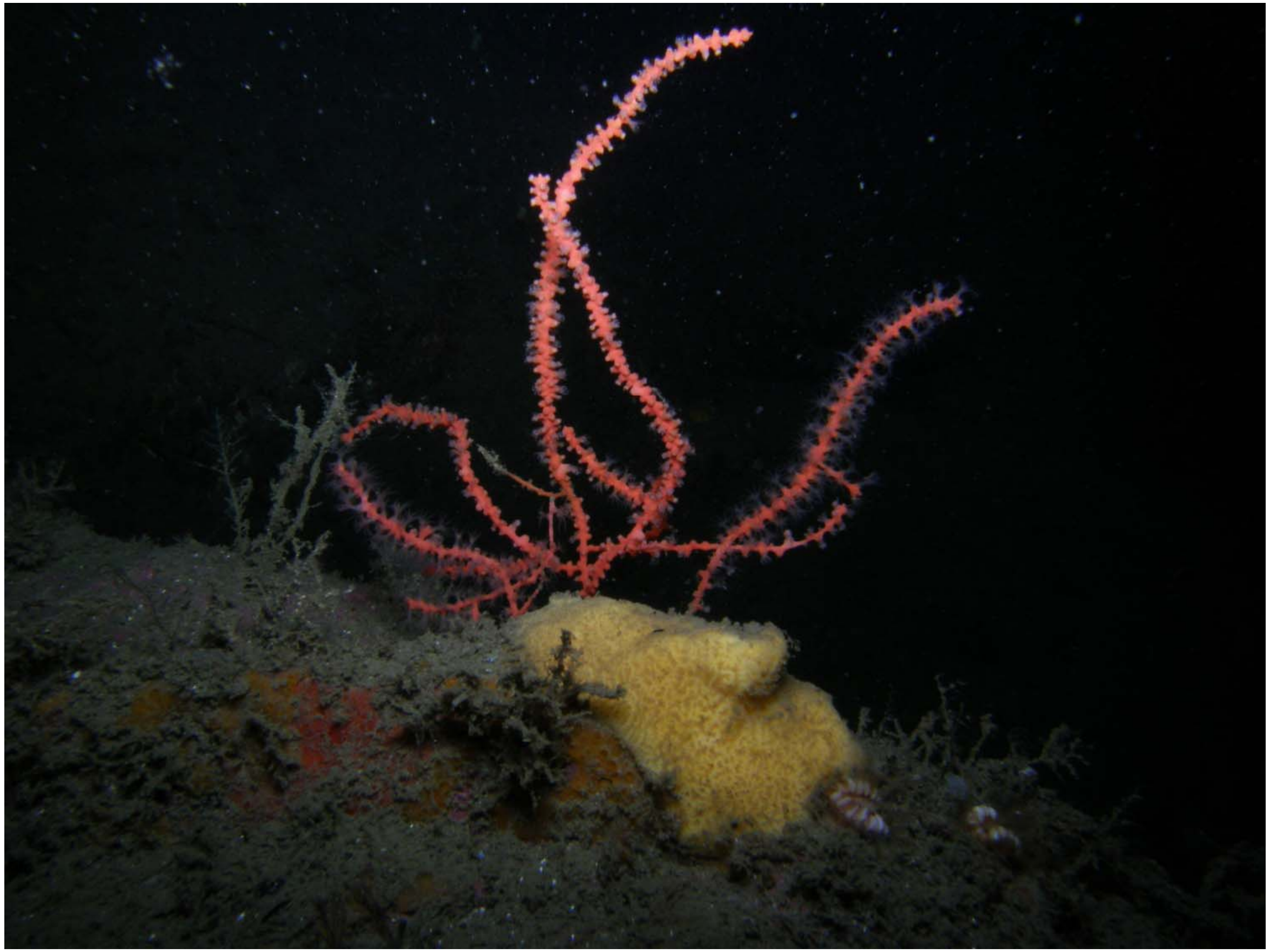
Analytical chemistry -sampling strategies



Dr. Pernilla Carlsson; carlsson@recetox.muni.cz, room 209, RECETOX

Outline

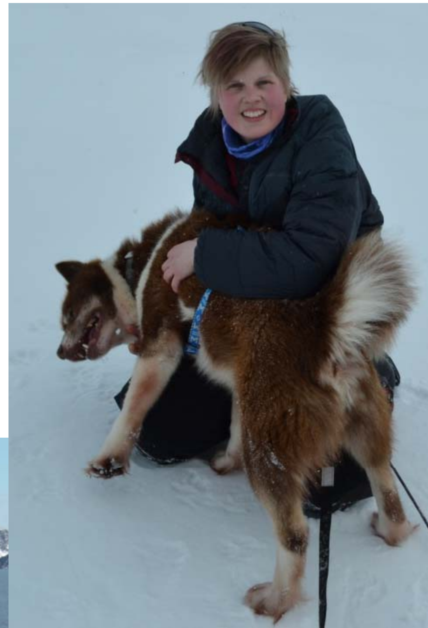
- Sampling strategies
  -general limitations
  -bioaccumulation and sampling strategy
- Your hypothesis and how to address it
- ”Chemical tools”
  -chirality: environmental processes and different sources
  -transport processes
  -fate of POPs
- Case study discussions

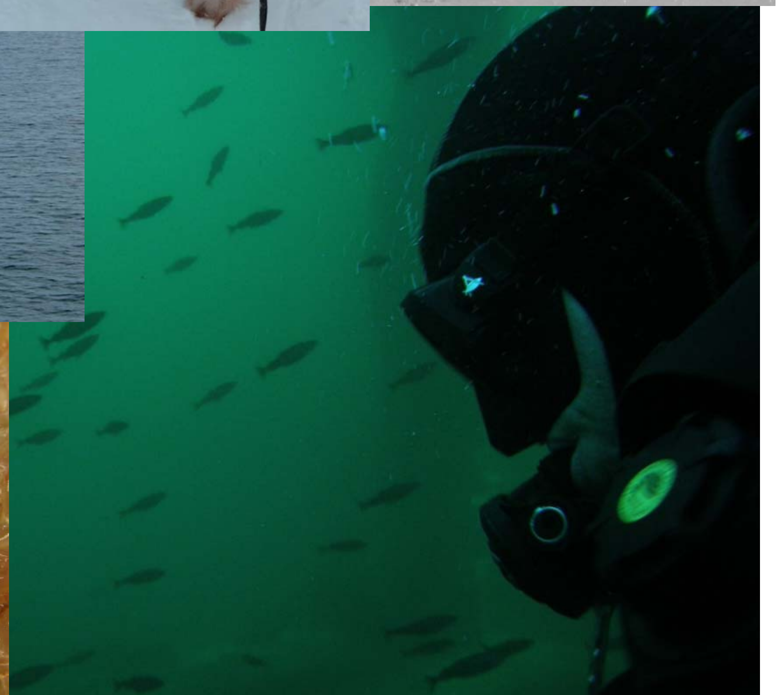
General issues

- Amount and type of data
- Seasonal distribution
- Instrumental limitations and infrastructure
- Legislation

Sampling strategy - biomagnification

Cover the whole food web!

