Thoughts on the Cold Condensation and Global Fractionation of Persistent Organic Pollutants

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Objectives

- Define Cold Condensation (»CC«) and Global Fractionation (»GF«) and analyze their interplay.

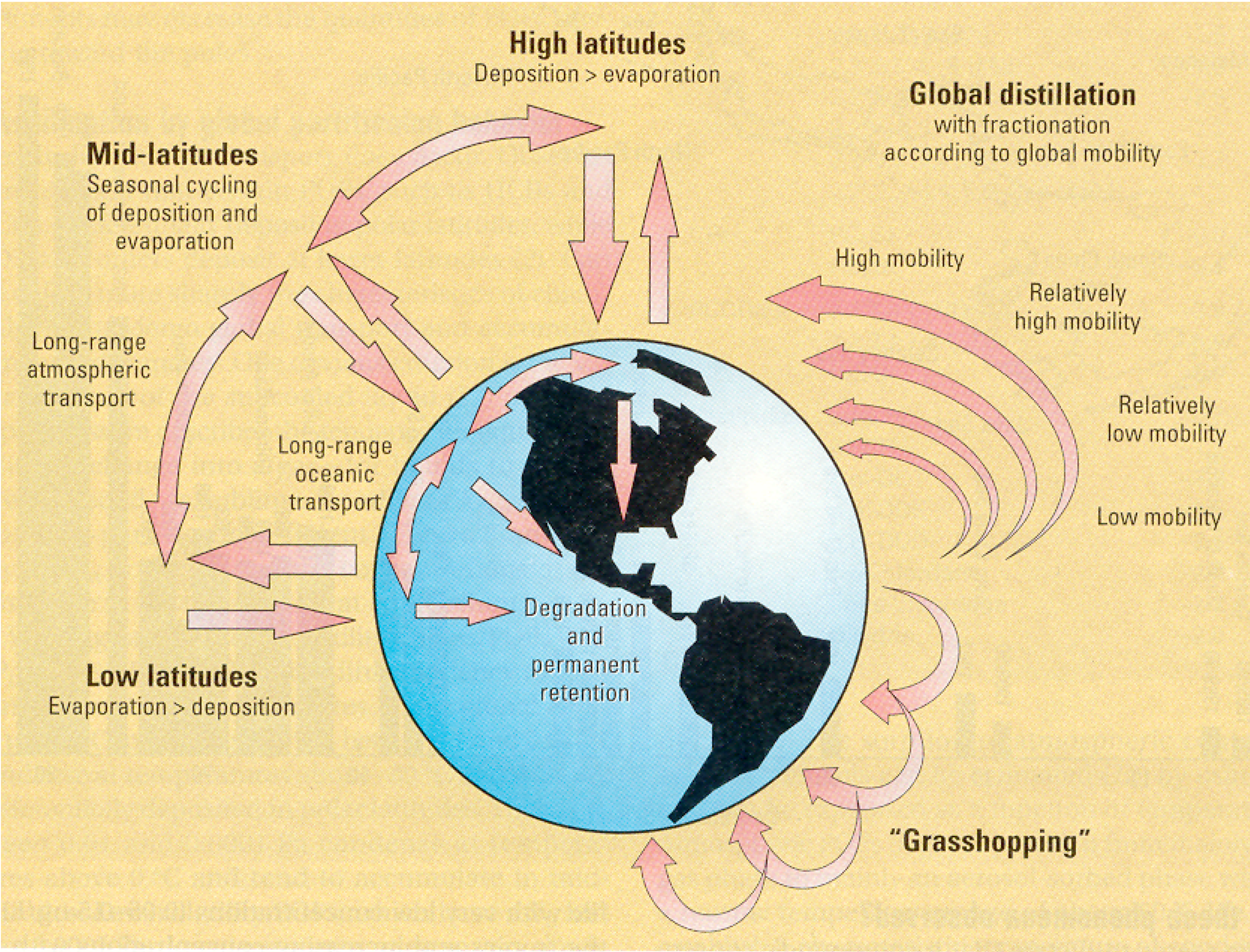
- Present suggestions for improving the interface between POPs science and politics.

History of CC and GF (I)

- Goldberg (1975): »global distillation«
  - Mobilisation and movement of SOCs
- Ottar et al., 2nd Symposium on Arctic Air Chemistry (1980): »cold trap«, »cold finger«
  - Influence of low temperatures
- Risebrough (1990): »global chromatography«
  - Different transport efficiencies of different compounds

History of CC and GF (II)

- Wania and Mackay (1993, 1996): »global fractionation«



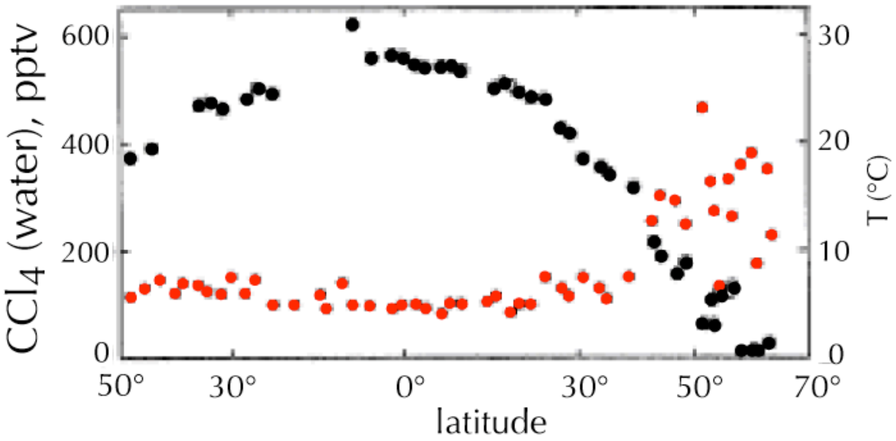
F. Wania, D. Mackay, Environ. Sci. Technol. 30 (1996), 390A–396A

Definition of CC and GF

- „Absolute amounts of HCB were found to increase with increasing latitude, suggesting that this compound is undergoing cold condensation and global fractionation.“
- CC refers to **individual** chemicals.
- GF refers to **several** chemicals in comparison.
- CC contributes to GF but does not fully explain GF.

