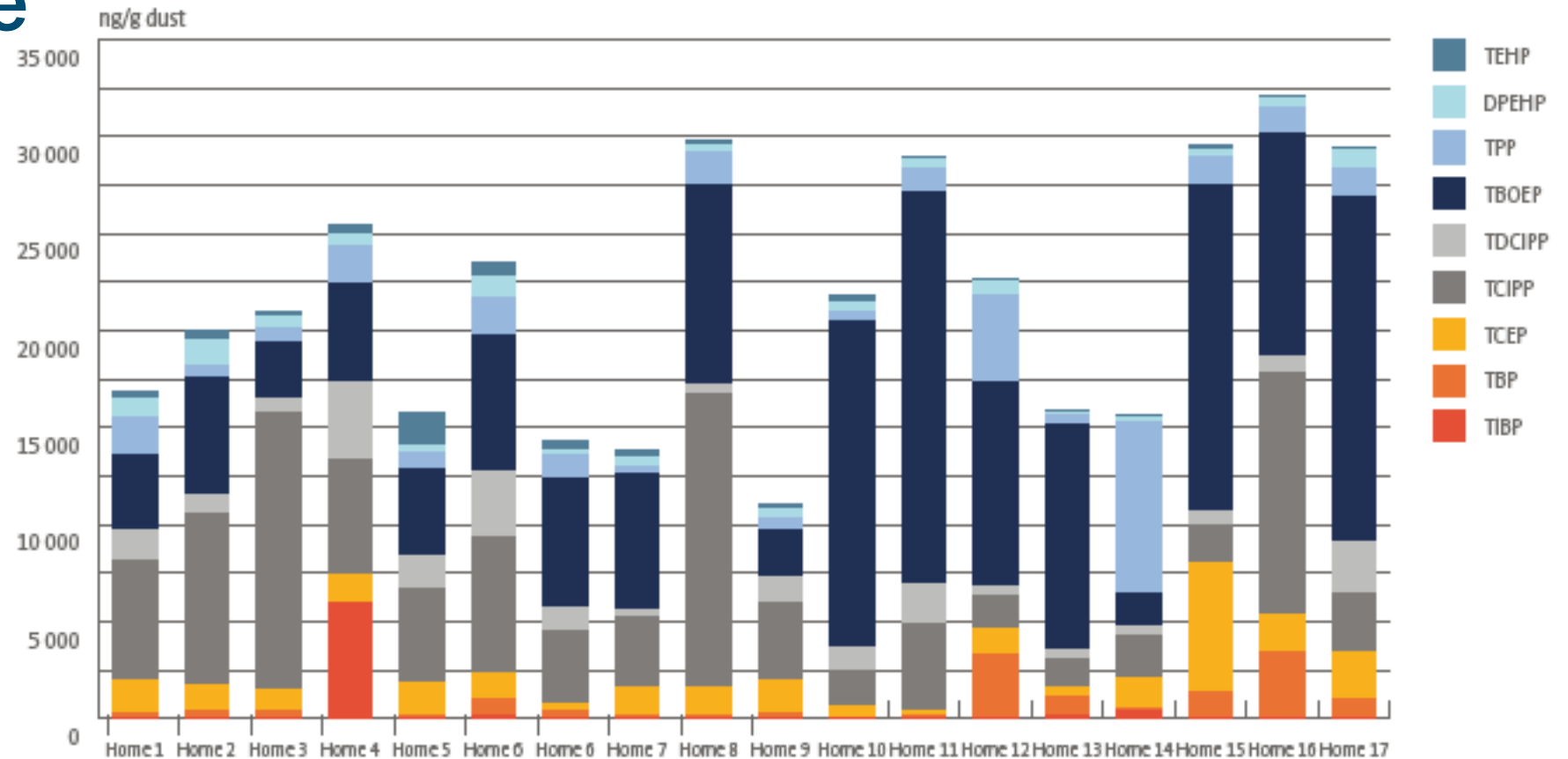
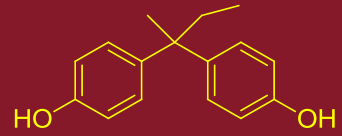
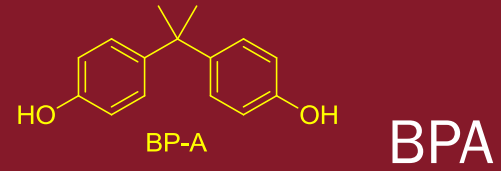


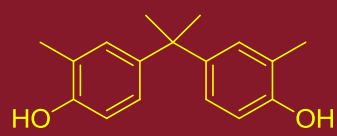
Figure 3.10.2. Individual PFR concentration (ng/g dust) profiles in dust from Swedish households (n=17) [13].

