Persistent Organic Pollutants (POPs)
From local contamination to global challenges

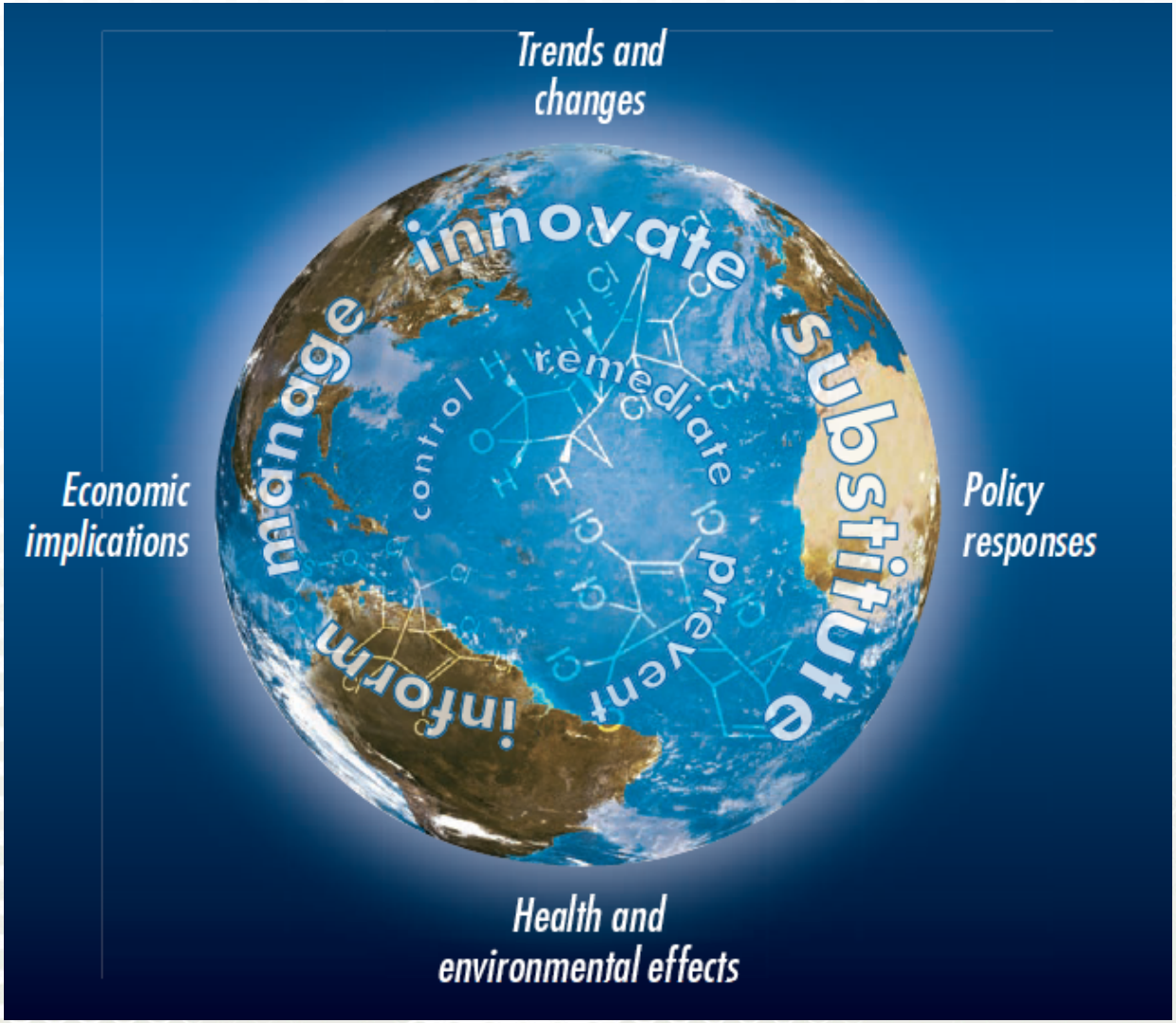
Miljøstabile organiske forurensinger: Fra Lokal utslipp til globale konsekvenser

NKS Lokalavdeling Rogaland

Roland Kallenborn

Department of Chemistry, Biotechnology and Food Sciences (IKBM)

The Chemical Universe



Source: UNEP: GCO (2012)

Persistent Organic Pollutants (POPs)

- remain intact in the environment for a long time;
- become widely distributed throughout the environment;
- accumulate in fatty tissue of living organisms; and
- are toxic to humans and wildlife

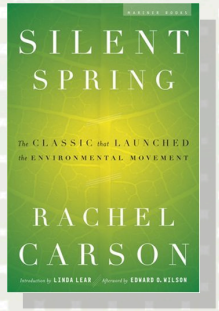
STOCKHOLM CONVENTION

History of POPs

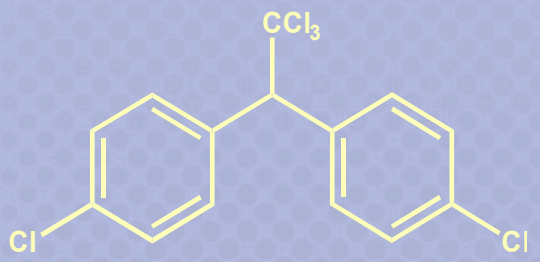
- Insecticidal effect of *p,p`*-di-chloro-diphenyl-trichloroethane (2,2`–DDT), Paul-Hermann Müller (Patent 1940), Nobel Price 1948

- Development of the ultra-sensitive Electron Capture Detector (ECD) by James Lovelock, 1957

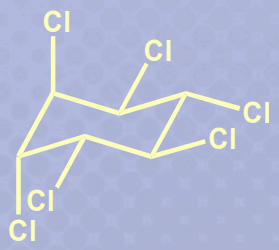
- Publishing of Silent Spring by Rachel Carson in 1962.