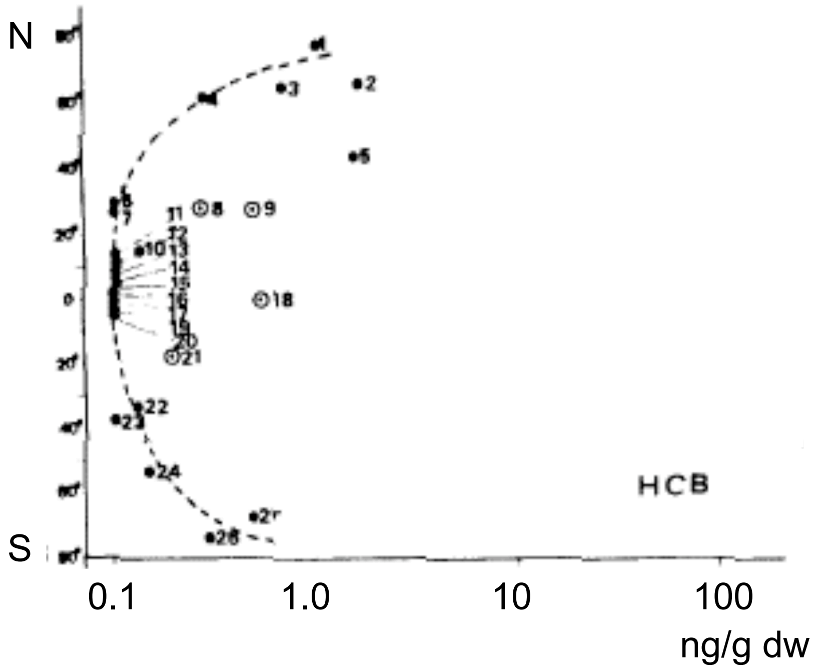
Cold Condensation

CCl_4 measured in ocean water



R.J. Hunter-Smith et al., Tellus 35B (1983), 170–176

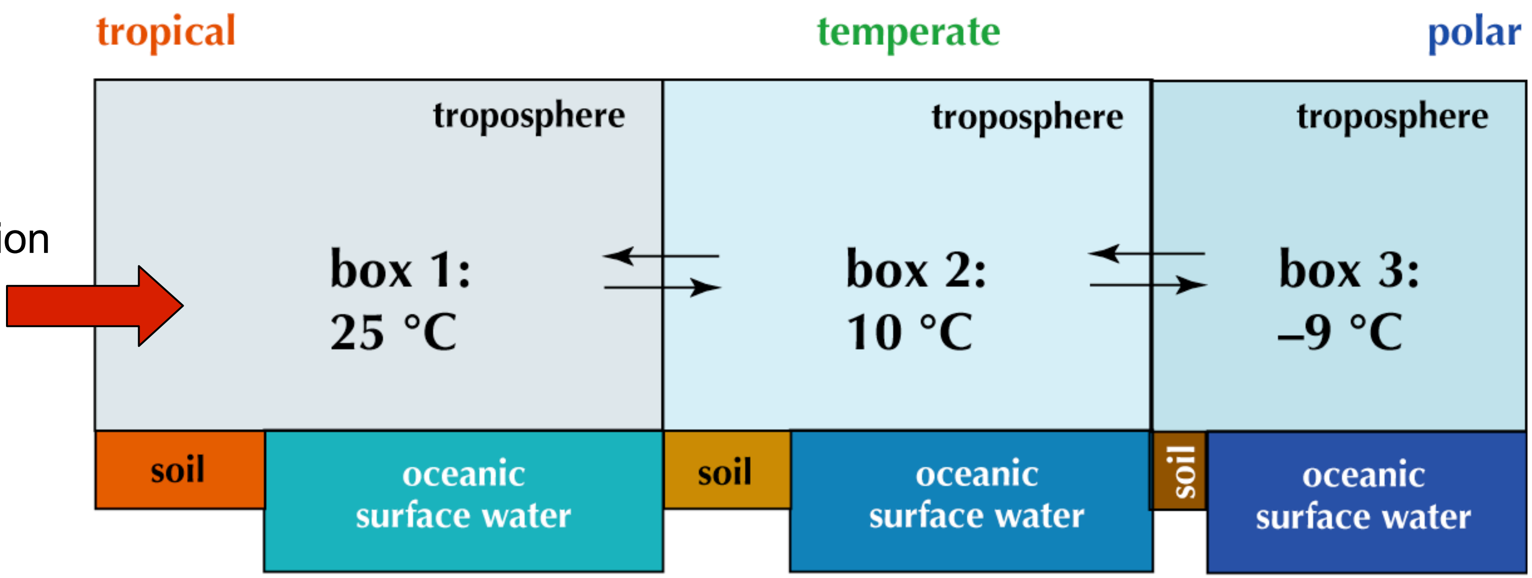
HCB measured in foliage



D. Calamari et al., Environ. Sci. Technol. 25 (1991), 1489–1495

Cold Condensation in a Simple Model

- Model 1: a 3-box model with different temperatures



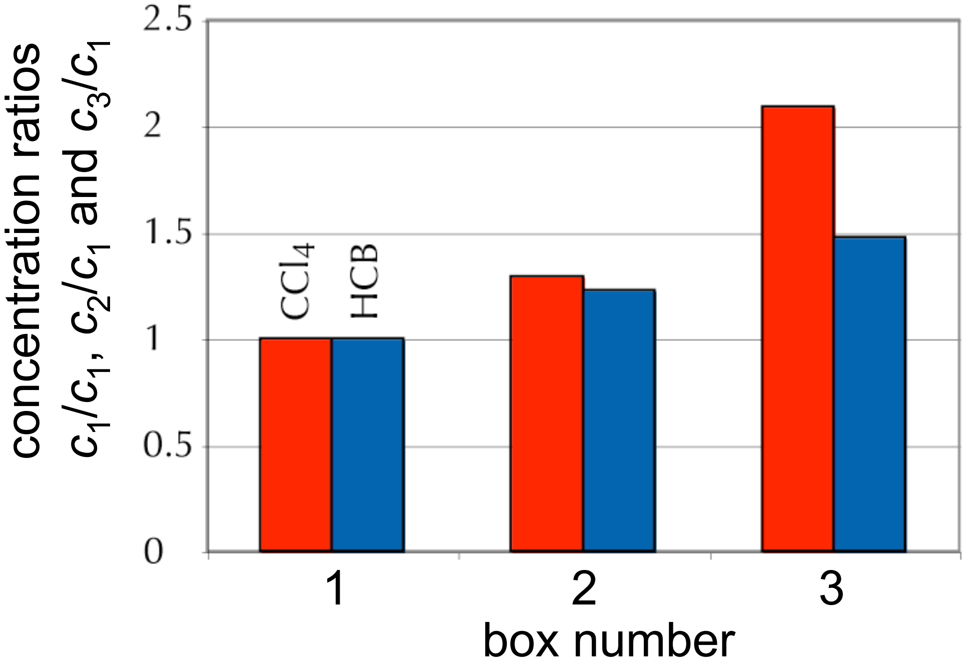
Based on:
T. Smieszek, P. Peter, U. Müller-Herold, M. Scheringer, under review for Ecological Modelling.

- Assumptions:
  - steady state
  - instant equilibrium between soil, water, air
  - diffusive exchange between boxes
  - temperature-dependent degradation rate constants and Henry's law constants (HLC)

Model 1
VOCs

Cold Condensation: CCl_4 and HCB

- Concentrations in soil relative to zone 1.



- Inverted concentration profiles in surface media,

Model 1
VOCs

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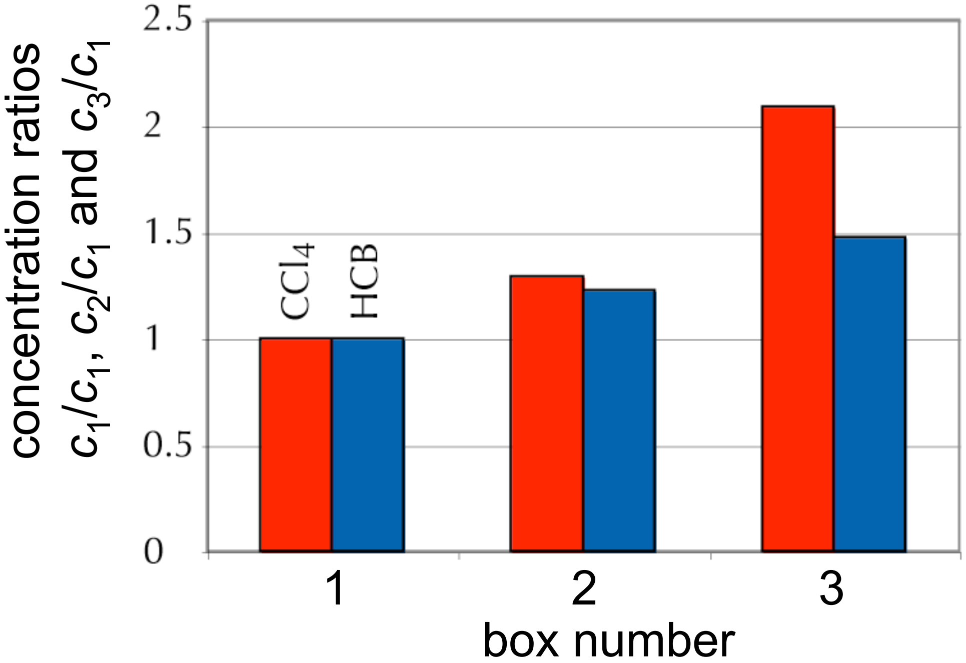
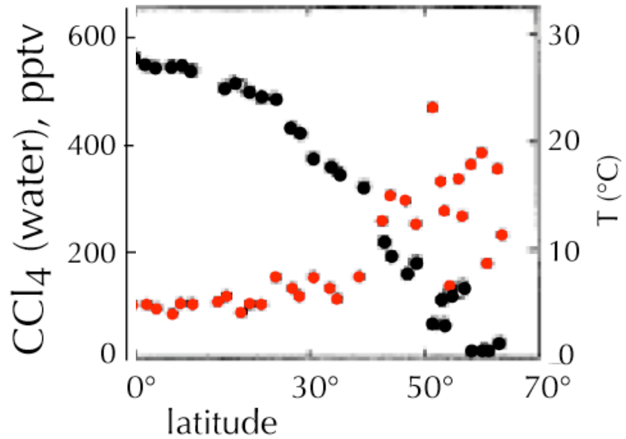