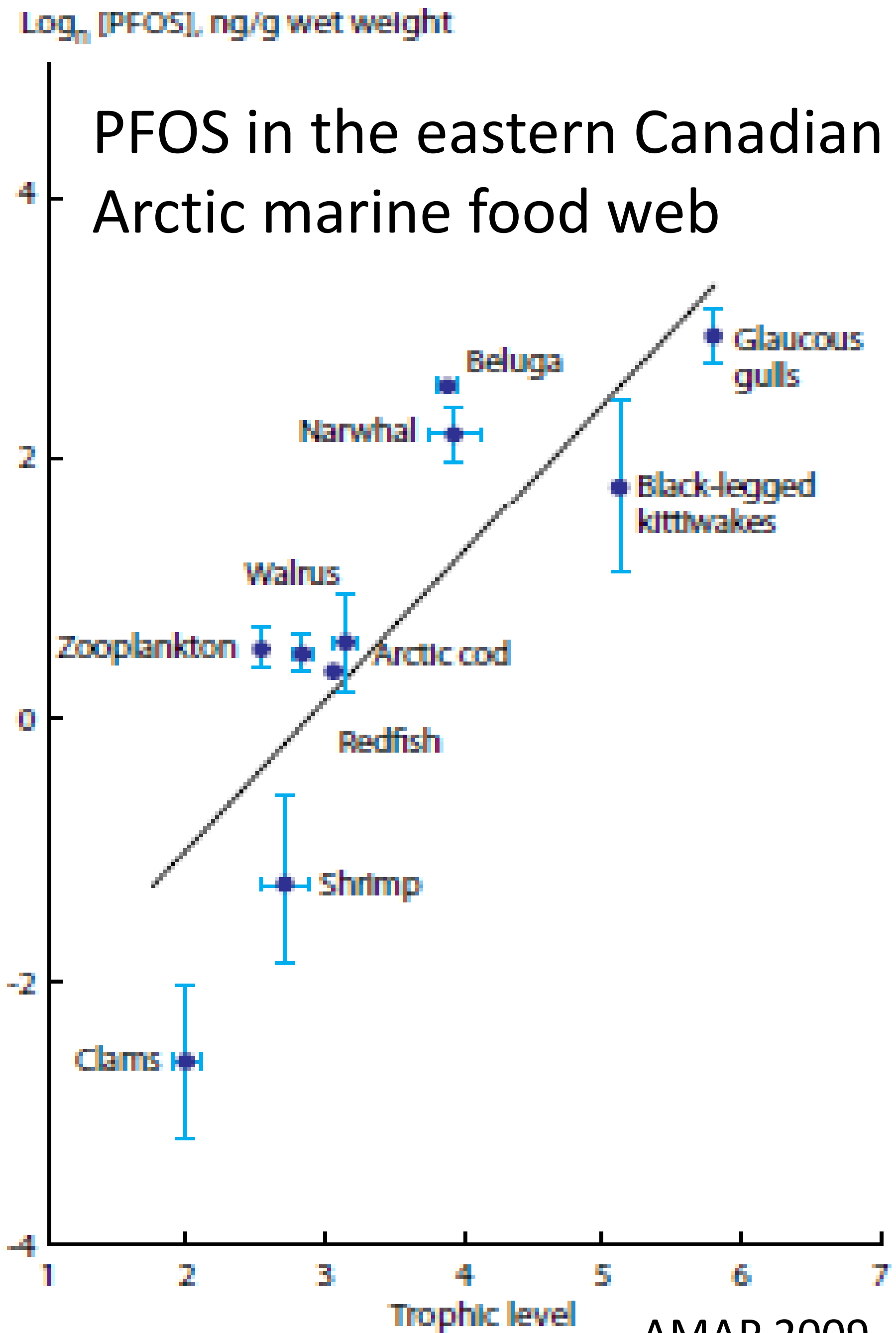




Biomagnification

- Who eats who?
- Benthic/pelagic couplings?

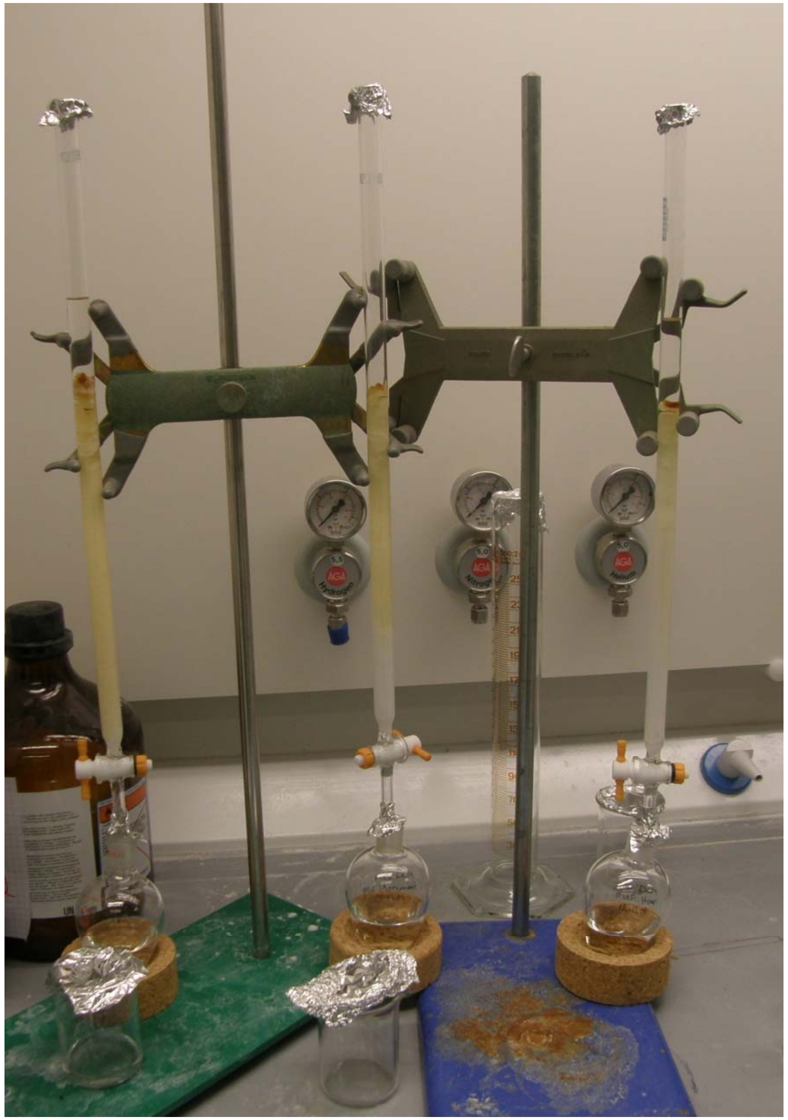
PFOS in the eastern Canadian Arctic marine food web



AMAP 2009

Your hypothesis and how to address it

- Clear research questions!
- Data needed
- Financial and time frames



Your hypothesis and how to address it

- An example:

Does fish from the Baltic Sea contain higher concentrations of PCB and dioxins compared to fish from the Atlantic ocean?”

Fish and POPs

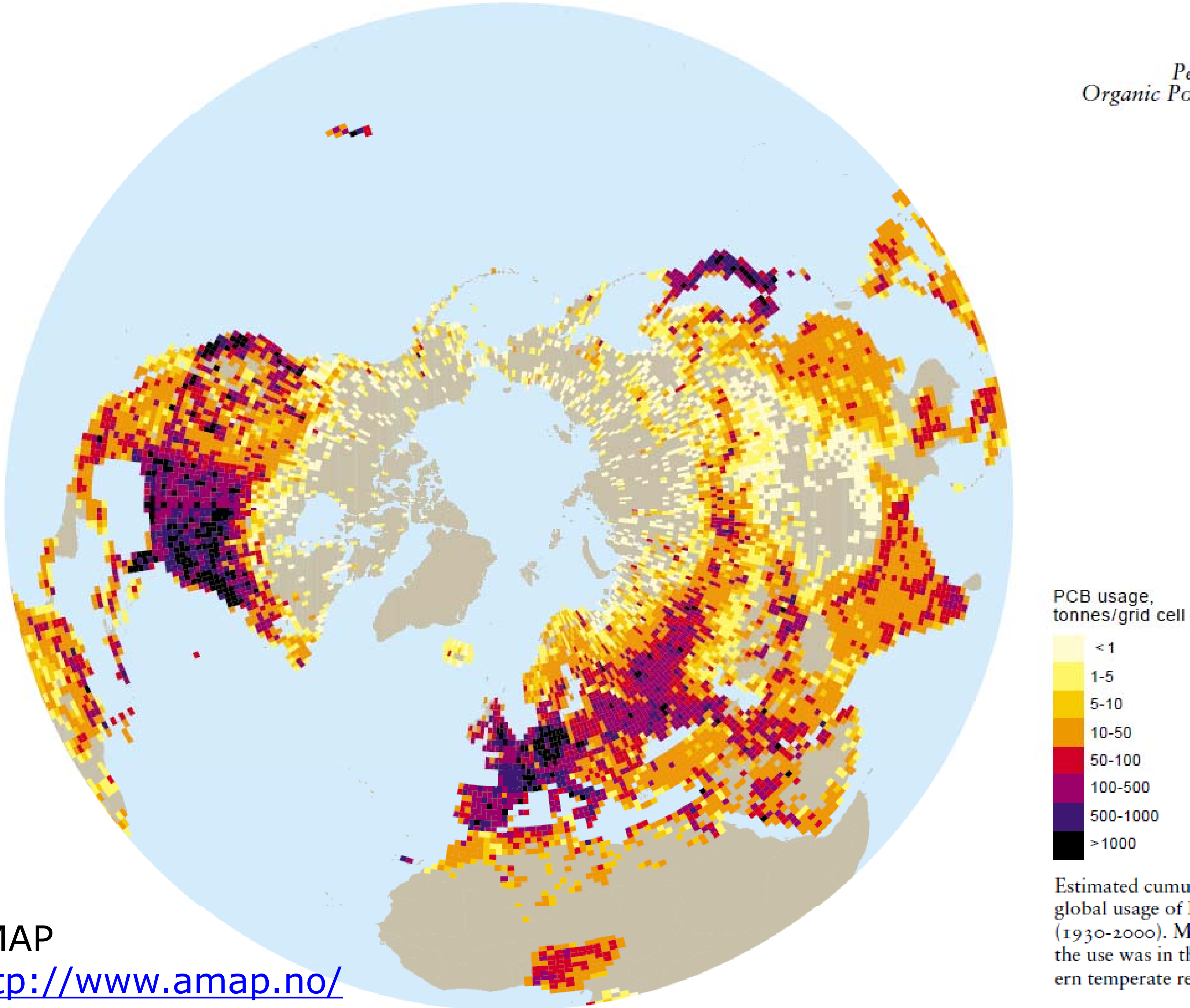
- Study design:
- Fish –species
- Sampling: fishing or buying?
- Transport
- Analyses
- Data interpretation
- Literature comparison

Chemical ”tools”