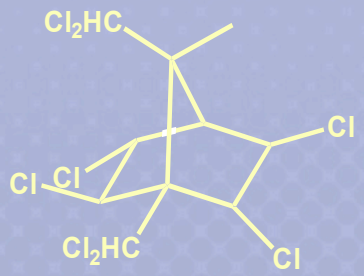
Early compounds of concern



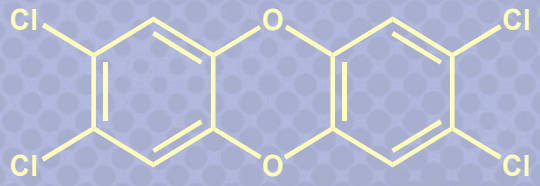
p,p'-DDT
1950-pres.: 2600kT



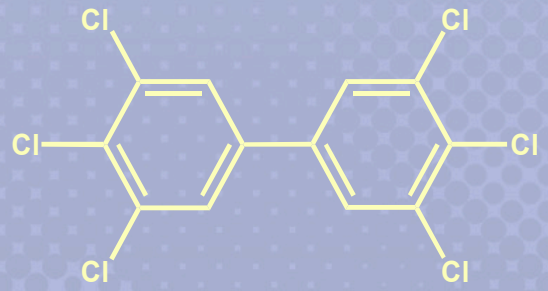
α-HCH
1948-1997: 10 000 kT



Tox 8/T2/26
1950-1996: 1300 kT

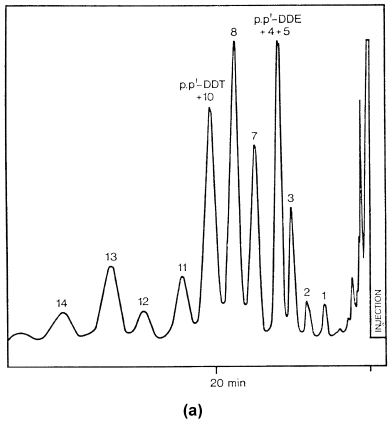


2,3,7,8-TCDD

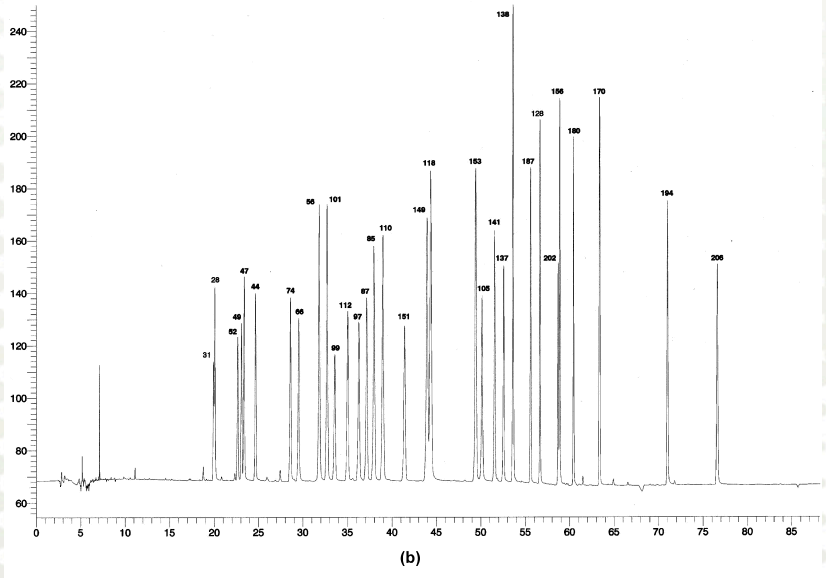


PCB 169
PCB, 1913-1992: 1300 kT

Further Technological Developments



(a)



(b)

Polychlorinated biphenyls (PCB): Separation on (a) packed and (b) capillary columns (DB-5 type of stationary phase).

Ref.: DeBoer & Law (2003) J. Chromatogr. A. 1000: 223-251

Early findings and events

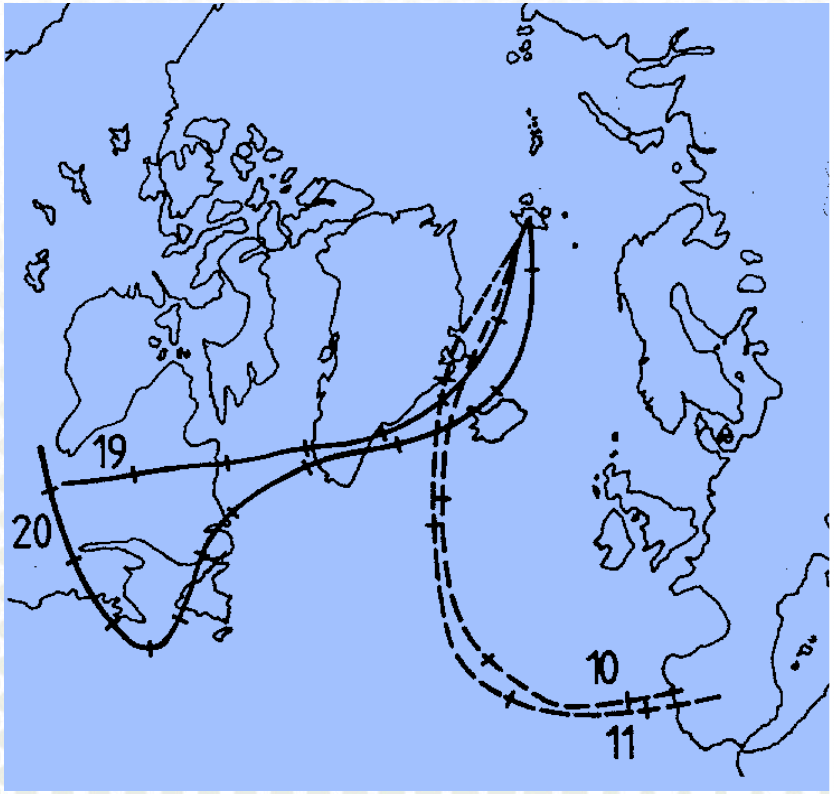
- 1962: Ratcliffe identified the connection between egg shell thinning and DDT usage (Nature, 1967).
- 1962: Silent Spring published (Carson)
- 1968 Yusho: Consumption of rice oil, contaminated with PCB/PCDF
- 1969: PCB detected in white tailed sea eagles (Jenssen, 1972)
- 1976 Seveso accident (80 kg PCDD/F released in Norhern Italy)
- 1984 Bophal, India (release of Methyl isocyanate and PCDD/F)