measured data:
CCl_4 in ocean water



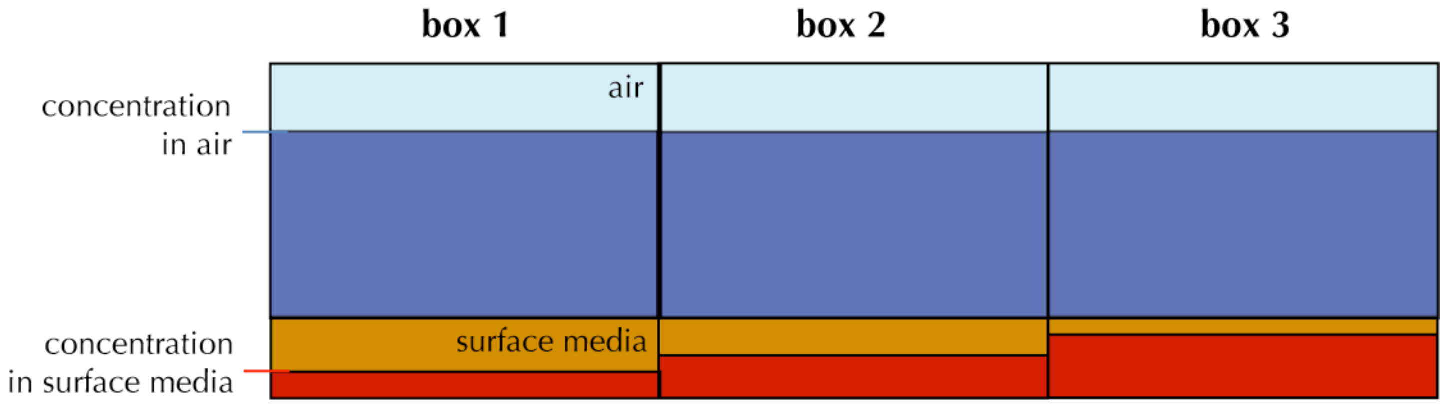
R.J. Hunter-Smith et al., Tellus 35B (1983), 170–176

- Inverted concentration profiles in surface media, in accordance with experimental findings.

Model 1
VOCs

CC of Volatile Compounds

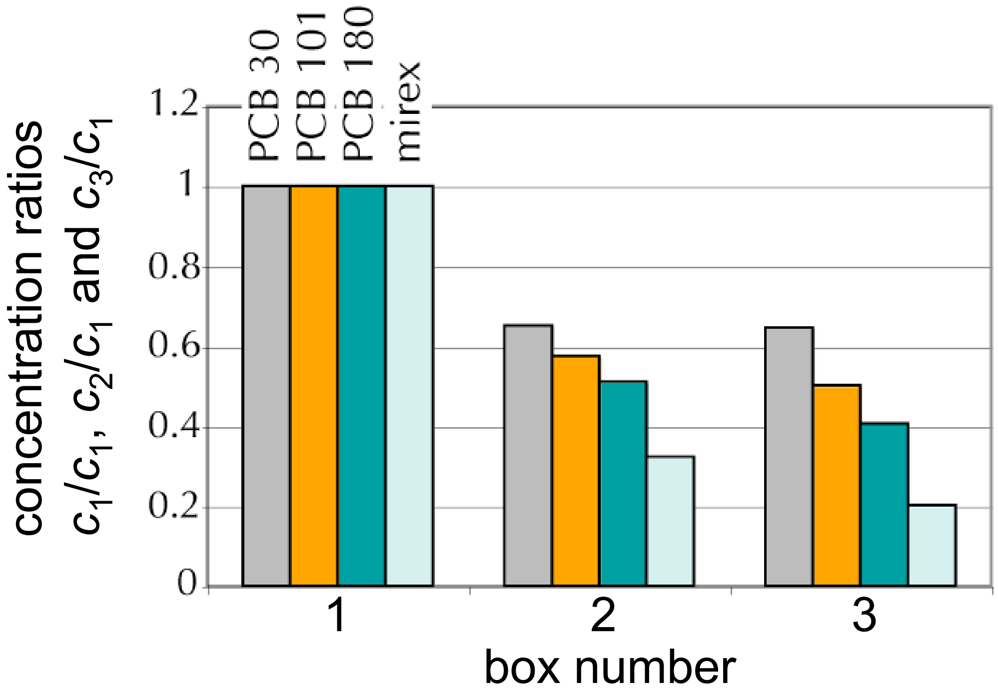
- Chemical evenly distributed in air
- Inverted concentration profile in surface media
- Purely thermodynamic effect: $H(T)$, $K_{air\text{-}soil}(T)$



Model 1
SOCs

CC of Semivolatile Compounds (I)

- PCB 30, PCB 101, PCB 180, mirex

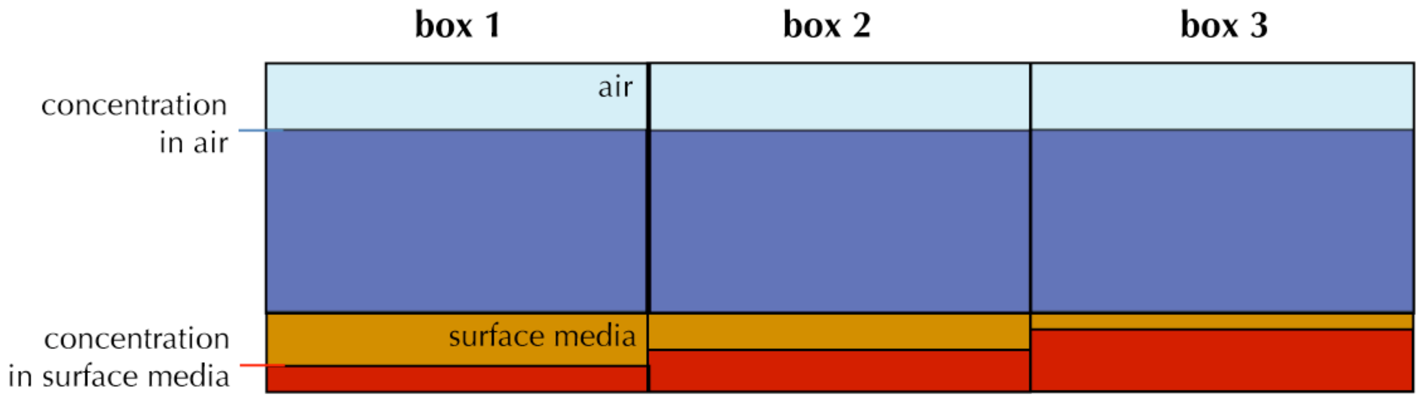


- Decreasing concentrations in soil,
  more pronounced for less volatile compounds.