- Relative distribution
- Degradation and metabolites
- Chirality
- Isotopes

Relative distribution

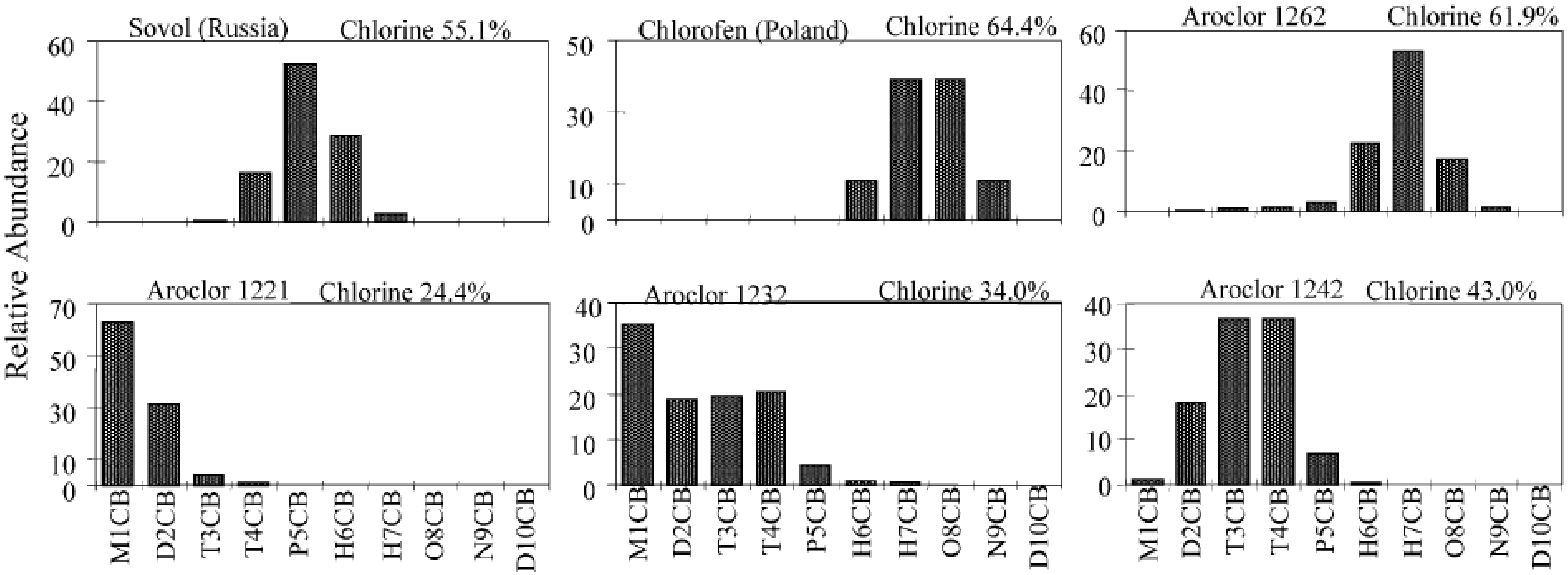
- PCBs: different mixtures had different ratio between congeners
- Low-chlorinated PCBs: Easily undergo long-range transport.



Estimated cumulative global usage of PCBs (1930-2000). Most of the use was in the northern temperate region.

AMAP
http://www.amap.no/

Relative distribution –technical PCB mixtures



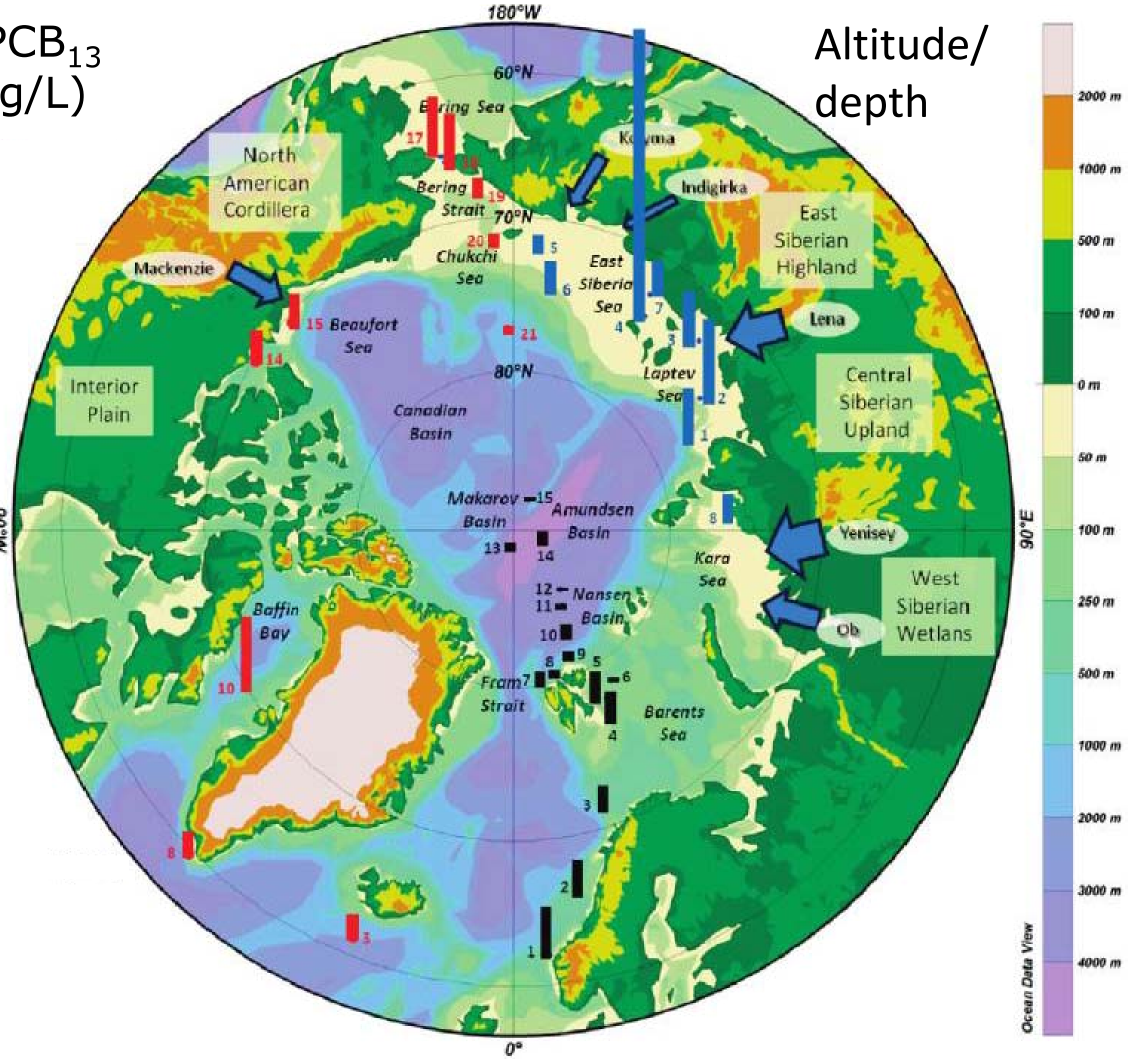
Arochlor: USA

Takasuga et al., 2006

PCB flux to the Arctic

ΣPCB$_{13}$ (pg/L)