Regulation strategies

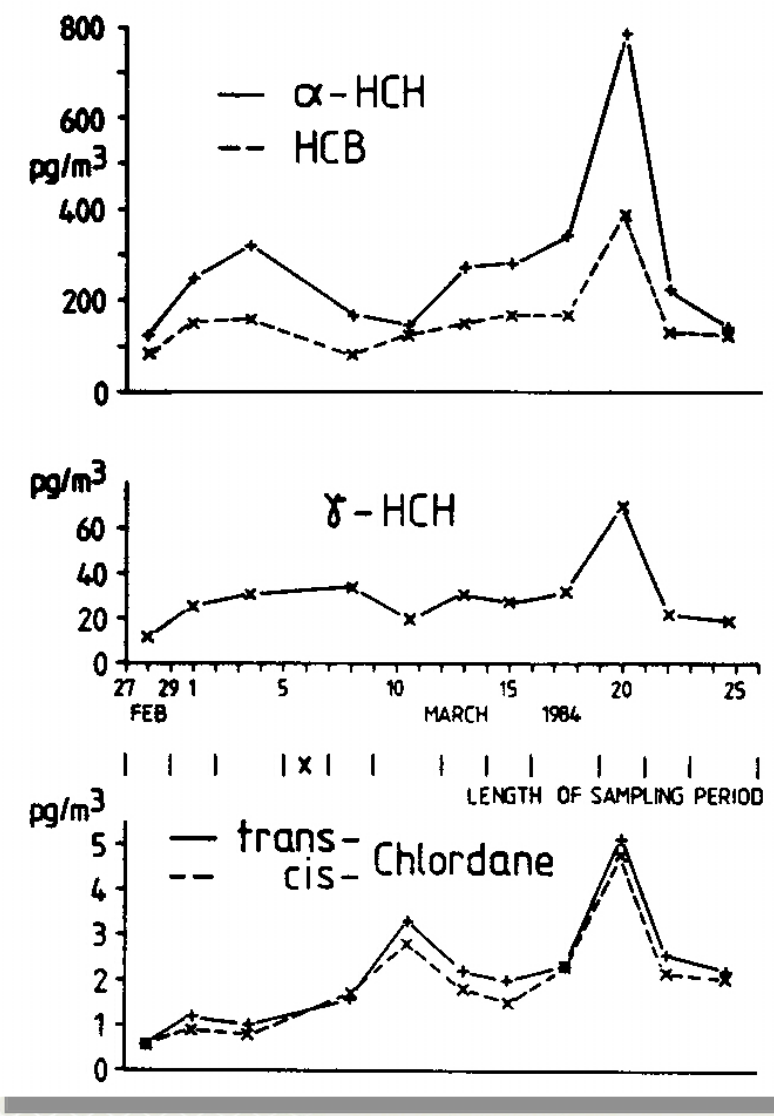
- Early regulatory considerations focused on local impact with minor regional implications
- National regulations in place already in the early 1970s for many compounds of concern
- First indications for regional distribution of POPs (atmosphere, sea currents, rivers) found I the late 1970.
- 1993 The Arctic Monitoring and Assessment Program established as a working group of the Arctic Council
- 1998 The Aarhus protocol includes POPS as priority compounds to the UN-ECE LRTAP Convention for transboundary pollutants.
- 2001 the UNEP Convention on global regulations of POPs ratified by the first nations (Stockholm Convention)

Hemispherical and Global dimensions.

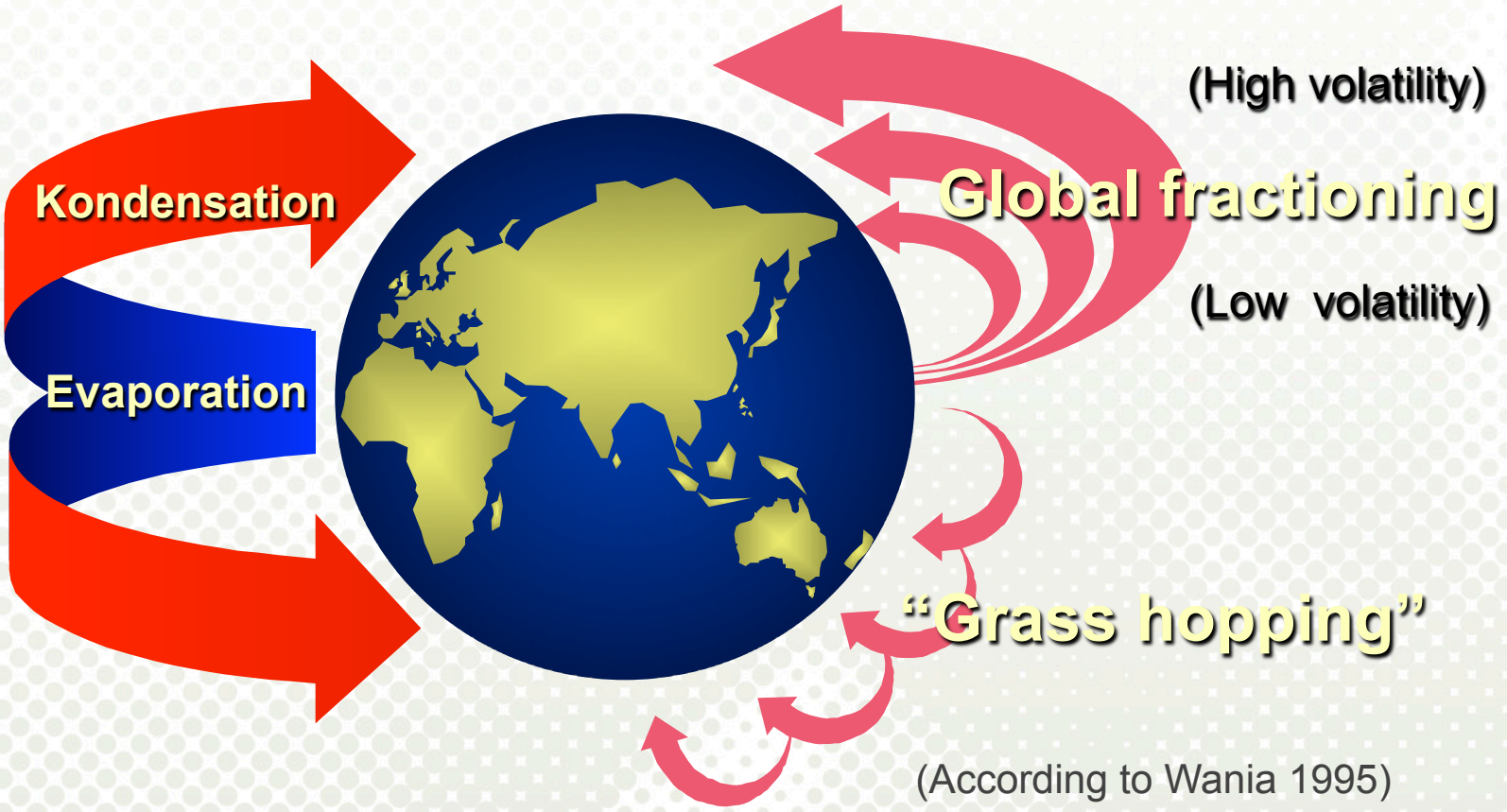
First evidence presented already in the early 1980s