Model 1
SOCs

CC of Semivolatile Compounds (II)

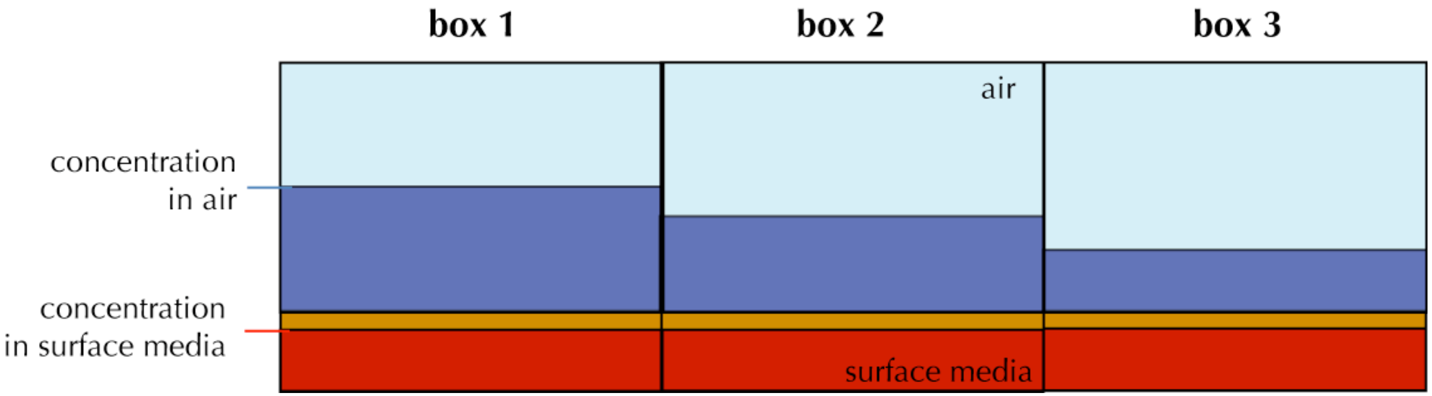
- CC of volatile compounds:



Model 1
SOCs

CC of Semivolatile Compounds (II)

- First scenario: SOCs, no loss in surface media



evenly distributed in surface media – LRT high!

Model 1
SOCs

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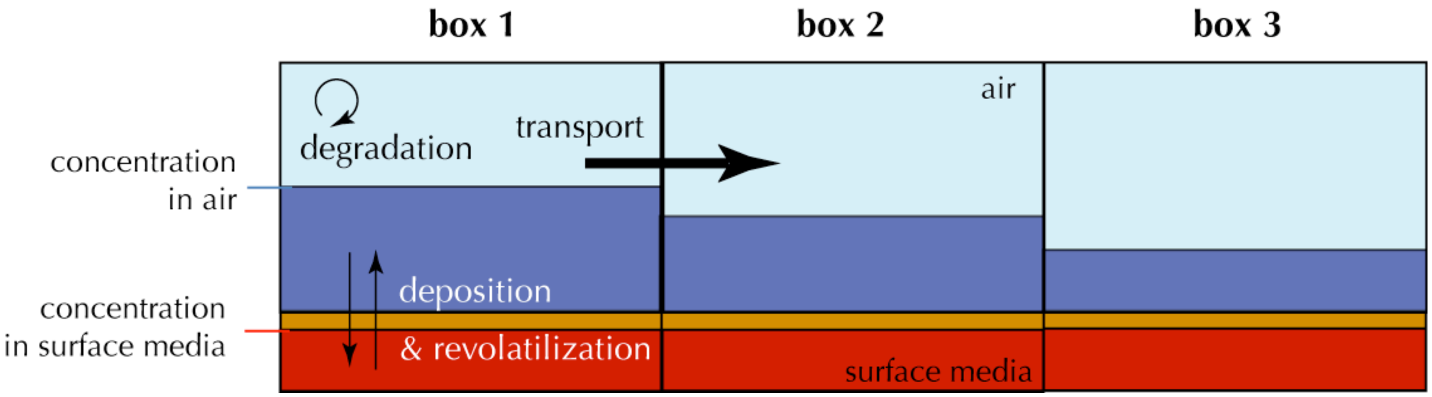

evenly distributed in surface media – LRT high!

- **Spatial distribution determined by loss versus LRT.**

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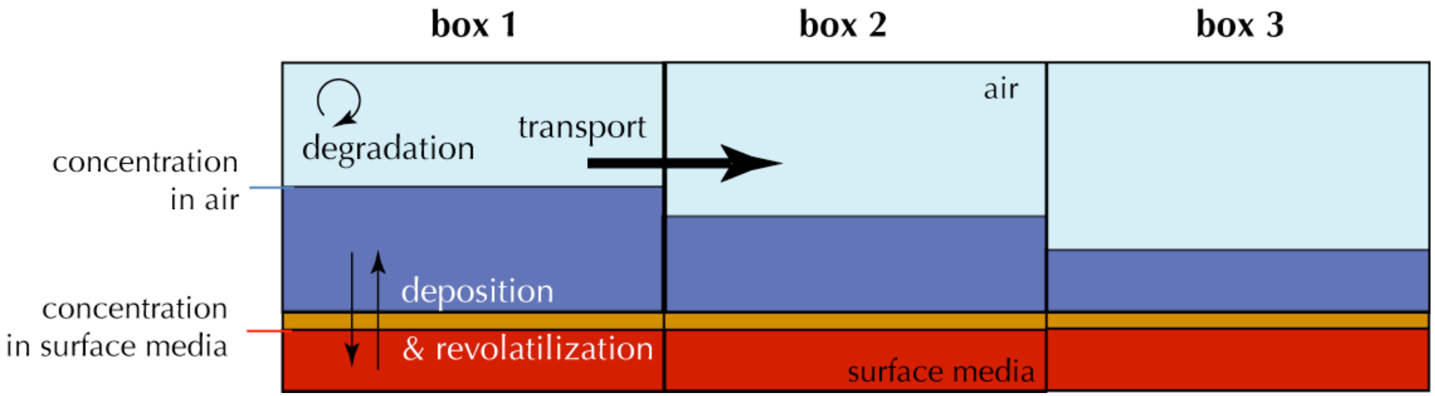
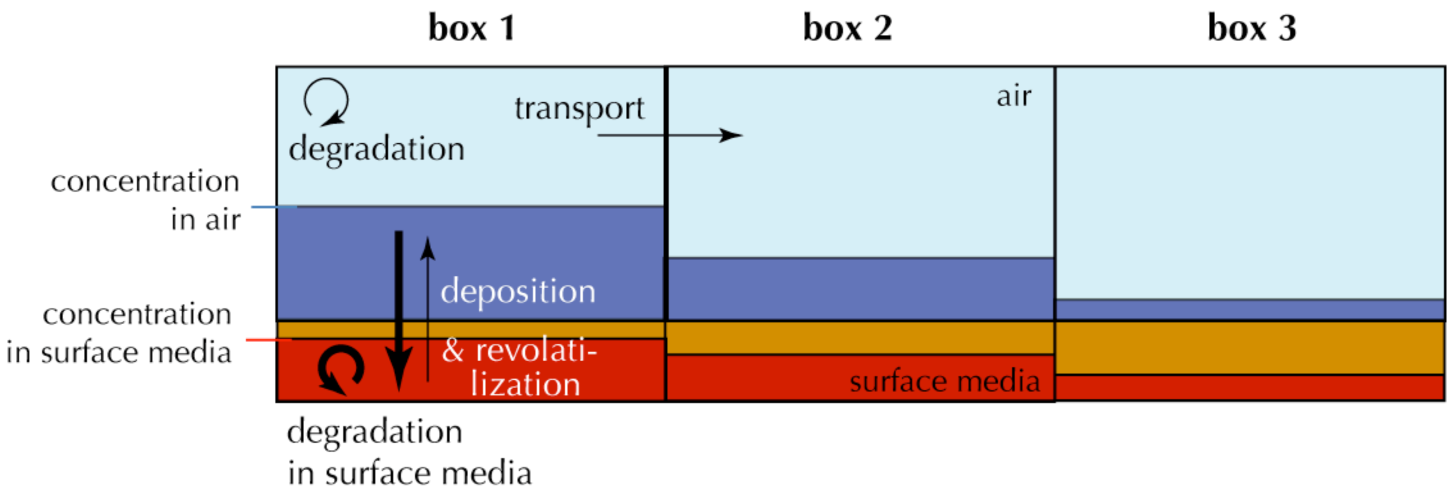


evenly distributed in surface media – LRT high!

- **Spatial distribution determined by loss versus LRT.**

- Second scenario: with loss in surface media



decreasing in surface media – LRT reduced.

CC of Semivolatile Compounds (III)

- In a steady-state model:
  low vapor pressure alone does not reduce LRT!