Altitude/ depth

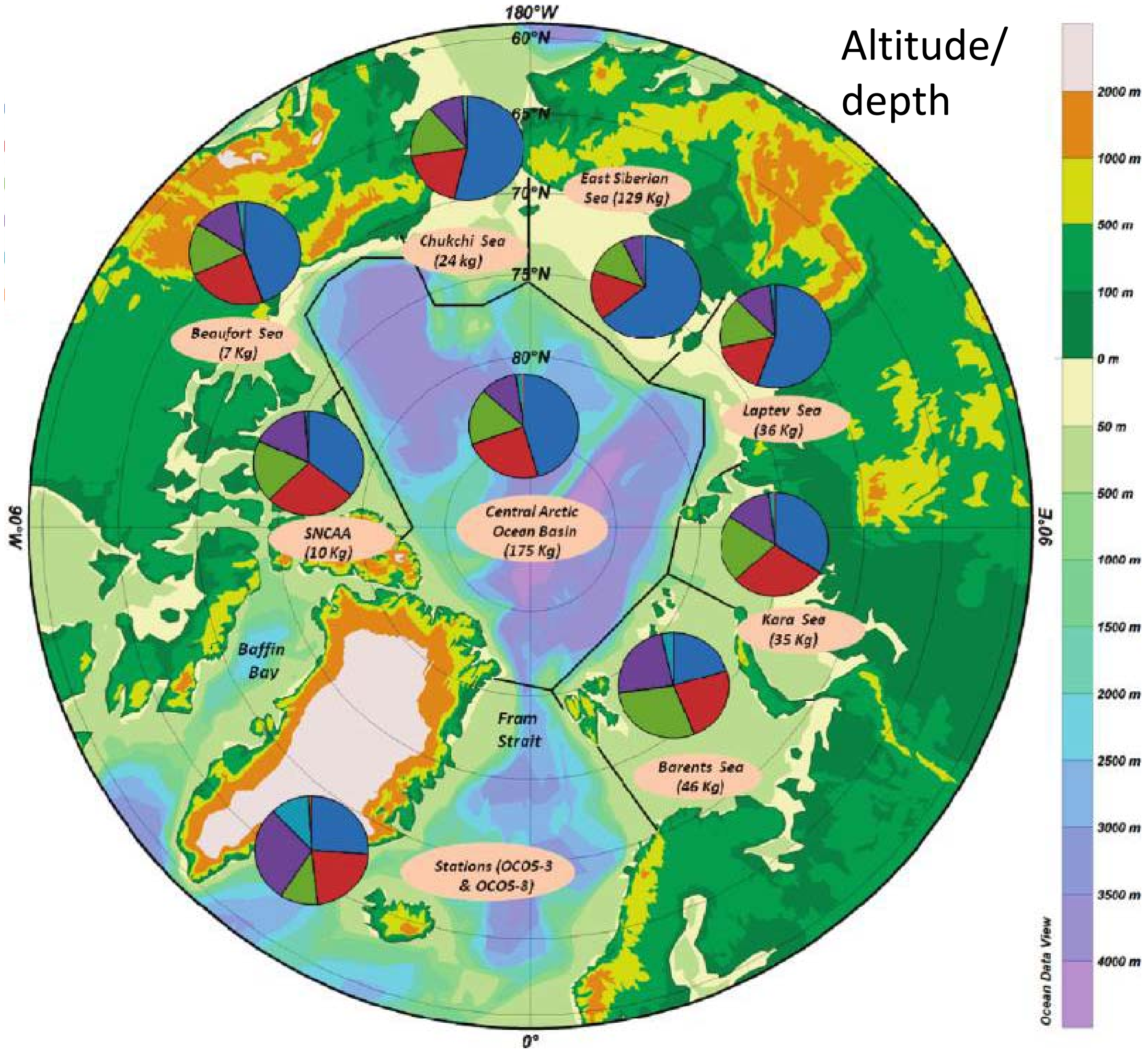


Carrizo, D.; Gustafsson, O. Distribution and Inventories of Polychlorinated Biphenyls in the Polar Mixed Layer of Seven Pan-Arctic Shelf Seas and the Interior Basins. *ES&T* 2011.

Carrizo, D.; Gustafsson, O. Pan-Arctic River Fluxes of Polychlorinated Biphenyls. *ES&T* 2011

PCB flux to the Arctic

- Tri-PCB
- Tetra-PCB
- Penta-PCB
- Hexa-PCB
- Hepta-PCB
- Octa-PCB



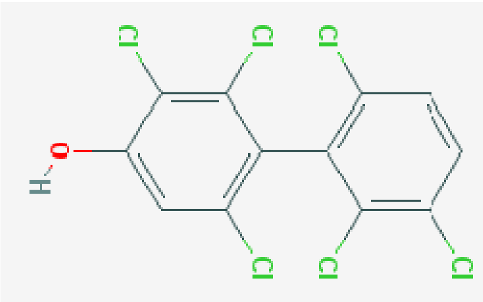
Carrizo, D.; Gustafsson, O. Distribution and Inventories of Polychlorinated Biphenyls in the Polar Mixed Layer of Seven Pan-Arctic Shelf Seas and the Interior Basins. *ES&T* 2011.
Carrizo, D.; Gustafsson, O. Pan-Arctic River Fluxes of Polychlorinated Biphenyls. *ES&T* 2011

Relative distribution

- Long-range transport: Will favour light, easy volatile compounds
  =>Changed ratio in Arctic compared to technical mixture
  =>"Non-changed ratio": Local sources

Degradation and metabolites

- Hydroxy-PCBs: Metabolism of PCBs to facilitate excreation of the compounds
- *Oxy*chlordane: Common, stable metabolite from *trans-/cis*-nonachlor and –chlordane
- DDE: Stable metabolite from DDT. Affect egg-shell thickness among birds

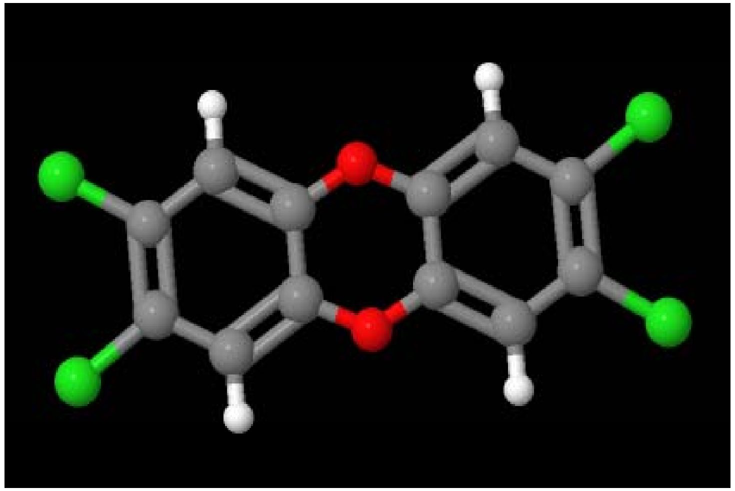


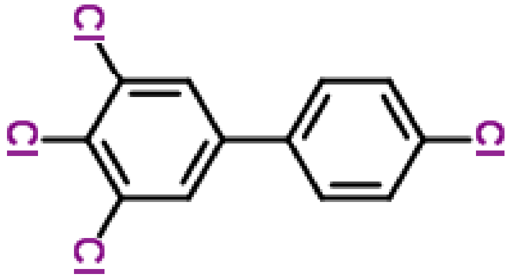
Degradation of POPs

- Cytochrome P450 (commonly known as CYP)
- A superfamily of proteins (enzymes) found in the entire kingdom of life
- They can transform the structure of organic chemicals
- CYP1A1 responsible for oxidation of many POPs
- By affecting chemical structures, CYP may make a given compound nontoxic.
- Or, drastically increase its toxicity…

CYP1A

- Most important subfamily among the P450.
- 2,3,7,8-TCDD, benzo(a)pyrene and dioxin-like PCBs (non- and mono-ortho-PCBs) can induce the transcription of CYP1A genes via the aryl hydrocarbon (Ah) receptor.





2,3,7,8-TCDD and PCB-81.

www.chemspider.com

Isotopes

Who eats who?

Trophic positions: “place in the food web”