(Oehme 1991

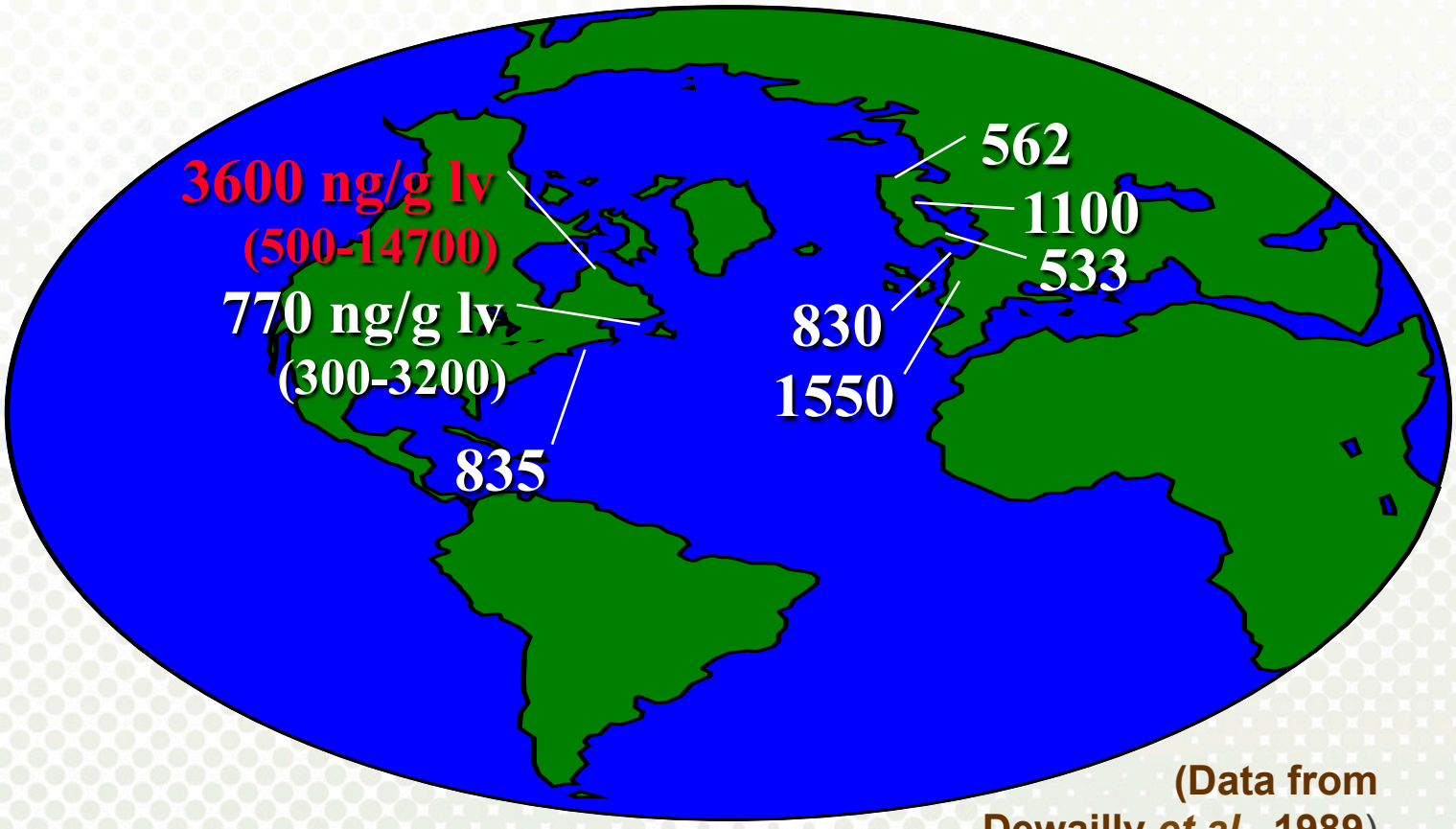


Atmospheric transport



(According to Wania 1995)