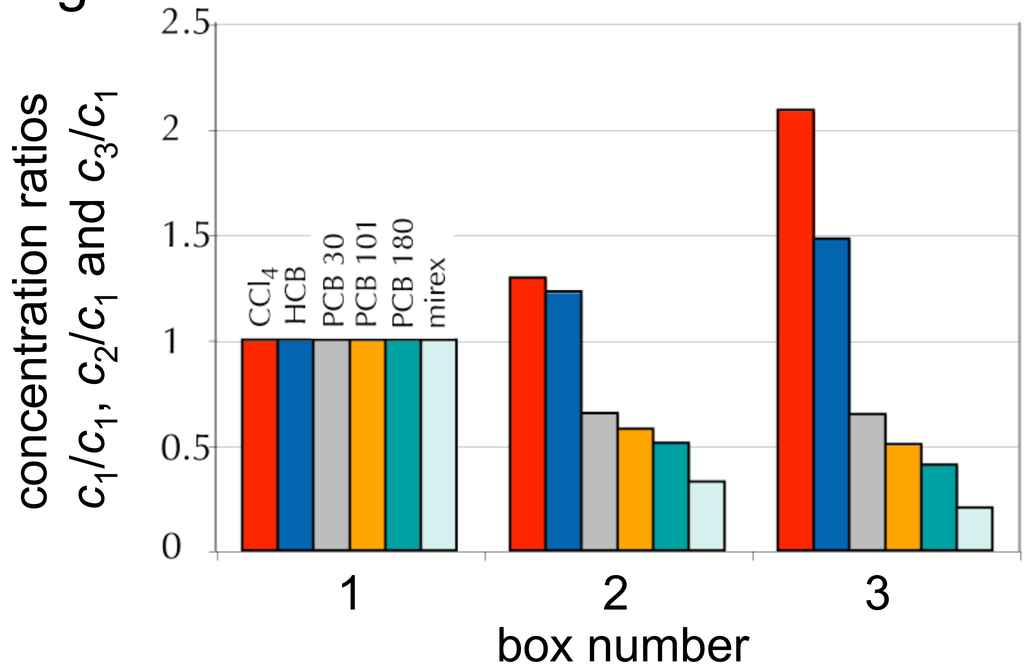
- Low vapor pressure in combination with degradation in surface media leads to reduced LRT and decreasing concentrations.

- Time-to-steady state: many decades;
  much longer than for volatile compounds.

Model 1

CC Contributing to GF

- Comparison of volatile and semivolatile compounds
  - fraction 1: CCl_4 and HCB; inversion
  - fraction 2: PCBs 30 and 101; absolute concentrations decreasing, fractions among SOCs increasing
  - fraction 3: PCB 180, mirex; absolute concentrations **and** fractions decreasing



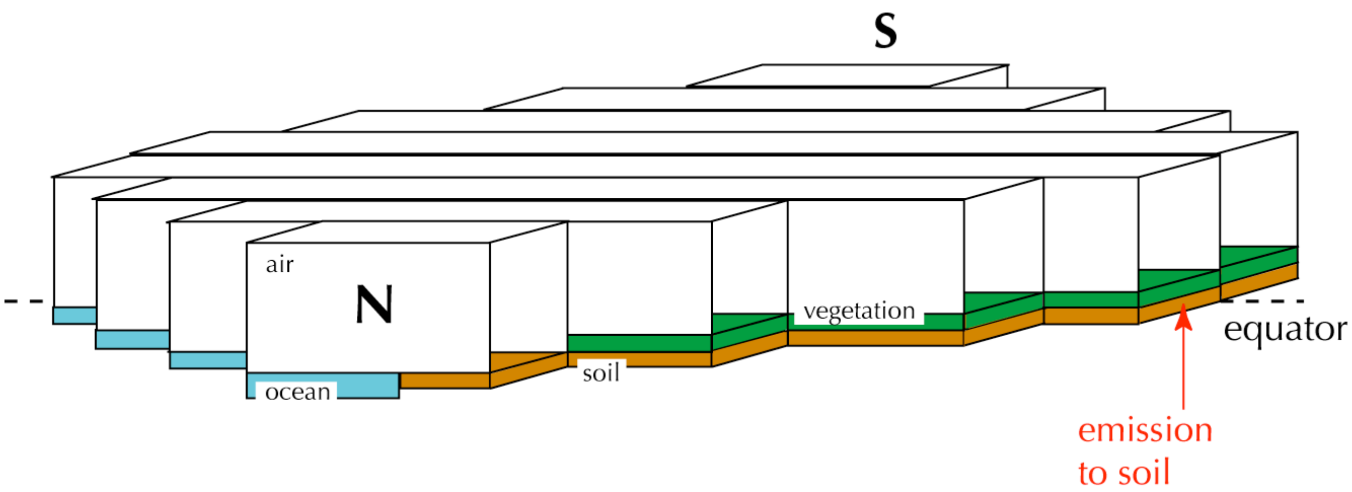
Results and Open Questions from the 3-Box Model

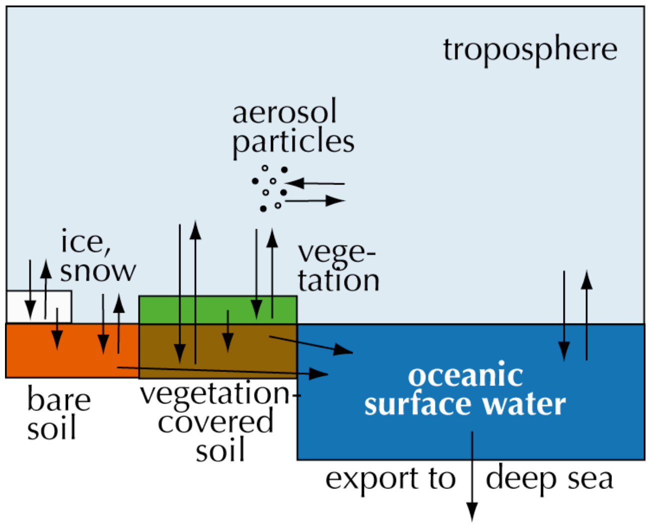
- CC of volatile compounds driven by $H(T)$, $K_{air\text{-}soil}(T)$.
- **Two drivers** of CC and GF of semivolatile compounds: (1) low vapor pressure, (2) loss in surface media.

- How does the fractionation pattern change over time?
- More detailed understanding of the influence of volatility versus degradability?

Model 2: CliMoChem

- Dynamic model (level IV).
- Different temperature, vegetation cover etc. in different latitudinal zones.
- Here: 10 zones, pulse release of PCBs 28, 101, 180 to soil of the zone north of the equator.