Chemical Pollution Challenges in the Yangtze River Delta  
 Editors: Ake Bergman, Anders Bignert, Yanling Qiu, Ge Yin  
 ISBN printed: 978-91-87355-31-8

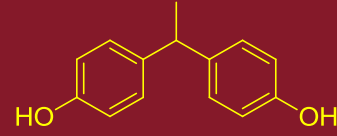
# Bisphenols



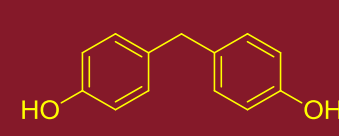
BP-B



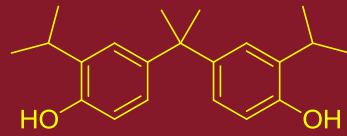
BP-C



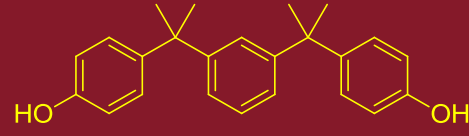
BP-E



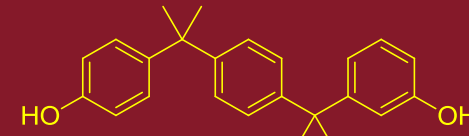
BP-F



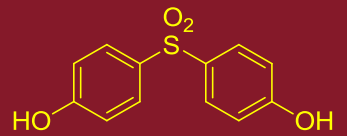