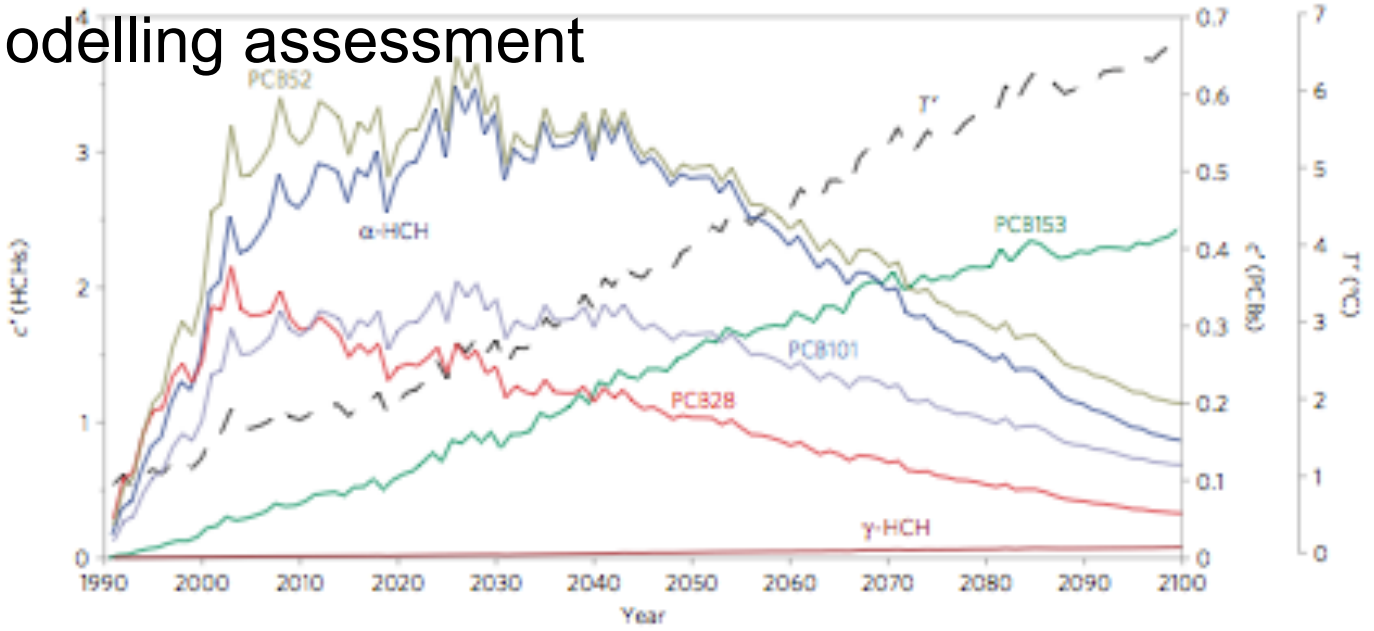
PCB in human breast milk samples



(Data from Dewailly *et al.*, 1989)

Todays situations

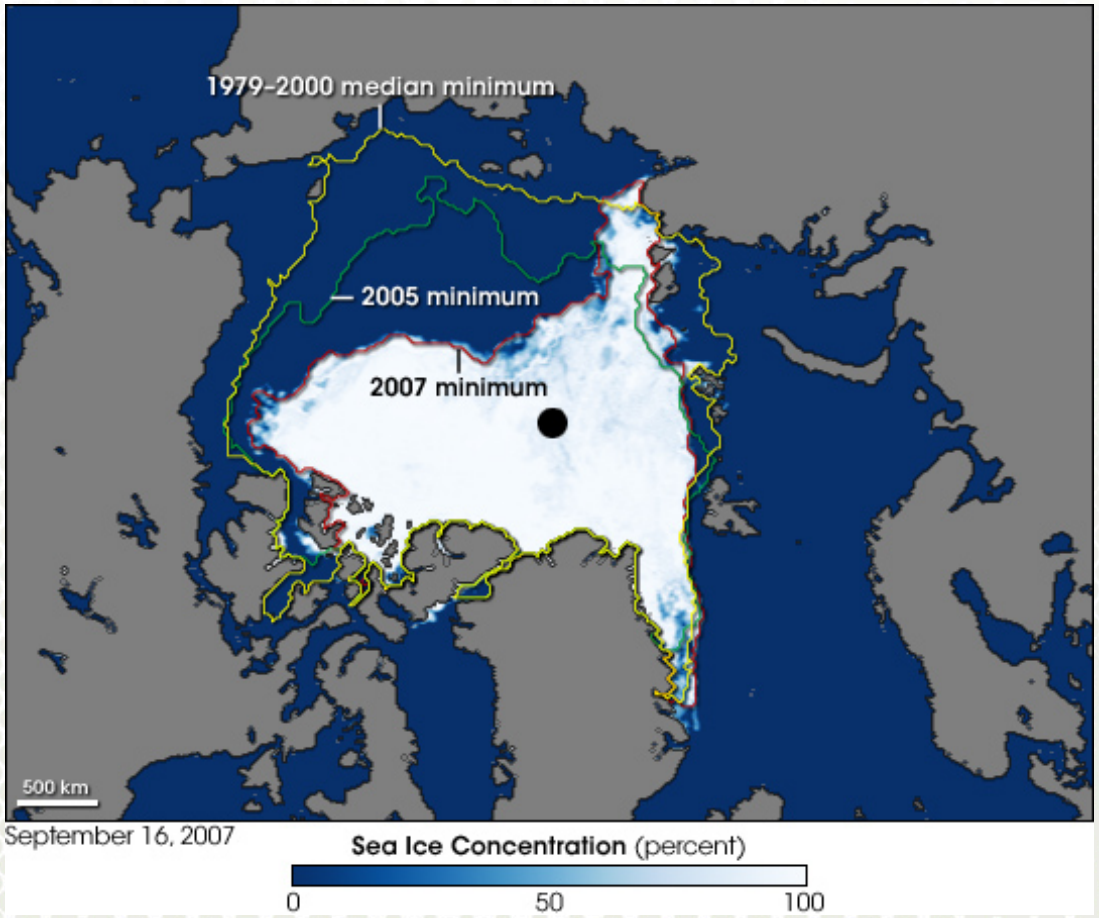
Modelling assessment



Zeppelin station (Svalbard) : POPs still present at measurable amounts, selected compounds are even showing concentration increase during the past decade, due to climate change influence (Ma et al. Nature Climate Change, 2011).