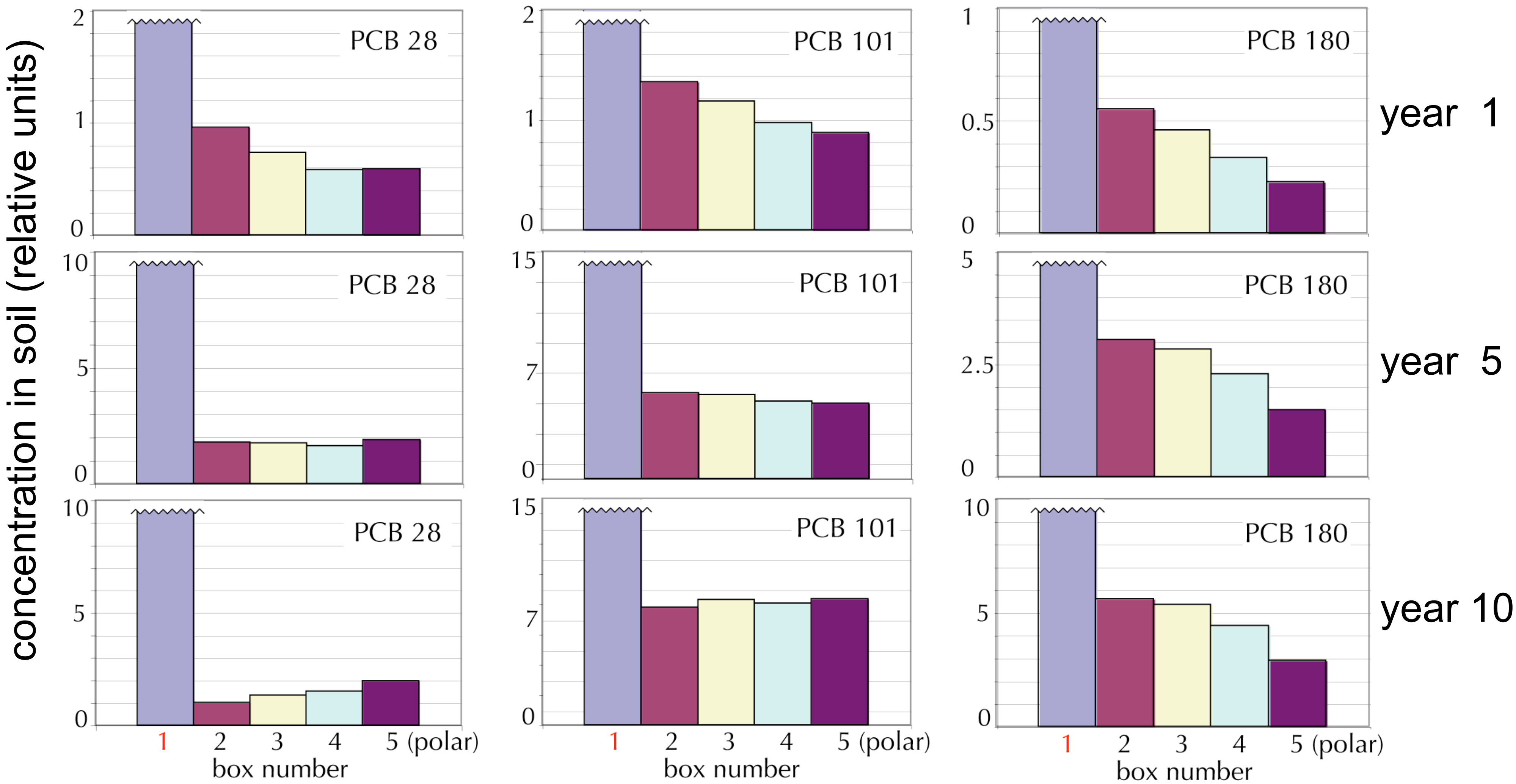




Model 2

Temporal Development of GF

✦ Spatial concentration profiles of PCBs as function of time



✦ Additional contribution to GF: **degradability differences**

Model 2

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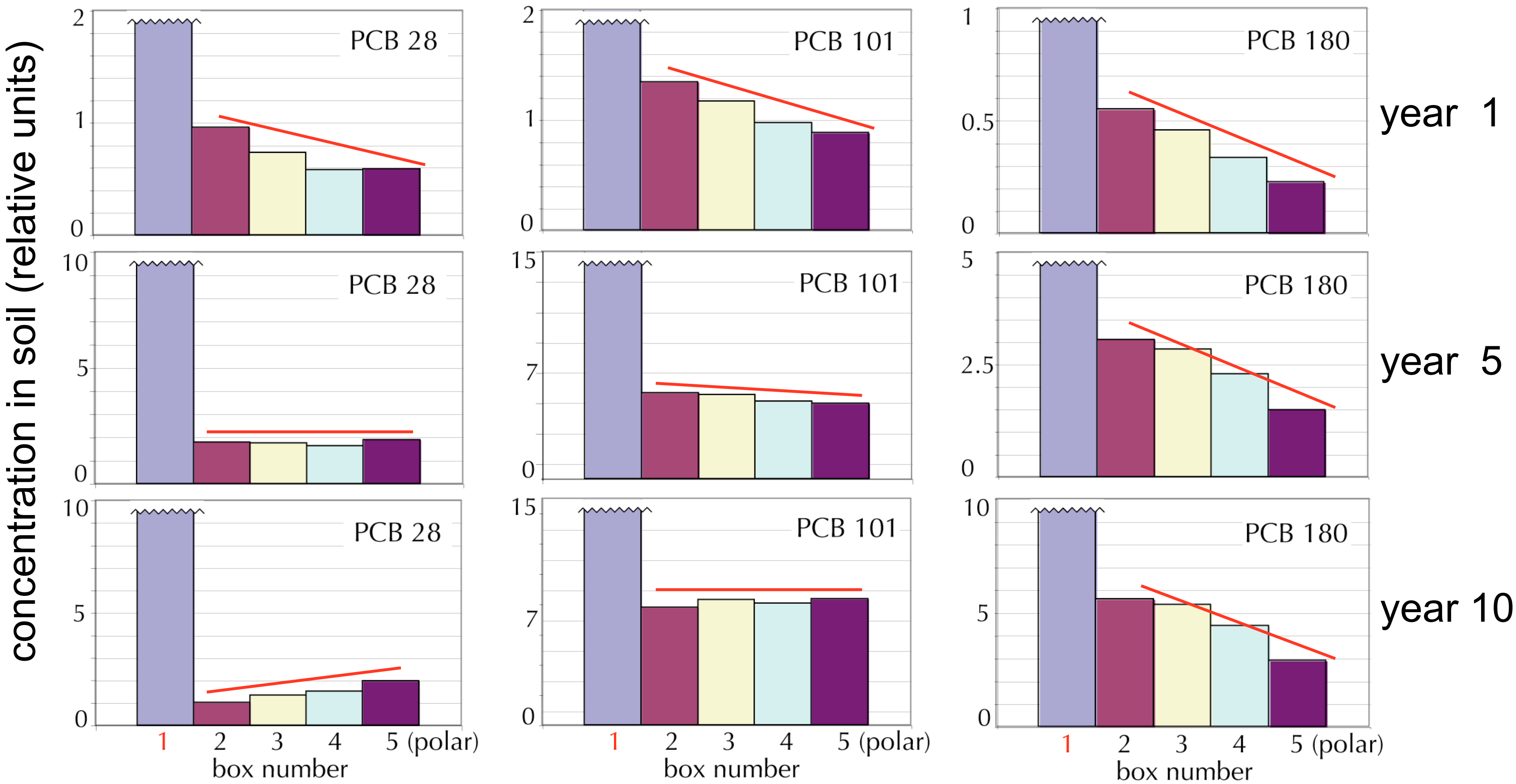
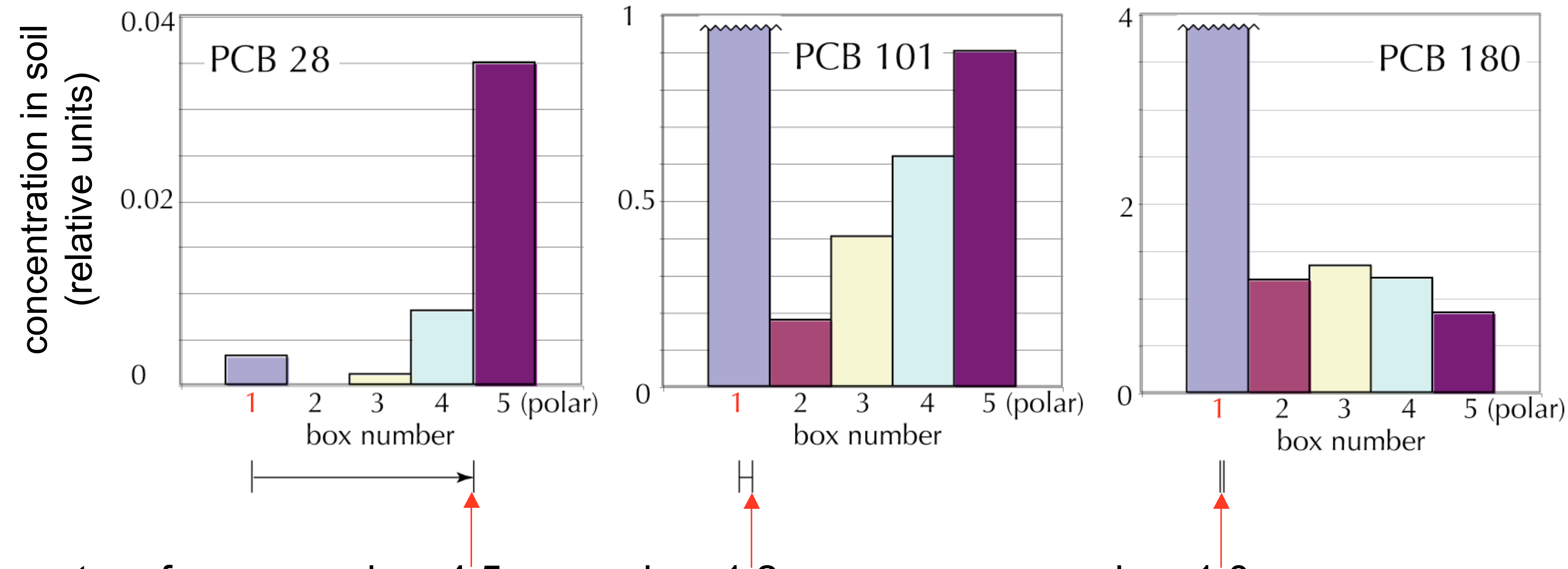