BP-G



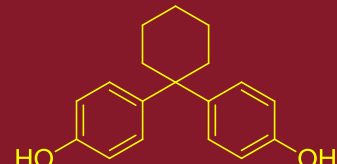
BP-M



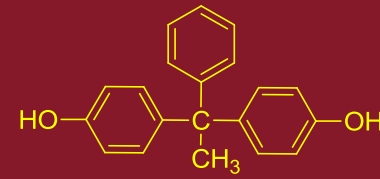
BP-P



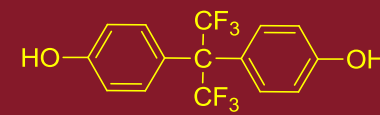
BP-S



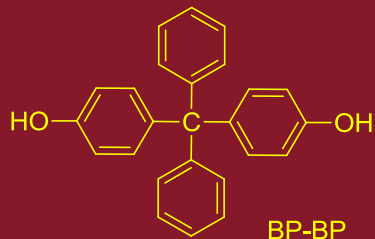
BP-Z



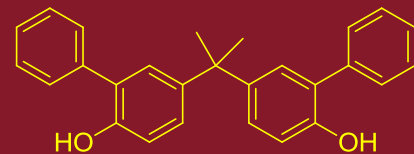
BP-AP



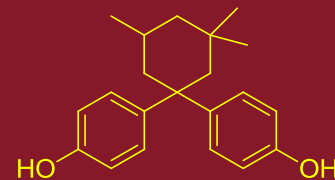
BP-AF



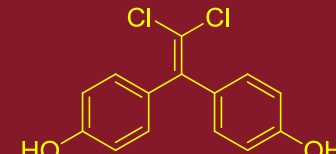
BP-BP



BP-PH

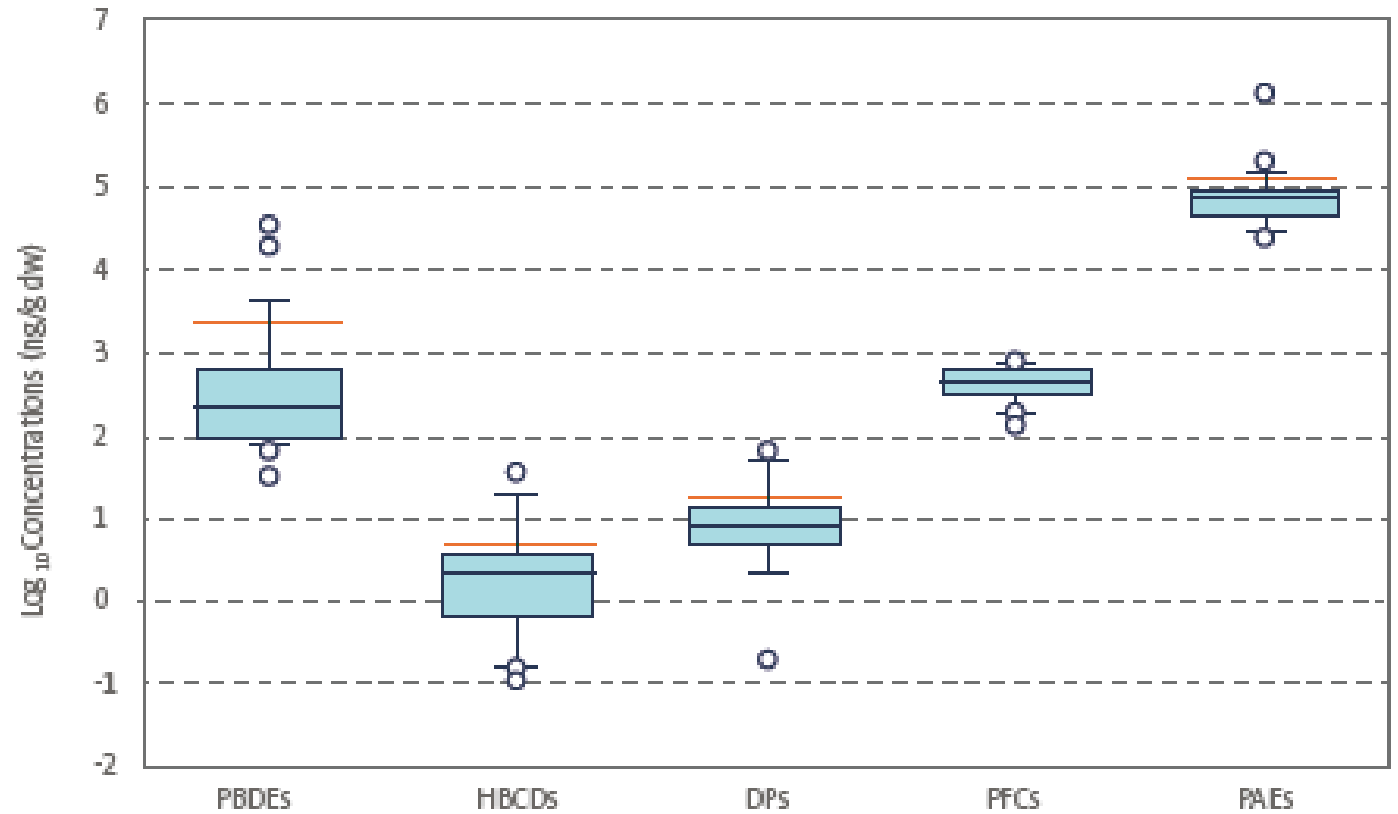
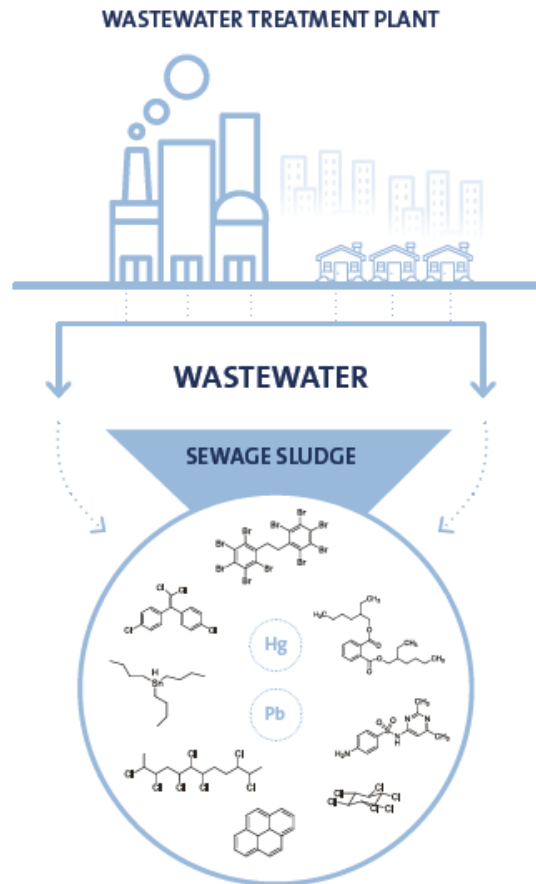