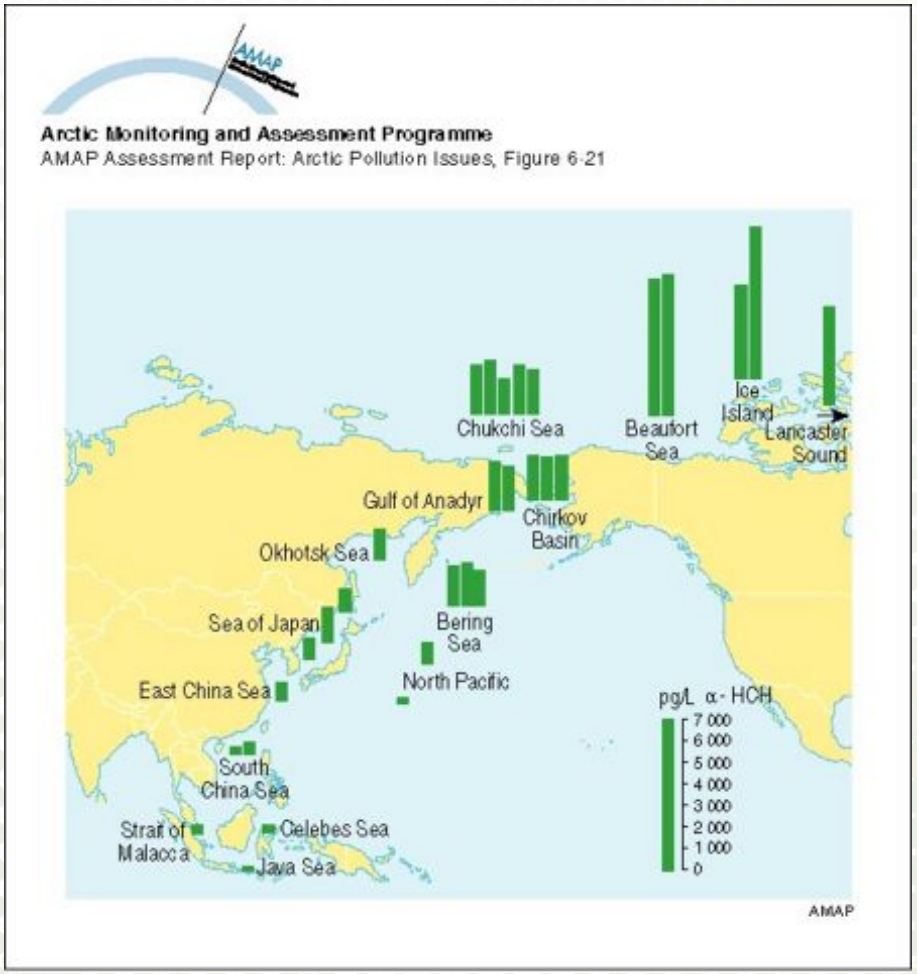
Todays situations: Regional implications

Arctic Climate change

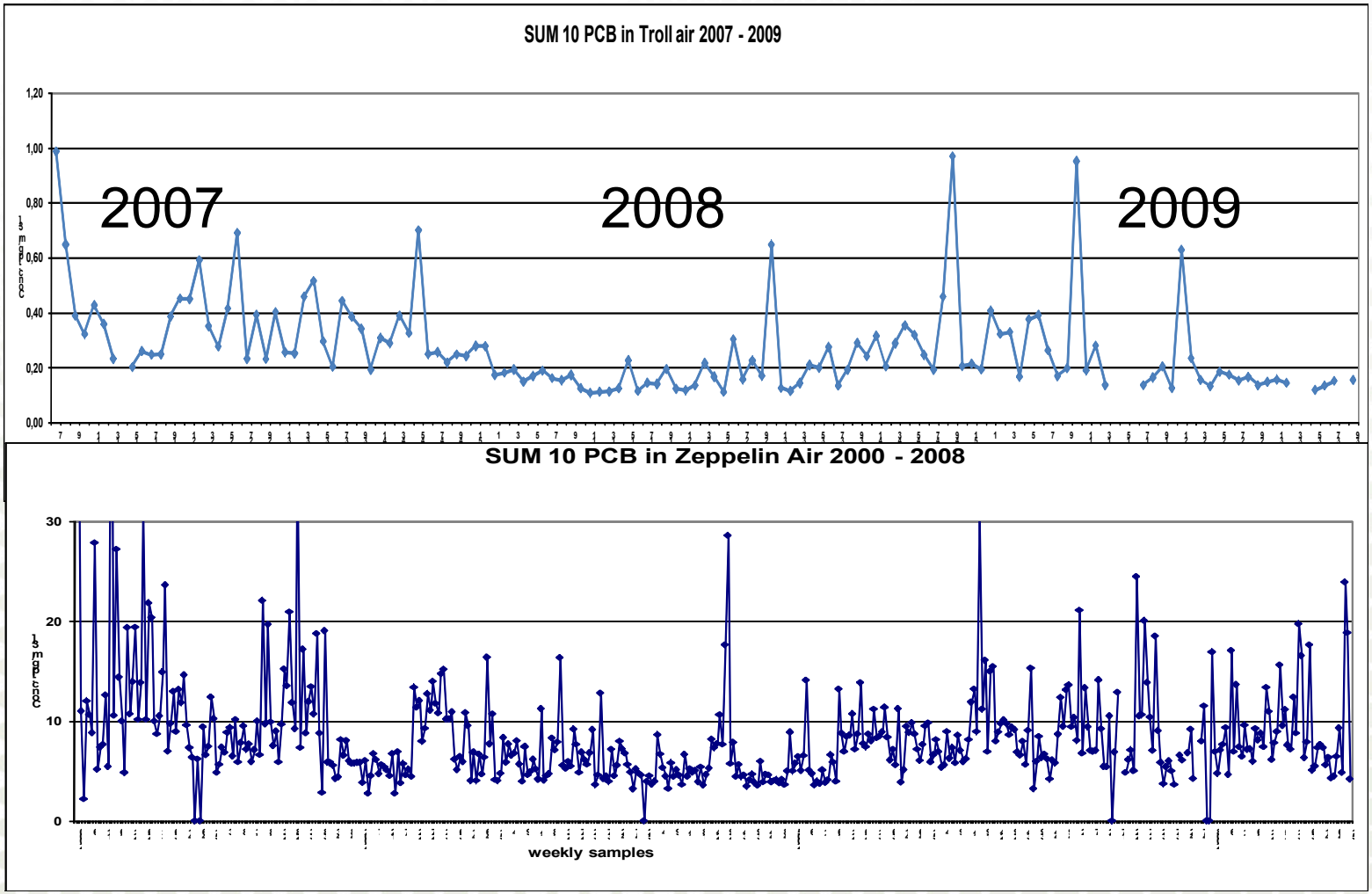


Hemispherical distribution

α-hexachlorocyclohexane (HCH) in seawater [ng/L]