✦ Additional contribution to GF: **degradability differences**

Model 2

GF in CliMoChem (I)

50 years after pulse release to zone 1



center of mass at t = 50 y | box 4.5 | box 1.2 | box 1.0

- Moving center of mass through degradation in warmer zones; faster for lighter, slower for heavier PCBs.

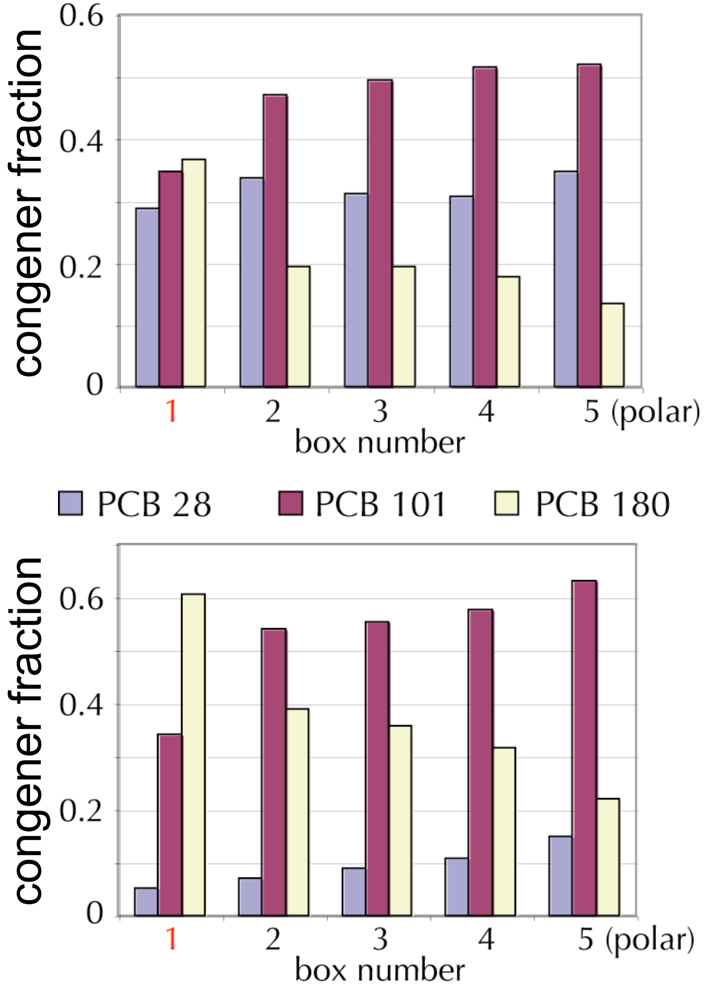
Model 2

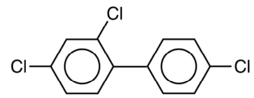
GF in CliMoChem (II)

Congener fractions of total PCB soil concentrations

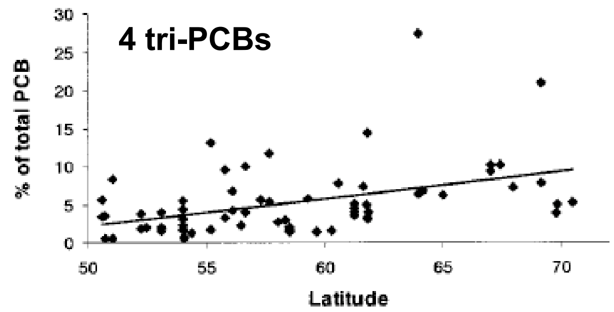
year 1

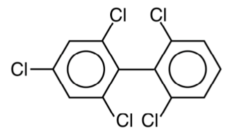
year 10



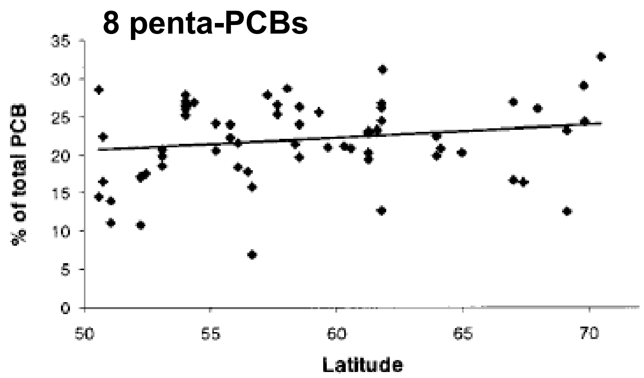


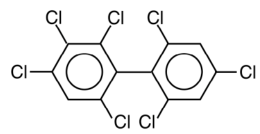
PCB 28



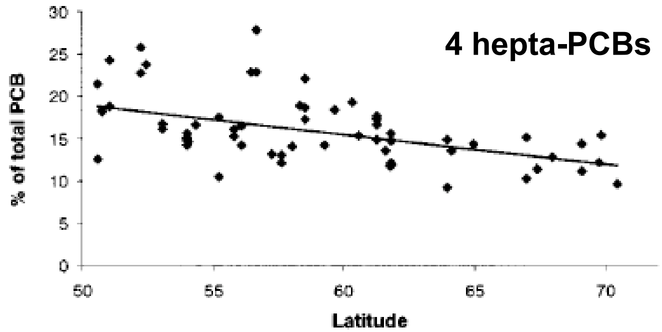


PCB 101





PCB 180



S. Meijer et al., ES&T 36, 2146–2153 (2002)

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Swiss Federal Institute of Technology Zurich

Open Questions from CliMoChem

- Transport efficiency:

  removal in given zone vs. **transfer** to next zone.

Model 2

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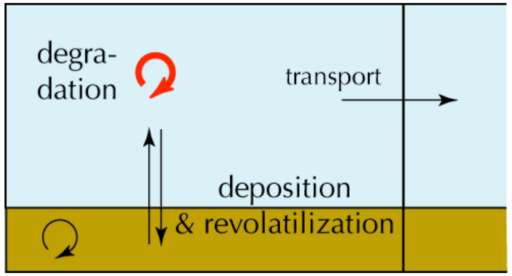
- Removal processes:

  - **degradation** in air: reaction with OH radicals



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Model 2

Open Questions from CliMoChem

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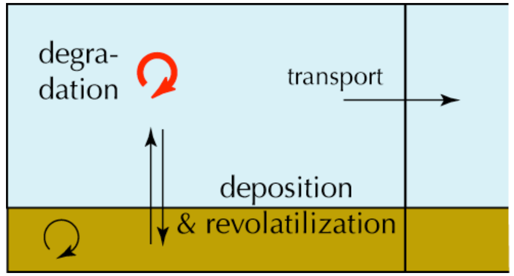
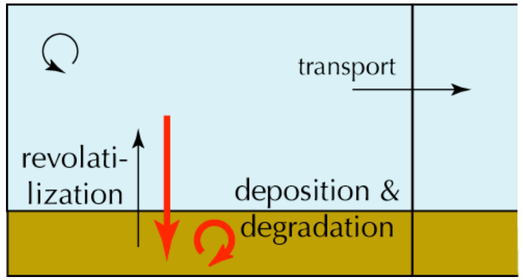
    absorption to organic matter,
    adsorption to mineral surfaces,
    uptake by vegetation, deep sea export, ...