$^{15}N/^{14}N = \delta^{15}N$

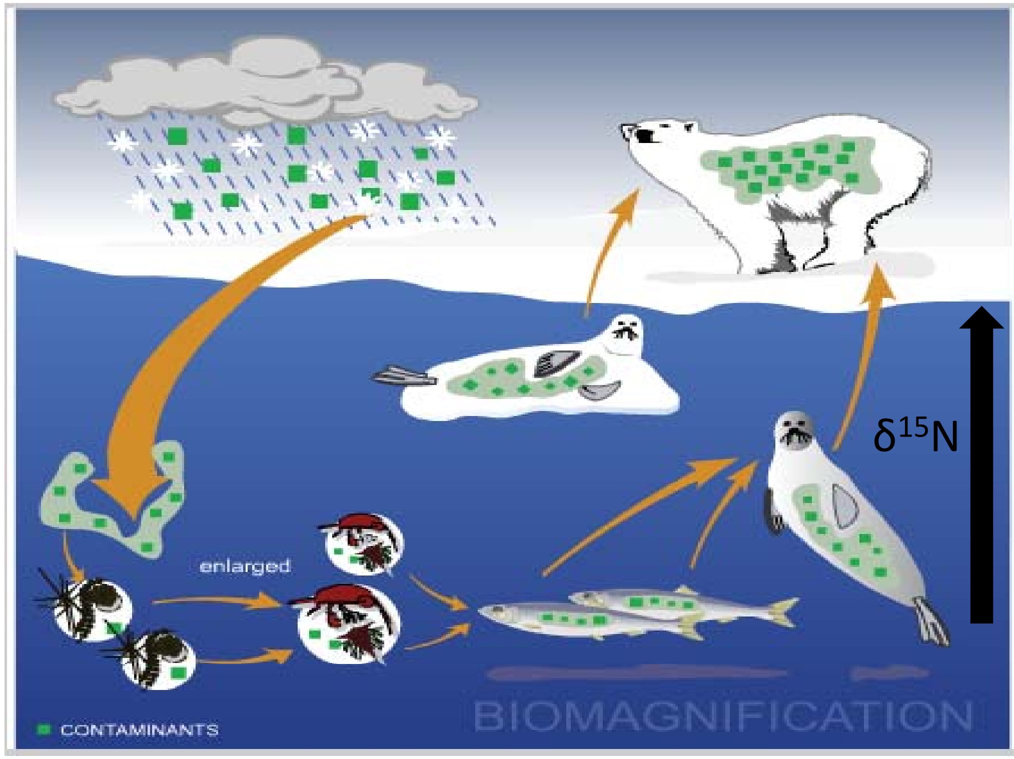
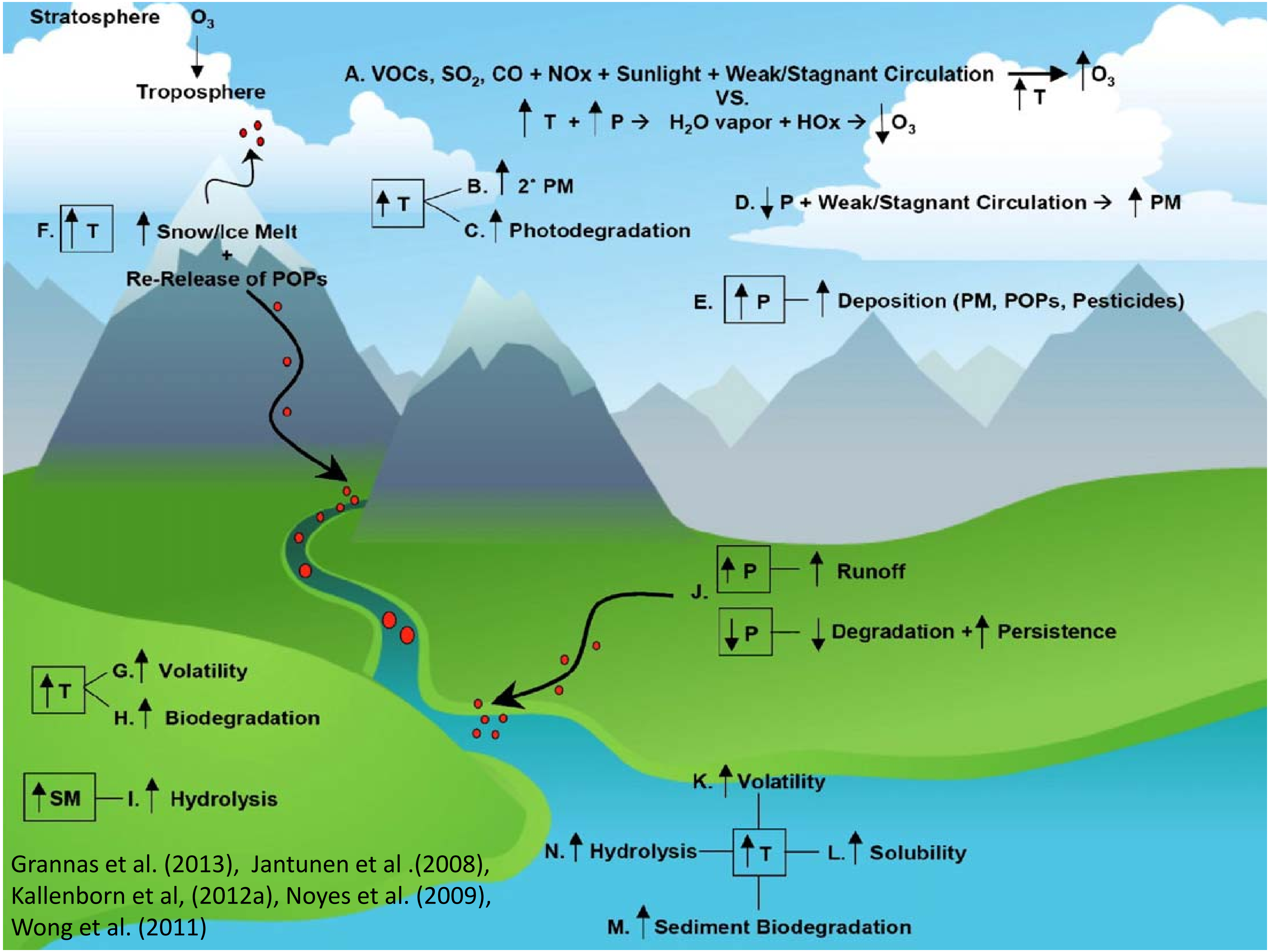


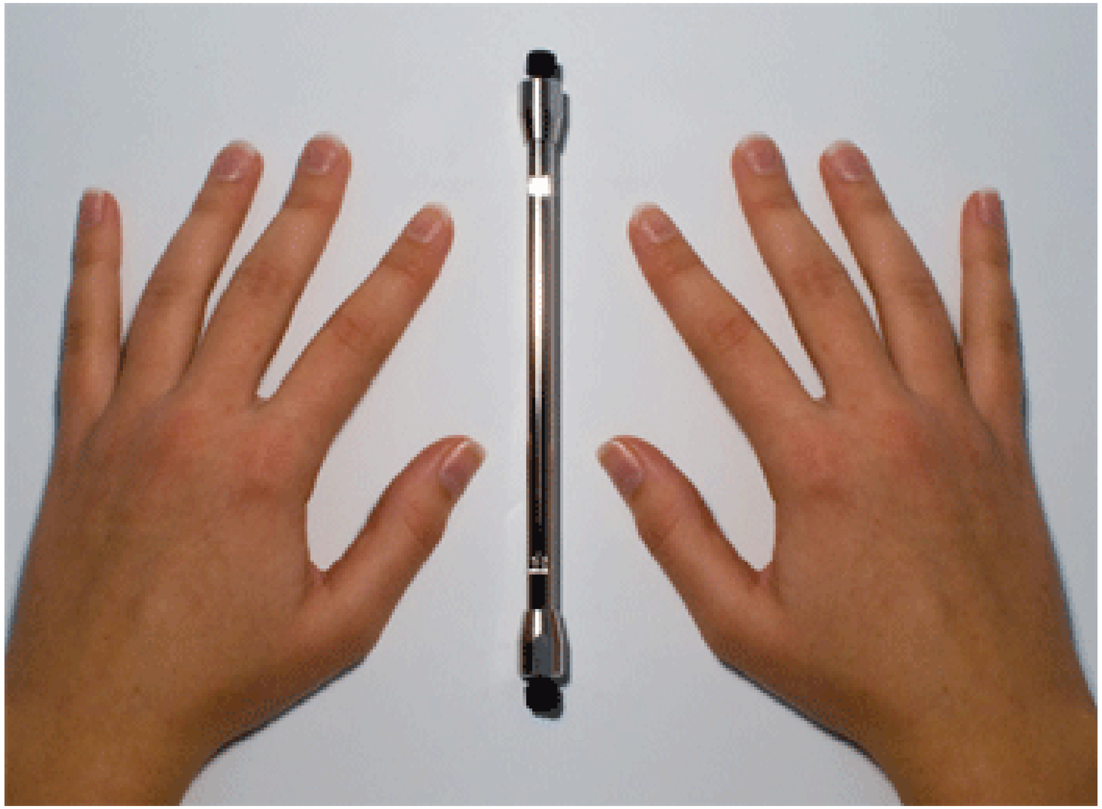
Illustration: Eldbjørg Heimstad

Transport processes
-tracking sources

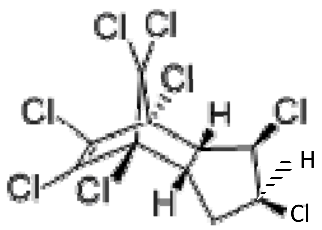


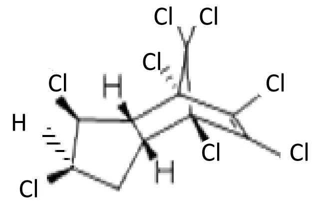
Grannas et al. (2013), Jantunen et al .(2008), Kallenborn et al, (2012a), Noyes et al. (2009), Wong et al. (2011)

Chirality
–tracing environmental processes and sources



Chiral pesticides: a-HCH*, trans-, cis-*, and *oxy*chlordane



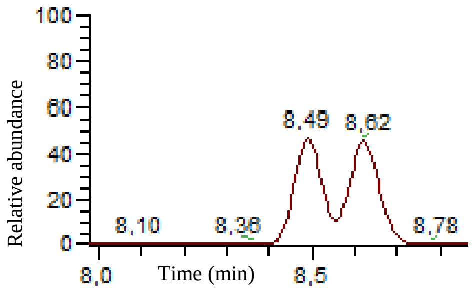


Enantiomer selective analyses

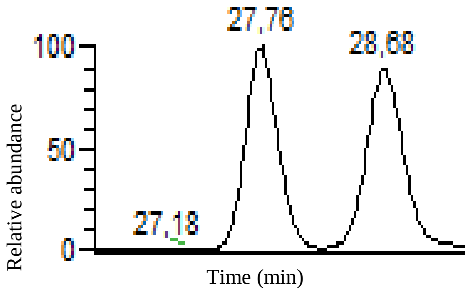
- GC-MS (ECNI, SIM)
- Enantioselective column: BGB-172 (chiral separator: 20% *tert*-butyldimethylsilyl-β –cyclodextrin)

- Enantiomeric fraction; $EF = \frac{[(E_+)]}{[(E_+)+(E_-)]}$

α-HCH: -, +



+*Oxy*chlordane (OC), -OC,



+*trans*-chlordane (TC), +*cis*-chlordane (CC), -CC, -TC

Enantiomer fractions of chiral pesticides in plankton as a tool to differentiate between water masses