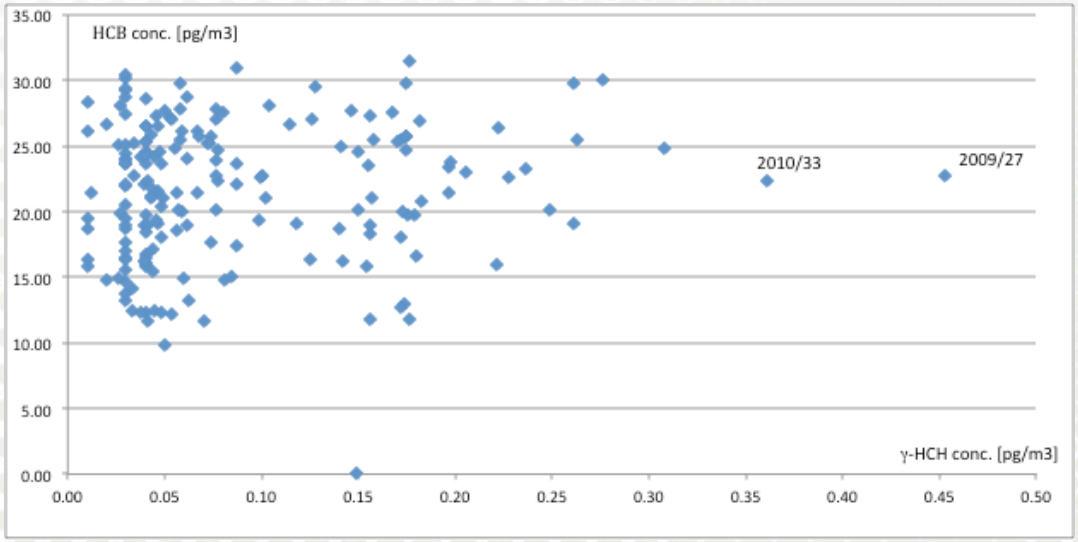


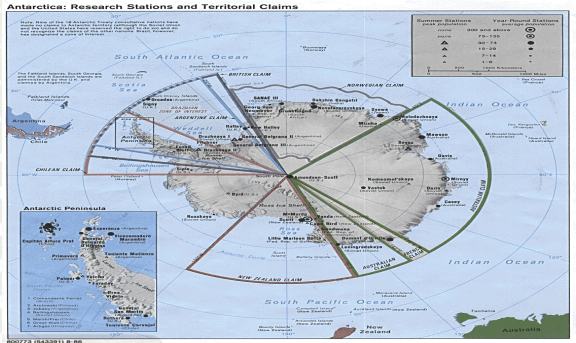
Polychlorinated biphenyls (PCB) concentration [pg/m^3]



Source elucidation and apportionment

POPs atmospheric monitoring at Troll (Antarctica), conc. [pg/m3]: 2007 - 2010

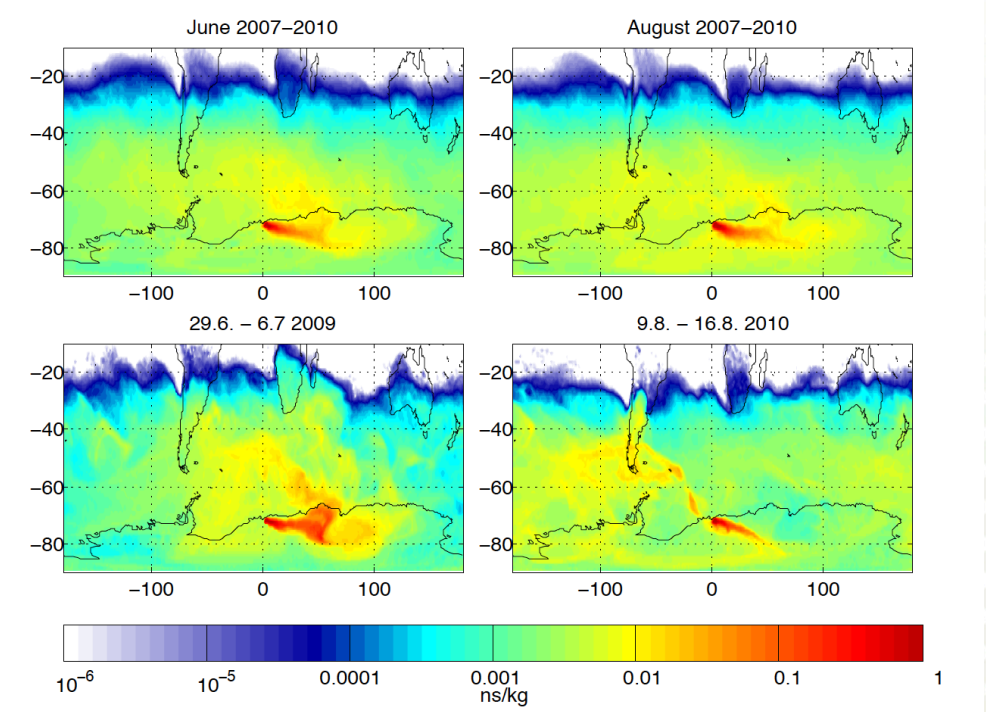




Source elucidation. Air mass Back trajectories

POPs atmospheric monitoring at Troll (Antarctica)

Week 2009/27



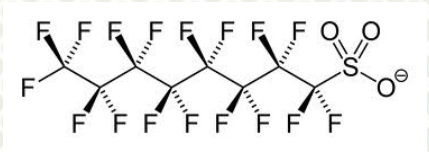
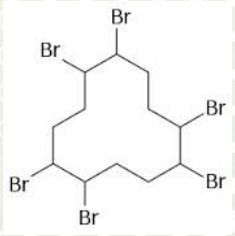
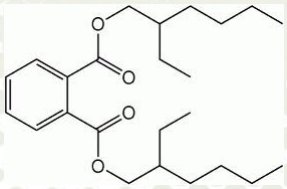
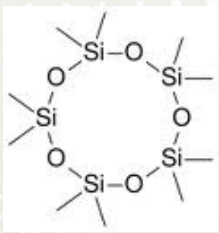
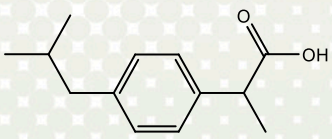
Week 2010/33

Footprint emission sensitivities calculated with FLEXPART (meteorological model)