BP-TMC



BP-C2

# Biosolids as a mirror of human activities



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

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# Acknowledge the semi-persistent chemicals

*Definition:* Persistent but readily metabolized

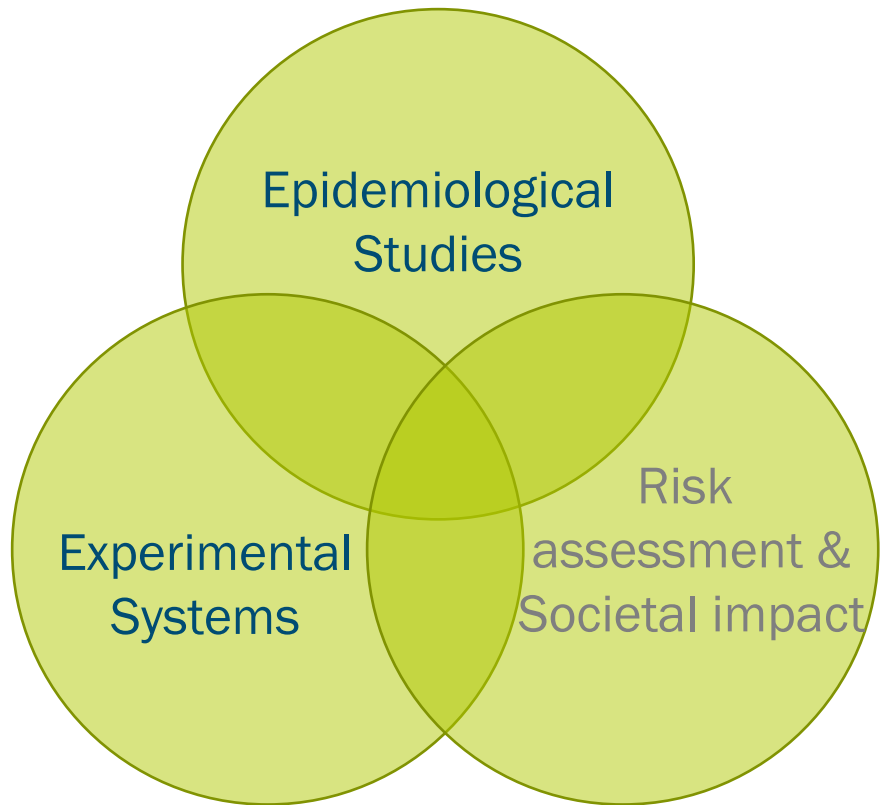
## *Bioaccumulativity*

Semi-persistent chemicals may bioaccumulate due to their **proteinophilic character** or because of **pseudopersistency**

Semi-persistent chemicals are of main concern, mainly due to a poor knowledge base.