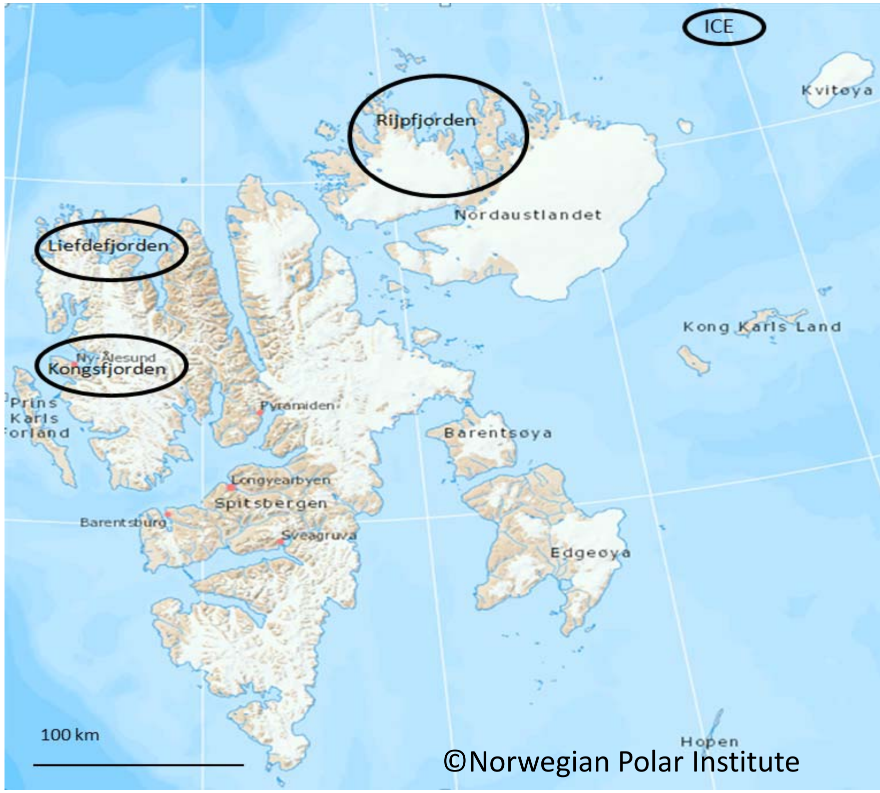
Chiral pesticides

⇒ non-racemic EFs: indicate biological transformation processes

Plankton

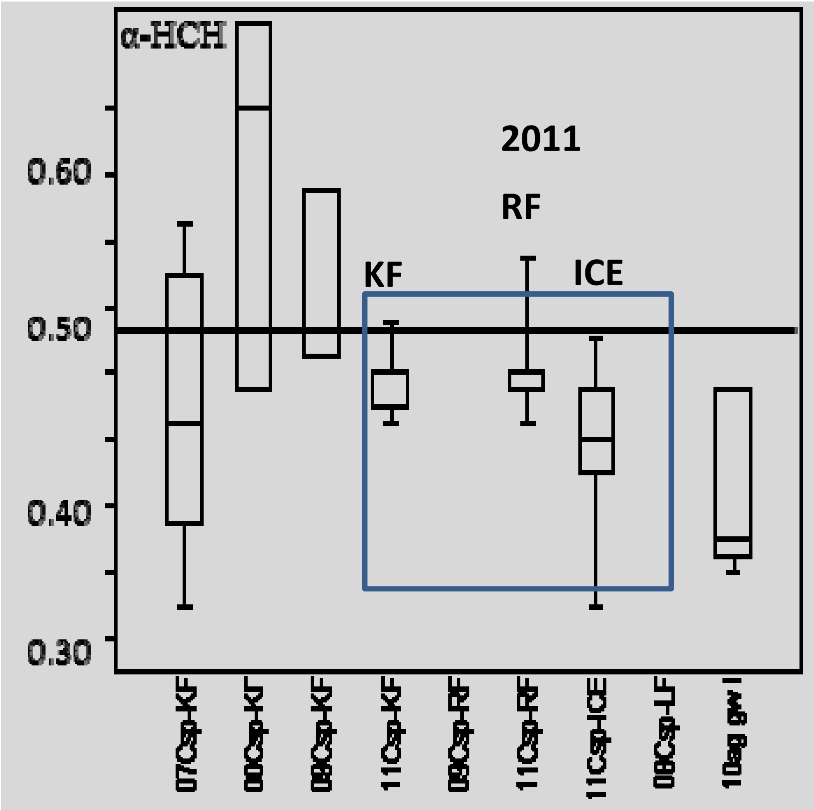
⇒ non-selective metabolism, reflect EFs of pesticides in the water mass

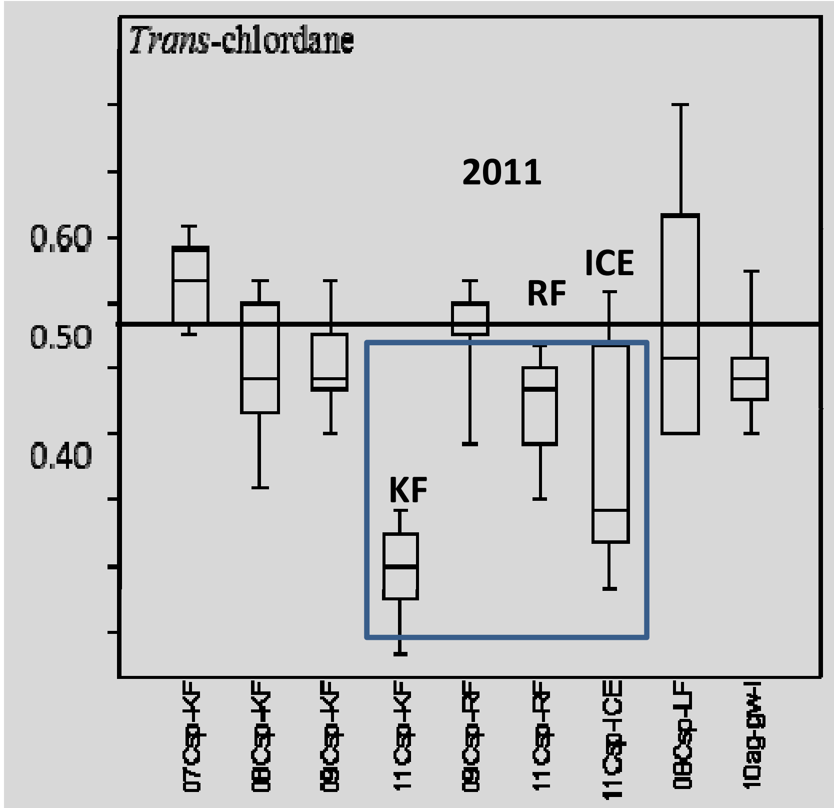
Carlsson et al, 2014



Sample area	2007	2008	2009	2010	2011	Dominating water mass	Winter ice conditions
Kongs-fjorden	Hallanger et al., 2011a	Hallanger et al., 2011b	Carlsson et al., 2014		Carlsson et al., 2014	Atlantic	None/partly covered
Liefde-fjorden		Hallanger et al., 2011b	Carlsson et al., 2014			Atlantic/ Arctic	March-July
Rijp-fjorden			Carlsson et al., 2014		Carlsson et al., 2014	Polar surface/ Arctic	Ice cover until July
Pack ice				Carlsson et al., 2014	Carlsson et al., 2014	Meltwater/ Atlantic	Annual ice cover

Median enantiomeric fractions in *Calanus* spp.





KF= Kongsfjorden
LF= Liefdefjorden
RF= Rijpfjorden

ICE = Ice stations (also represented by ag=*Apherusa glacialis,* gw=*Gammarus wilkitzkii* in 2010).

Carlsson et al, 2014

Chiral pesticides and water masses

•Ice cover and α-HCH
⇒(hindering of) volatilisation

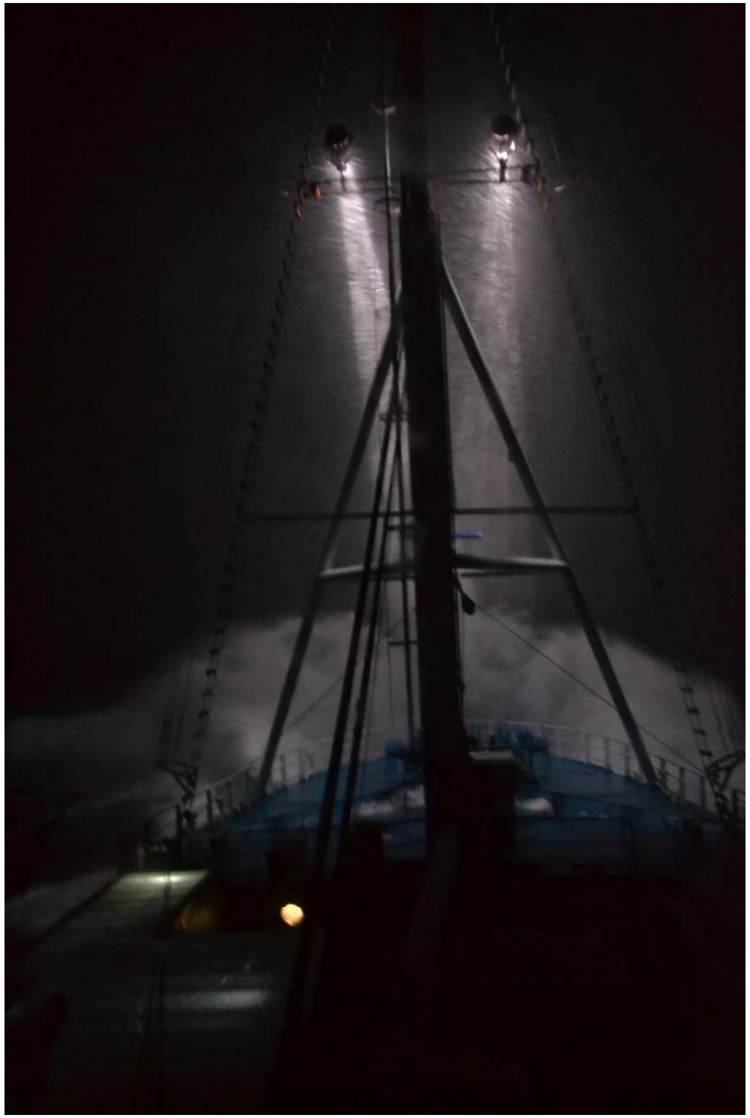
•Chlordanes and 2011
⇒Large deviations from racemic *trans*-chlordane

•Water masses and ice cover are important for the EF distribution.