New challenges

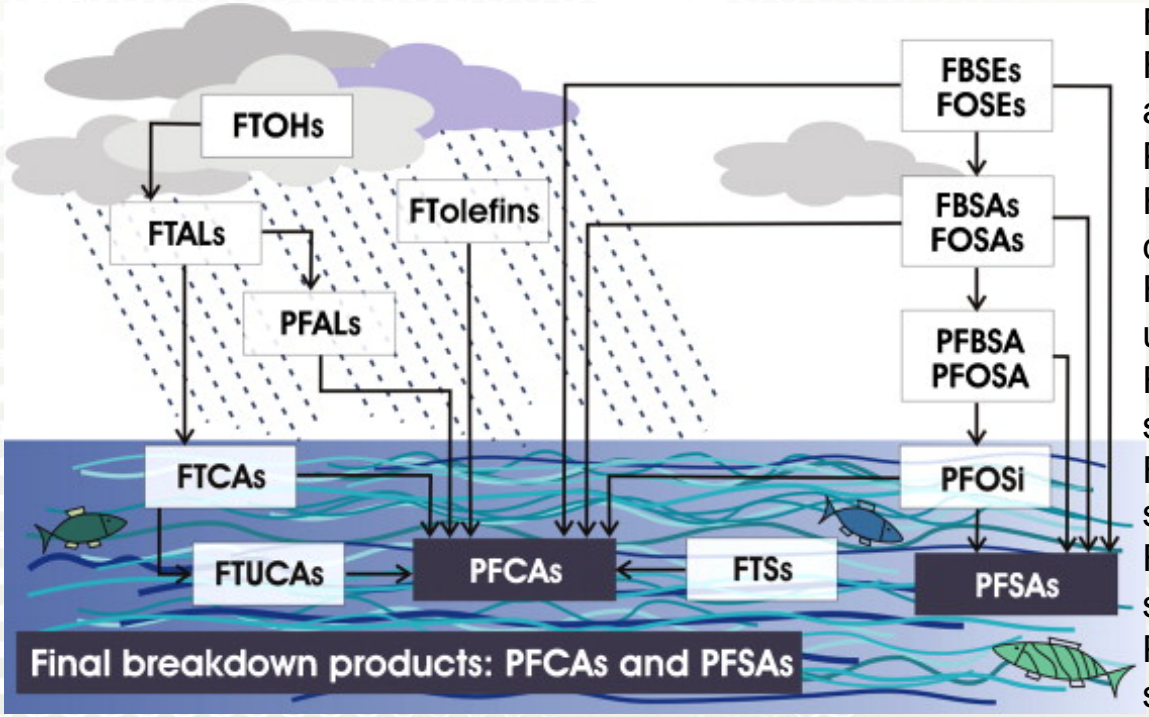
- The breath-taking technological development in chemical analytical methods and instrumentation continues – UPLC-Mass Spectrometry; GCxGC-ToF, UPLC-QToF, Proton-Transfer-reaction-MS, -Ion-Mobility-MS …….
- New and emerging POPs identified

  Perfluorinated alkylated substances (PFAS)
  Pharmaceutical residues and personal care products
  Flame retardants (brominated, phosphorous containing)
  Additives (plasticizers, softeners)

New Transport and distribution processes

- Perfluorinated substances



FTOH: Fluoro-Telomer OH
FTAL: Fluoro-telomer-aldehyde
PFAL: Perfluoro-Al
FTCA: Fluror-telpmer-caboxylic acids
FTUCA: Fluor-Telomer unsaturated carboxylic acids
FBSE: Fluorobutan-sulfonamido-ethanol
FOSE: Fluoro-Octan sulfonamido-ethanol
FBSA: Fluoro butan sulfonamide
PFOSi Perfluoro otan sulfinate

Ref. Jahnke & Berger (2009) Trace analysis of per- and polyfluorinated alkyl substances in various matrices—How do current methods perform? J. Chromatogr. A. 1216/3: 410-421

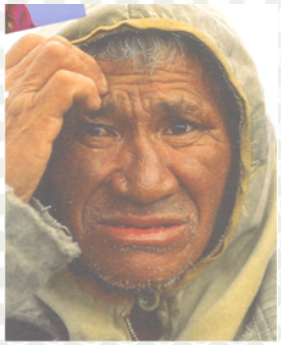
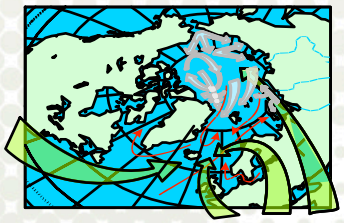
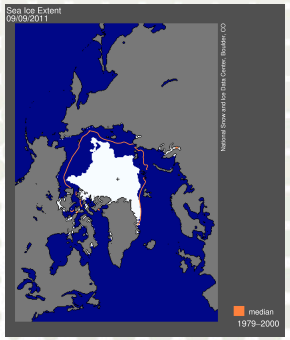
New challenges

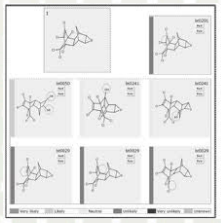
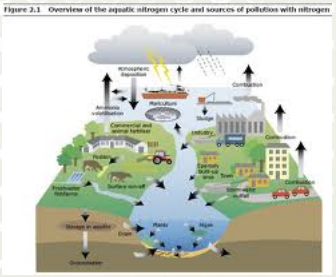
- UNEP definition of “POPs” need revision.
- New sophisticated methods for ultra-trace levels of emerging POPs not suitable for monitoring and assessments due to:
  - costs
  - Not applicable for multi-compound analysis
  - Sample preparation often difficult to automatise (Sample throughput).
- **Priority research:** Adjust chemical analytical methods for the combination with environmental toxicology assessments (e.g., aquatic toxicology)

Source: Frauenhofer institute, IME, Aachen (Germany)

Perspectives

- Global and applied/ interdisciplinary aspects are currently dominating international POP research.
  - ✓ Global effects of POP releases
  - ✓ Distribution and transport pathways
  - ✓ Effects of Climate change on distribution and Fate of POPs
  - ✓ Transformation pathways and environmental stability under different conditions.
  - ✓ Sources and environmental characterization of new and emerging contaminants

Conclusions

- POPs research ongoing for more than 55 years
- POPs still present in the global environment
- 50 years ago: regulations of primary emissions (industry, agricultural emissions), today: secondary source predominant (remissions, vaporization from former application sites)
- Technological development contributes to the detection of new POP-like contaminants
- Todays analytical methods / monitoring approaches not suitable anymore for the environmental control of such a large number of priority chemicals
- New strategies required ….. Any ideas?

Aknowledgement

I thank numerous colleagues and students for open-mind discussions on the above scientific topics:

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The AMAP POP expert group members
The SWIPA expert group
Fellow experts from the UNEP WEOG group (Stockholm convention)

Thank you for your attention