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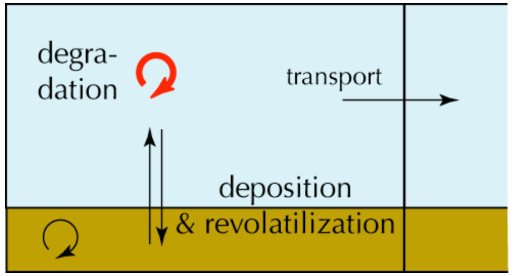
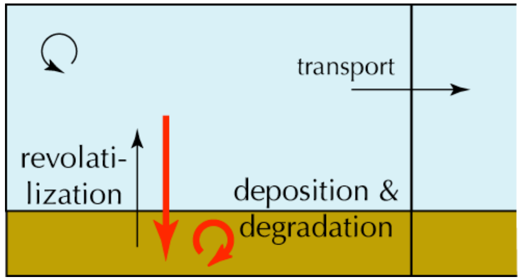


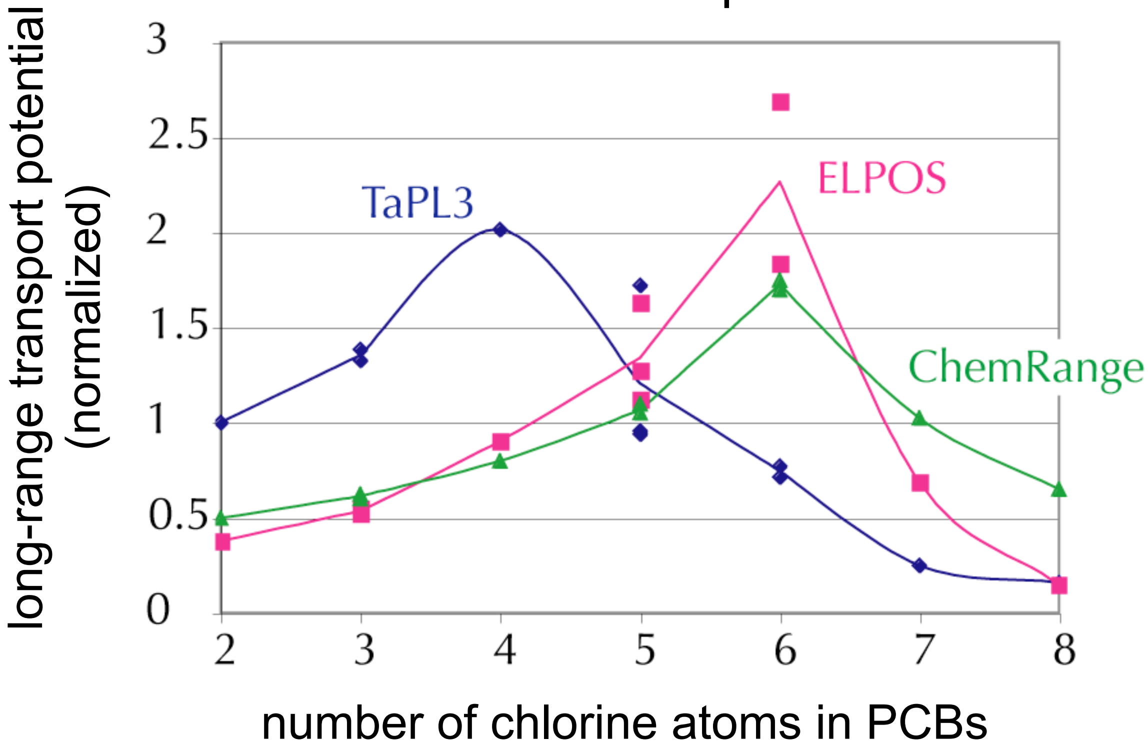


- Degradation in air limiting: removal of **lighter** PCBs
- Deposition to surface limiting: removal of **heavier** PCBs

Models
3, 4, 5

Degradation or Net Deposition?

Three steady-state multimedia models
for LRT in comparison



Data from: Wania & Dugani,
Environ. Toxicol. Chem. 22, 1252–1261, 2003

TaPL3:
deposition to and loss in surface media limits LRT.

ELPOS and ChemRange:
degradation in air limits LRT.

»Big Open Questions«

- **Degradation in air:**
  - Pathways and efficiency in the gas phase?
  - Pathways and efficiency in the particle-bound phase?
  - How and how long do POPs survive LRT in air?
- **Net deposition to surface media:**
  - For which compounds are surface media and air at equilibrium?
  - What is the influence of soil type, vegetation cover, local/recent emissions, etc.?
  - For which compounds is „grass hopping“ important?

Open Questions and Tasks

- Improve data bases for chemical properties
  - partition coefficients
  - degradation rate constants, in particular in the air
  - toxicity
- Historical emission inventories of POPs
- Long-term monitoring
- Modeling

From POPs Science to Politics

- Improve political support of research into transboundary chemical pollution.
- Is it desirable to establish an »**Intergovernmental Panel on Chemical Pollution**«?

The Intergovernmental Panel on Climate Change (IPCC)
has been established by WMO and UNEP
to assess scientific, technical and socio-economic information
relevant for the understanding of climate change,
its potential impacts and options for adaptation and mitigation.

www.ipcc.ch

An »Intergovernmental Panel on Chemical Pollution« – Why?

- Many chemical property data and findings on exposure and effects not harmonized!?
- High uncertainties limiting a science-based treatment of transboundary chemical pollution!?
- Support and funding for measuring chemical properties, compiling emission inventories, conducting monitoring programs, performing modeling studies still too low!?
- Existing organizations limited in their geographical scope; not entirely focused on chemicals.

An »Intergovernmental Panel on Chemical Pollution«?

- Existing institutions in the fields of chemicals:
  - EMEP: European Monitoring and Evaluation Programme (1977)

Provide sound scientific support for the Convention,
in particular in the areas of: atmospheric monitoring and modelling,
emission inventories and emission projections,
and integrated assessment modelling.

LRTAP 25th Anniversary
Long-range Transboundary Air Pollution

www.unece.org/env/emep/welcome.html

An »Intergovernmental Panel on Chemical Pollution«?

- Existing institutions in the fields of chemicals:
  - EMEP: European Monitoring and Evaluation Programme (1977)
  - AMAP: Arctic Monitoring and Assessment Programme (1991)

The primary function of AMAP is to advise the governments of the eight Arctic countries (Canada, Denmark/Greenland, Finland, Iceland, Norway, Russia, Sweden and the United States) on matters relating to threats to the Arctic region from pollution.

www.amap.no

An »Intergovernmental Panel on Chemical Pollution«?

- Existing institutions in the fields of chemicals:
  - EMEP: European Monitoring and Evaluation Programme (1977)
  - AMAP: Arctic Monitoring and Assessment Programme (1991)
  - EEA: European Environment Agency

EEA aims to support sustainable development and to help achieve significant and measurable improvement in Europe's environment, through the provision of timely, targeted, relevant and reliable information to policy making agents and the public.

European Environment Agency
Information for improving Europe's environment

www.eea.eu.int

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  - EEA: European Environment Agency
  - Others

The IPCC – A Model?

- Influential institutions related to international treaties:
  - EMEP and the Convention on Long-Range Transboundary Air Pollution
  - IPCC and the Framework Convention on Climate Change
  - »IPCP« and the Stockholm Convention on POPs?

- IPCC monopolized debate; deviant positions less accepted.
- Stronger involvement <–> lower autonomy of science.

»Greenhouse Gases« and »Chemicals«

- Problem areas
  - Scale of problem exceeds national boundaries.
  - Very high uncertainties; lack of information.
  - Political support/funding of research often limited by limited national responsibility.
- Needs
  - Efficient use of existing information.
  - Long-term scientific efforts.
  - Public awareness.
  - Consensus about political action – not too late.

Next Steps?

- Is an »Intergovernmental Panel on Chemical Pollution« desirable?

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