•Impact from benthic-pelagic processes not completely understood yet.

Case studies of environmental pollution

PCBs in a changing Arctic: Towards understanding their input, transfer and uptake into Arctic biota and humans under climate change



- *Eva Brorström-Lundén*
- *John Munthe, Hanna Andersson, Crispin Halsall, Roland Kallenborn, Pernilla Carlsson, Henry Wöhrnschimmel, Matthew MacLeod, Ian Cousins, Deguo Kong, Gerhard Lammel, Arja Rautio, Khaled Abass*

Aim of PCB-case study:

•Synthesize ArcRisk results using PCBs as model substances
•Link sources and pathways to transfer processes and uptake in biota and assess human exposure and effects
•Effect of future climate change on uptake processes

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Describing the full sequence from emissions to exposure

- **Review of the current status**
- **What will happen when the climate changes?**

PCB emissions and pathways to the Arctic

- Sources, releases
- Air and water transport and deposition fluxes
- Key intercompartmental transfer

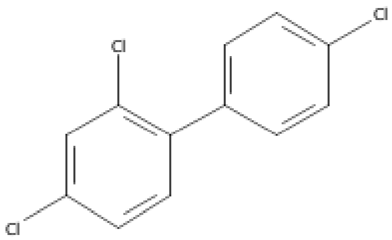
PCB occurrence in the Arctic

- Levels in abiotic matrices and biotic matrices (key biota)
- Time-series of concentrations

Human exposure of PCB

Policy, directives

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL



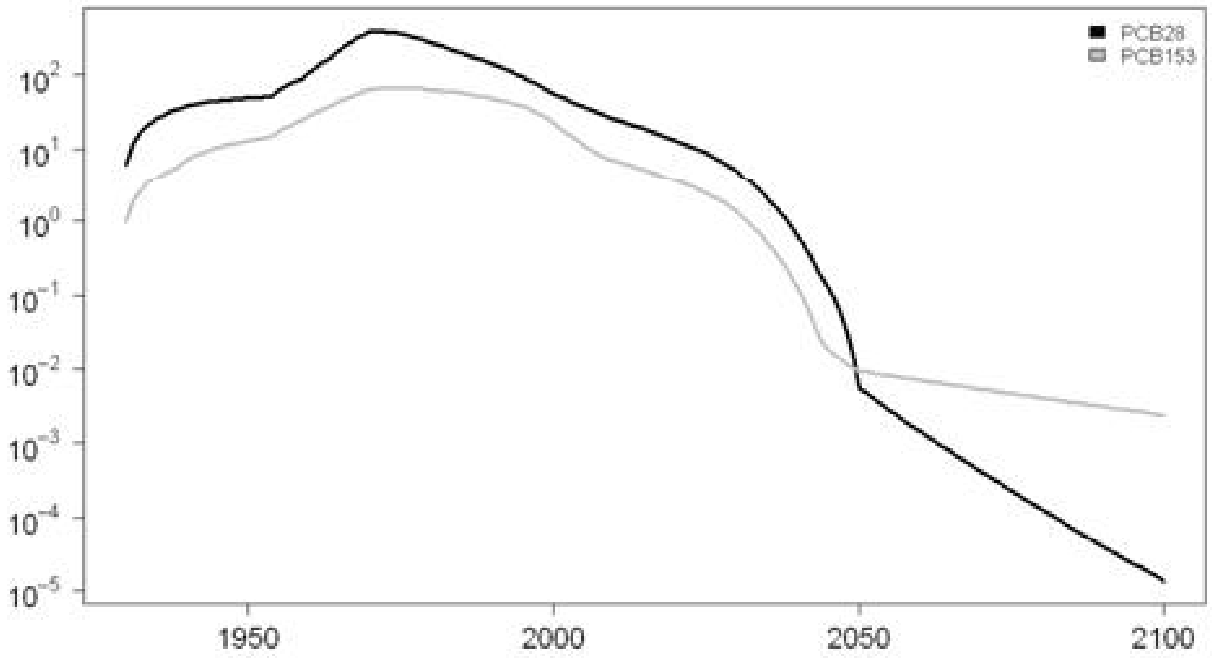
WHY PCBs?

- Banned, but still present in large quantities in the environment.
- Studied extensively in the Arctic for more than three decades.
- Well-understood physical-chemical properties, emissions, pathways and environmental concentrations

=> PCBs are perfect to evaluate models and as a benchmark for assessment of how other substances are influenced by climate change.

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

PCB emissions (tons/year)



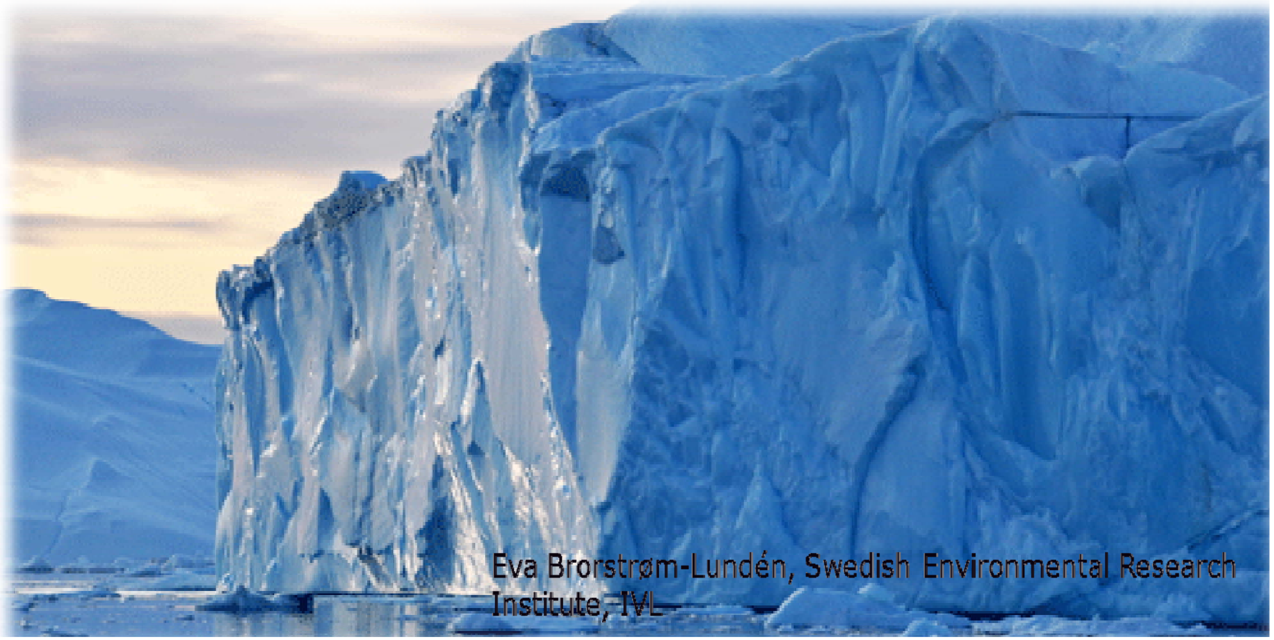
Global primary emissions of PCB-28 and PCB-153 to air (high-end estimate), according to Breivik et al. (2007).

- Primary emissions from constructions and waste dumps.
- Secondary emissions of PCBs will become more important than primary sources.
- Climate change will most likely increase these secondary emissions.

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

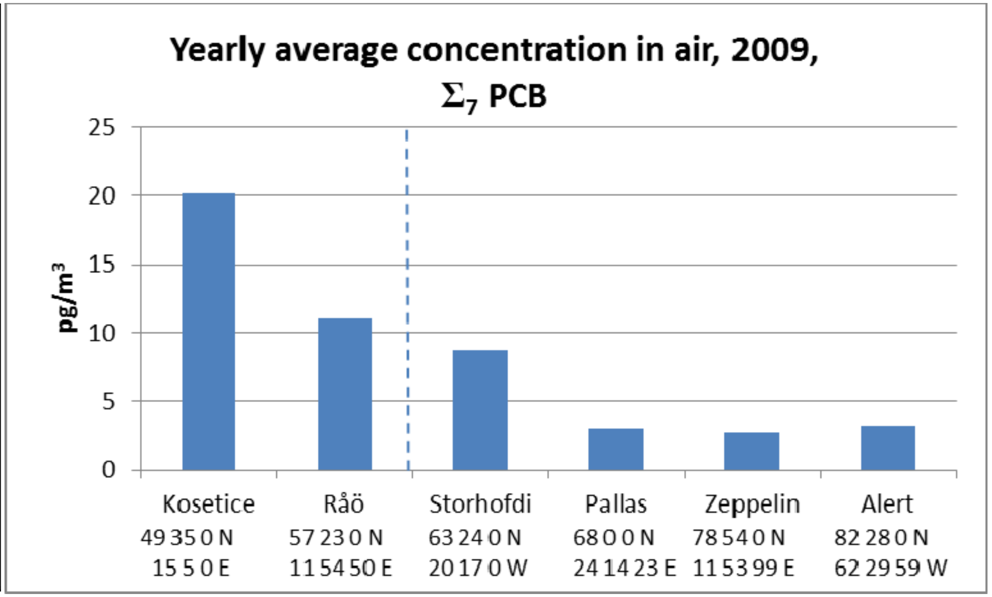
Identification of the most important pathways of PCBs to the Arctic

- Atmospheric long range transport is the major route for global distribution of PCBs to the Arctic.
- Long-range transport via oceanic currents is also of high importance.
- Climate change is likely to affect these pathways and therefore the environmental fate of PCBs.