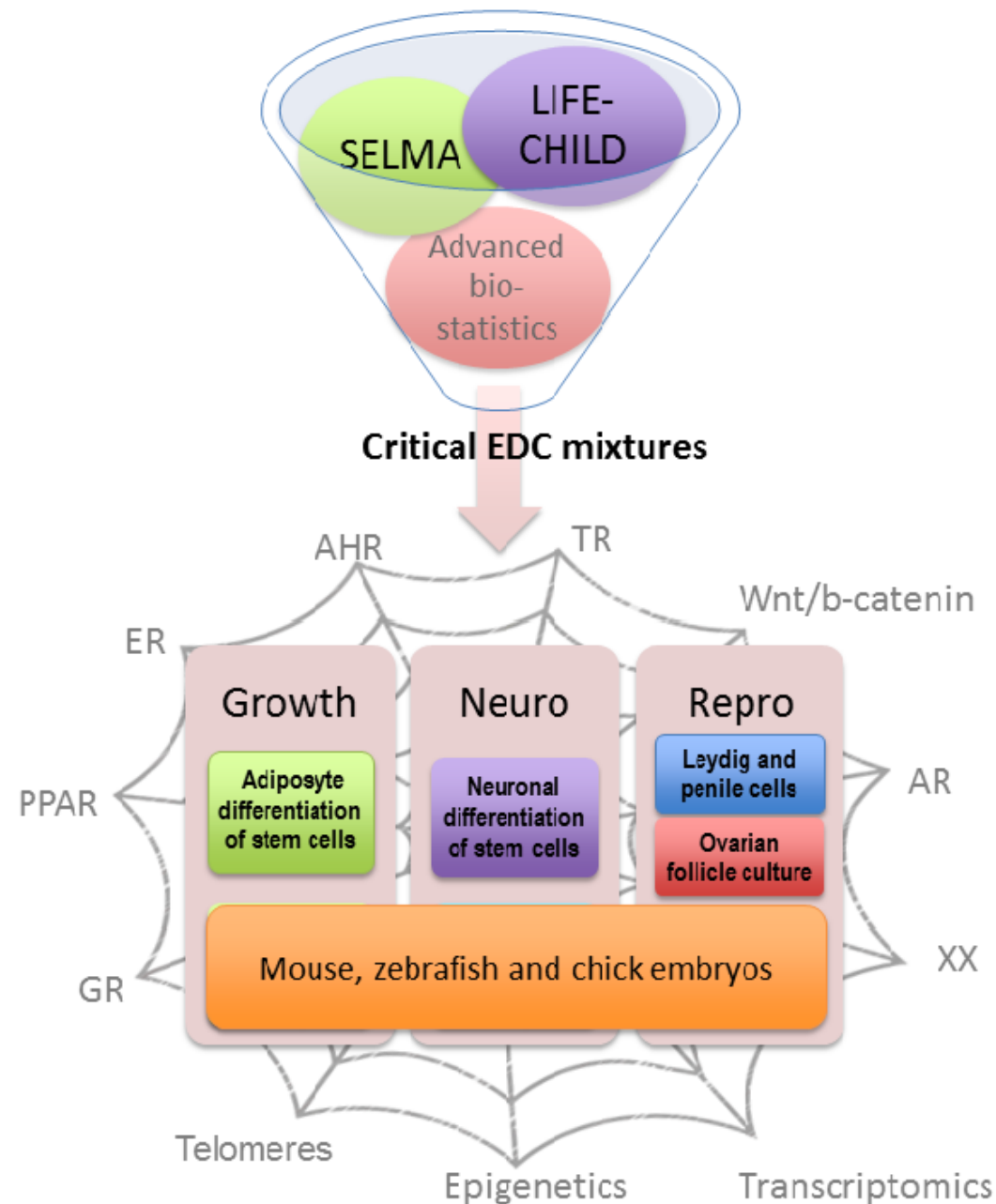
## EDC-MixRisk addresses EDC mixtures associated with adverse health outcomes:



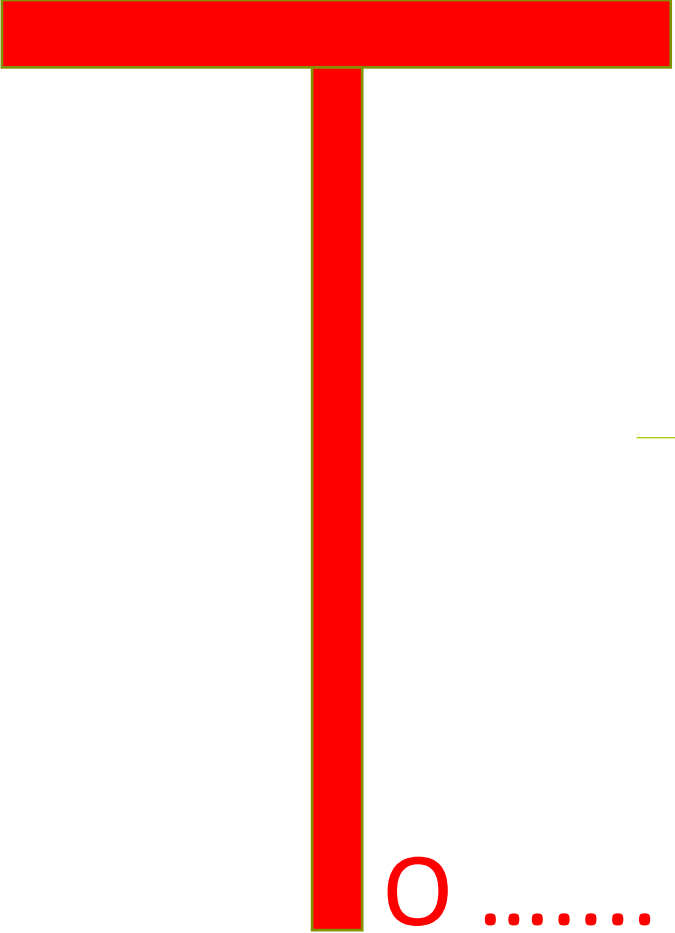
in two pregnancy cohort regarding:

- Growth and metabolism,
- Neurodevelopment &
- Sexual development

# Mixtures of anthropogenic chemicals: Hazard and risks



# The possibility and responsibility in environmental chemistry



- develop the society in the direction of safe production, use and applications of chemicals to meet the goals of environmental sustainability & good health through interactions with authorities, industry/business and NGOs

- meet the societal needs of information, communication and new knowledge, via all available channels.

---

- develop and manage teaching in environmental chemistry

- work interdisciplinary and across faculty borders; with other actors in the society

- contribute with environmental chemistry into other areas of chemistry/natural science and health

- use our fundamental knowledge in chemistry to develop the depth of environmental chemistry contribution to the science



# The possibility and responsibility in environmental chemistry

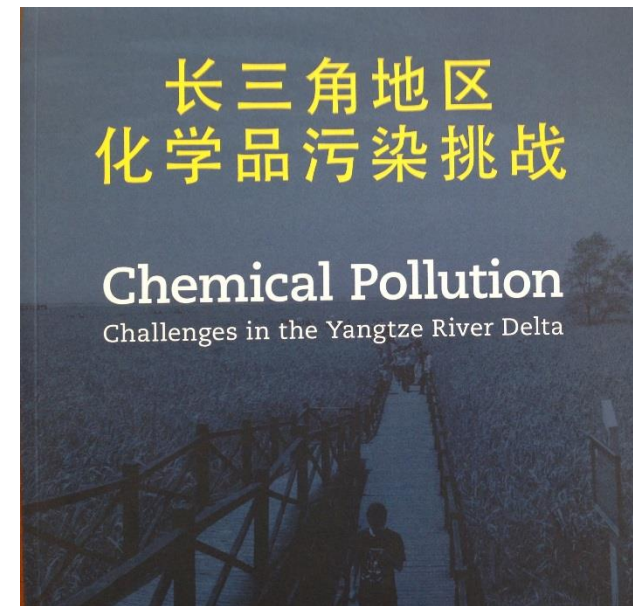
O .....

- Please be aware of the lobbying seeding doubt on science**
- develop the society in the direction of safe production, use and applications of chemicals to meet the goals of environmental sustainability & good health through interactions with authorities, industry/business and NGOs
  - meet the societal needs of information, communication and know knowledge, via all available channels.
  - develop and manage teaching in environmental chemistry across faculty borders; with other actors in the society
  - work interdisciplinary and across faculty borders; with other actors in the society
  - contribute with environmental chemistry into other areas of chemistry/natural science and health
  - use our fundamental knowledge in chemistry to develop the depth of environmental chemistry contribution to the science
- as for risk of tobacco smoking**
- as for exposure to brominated flame retardants**
- as related to Climate change**
- and hazard & risk of Endocrine Disrupting Chemicals (EDCs)**

# Acknowledgements

With great and special thanks for all support from Colleagues and Ph.D. students at Stockholm University & Swetox and to dear colleagues in Sweden and around the world that have made my scientific career possible such a joy

For all financial support from Sweden, the European Union and China



**Thank you for listening  
Happy Midsummer!**