Atmospheric concentrations of PCBs

Long term monitoring of PCBs are carried out in Arctic and Europe

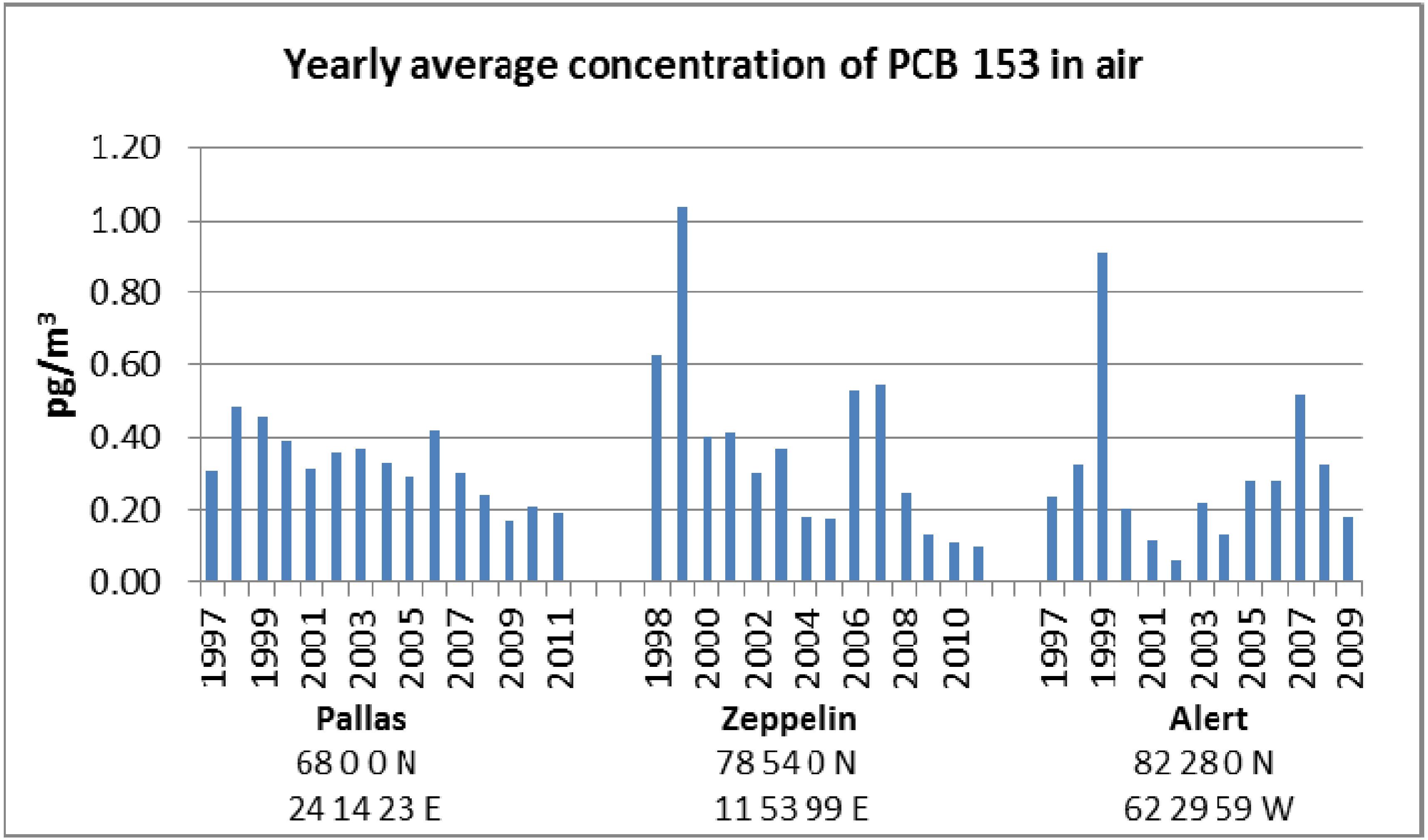


AMAP- and EMEP databases hosted by NILU EBASE (www.ebas.nilu.no).

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Atmospheric concentrations of PCBs

- Long term monitoring



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Arctic inter-compartmental transfer of PCBs
-Processes of importance for climate change

- Precipitation: Important factor for PCB levels in snowpack surface
- Climate change related effects: Changes in precipitation patterns and snow melt periods

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Arctic inter-compartmental transfer of PCBs
-Processes of importance for climate change

- Accumulation of PCBs in sea ice =>”chemical storage”
- Ice melting: Release of PCBs to the water and the marine food web, especially during early spring.
- Climate change will affect pathways and mobility of PCBs in Arctic sea ice.

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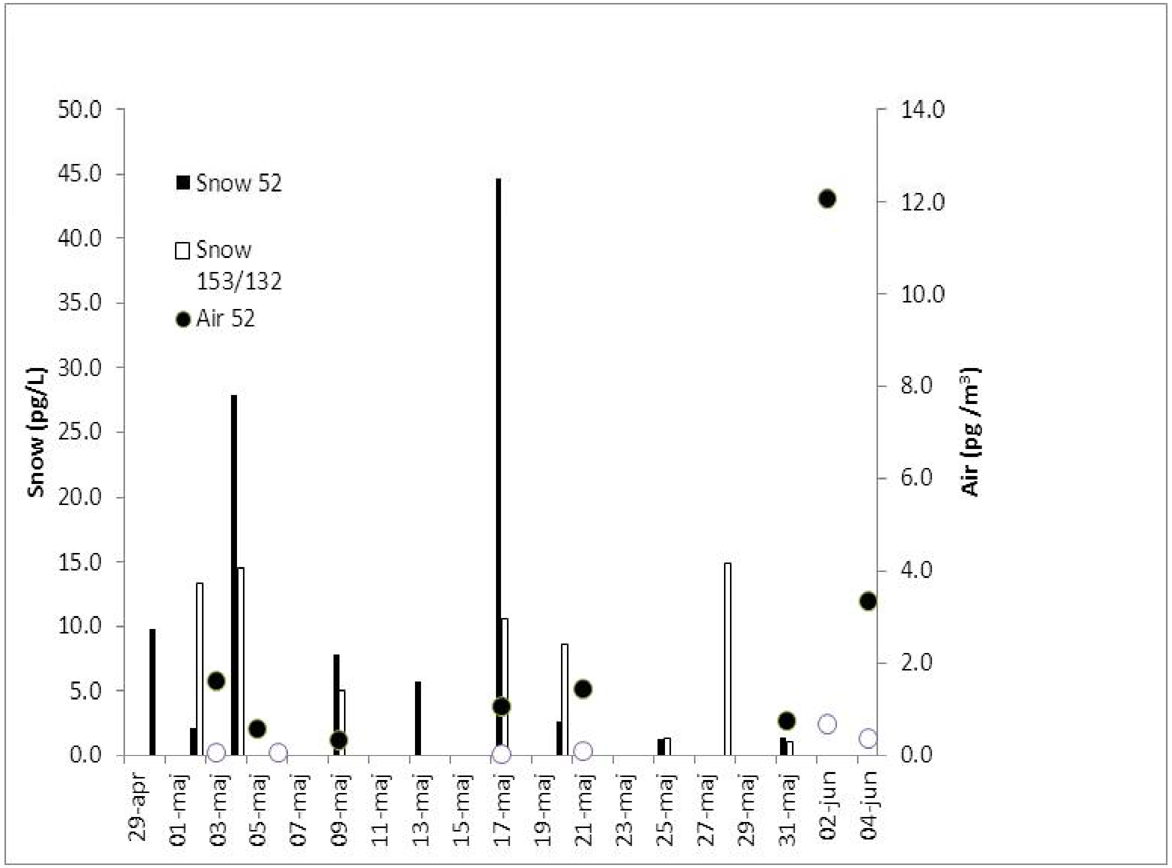
Arctic inter-compartmental transfer of PCBs
-Processes of importance for climate change



Concentrations of PCB-52 and PCB-153/132 in the ice-rafted snowpack of the Beaufort Sea (Canada) during late winter.

PCB-52 declines when the air temperatures increase above 0°C.

The heavier PCB-153/-132 do not show this trend.

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

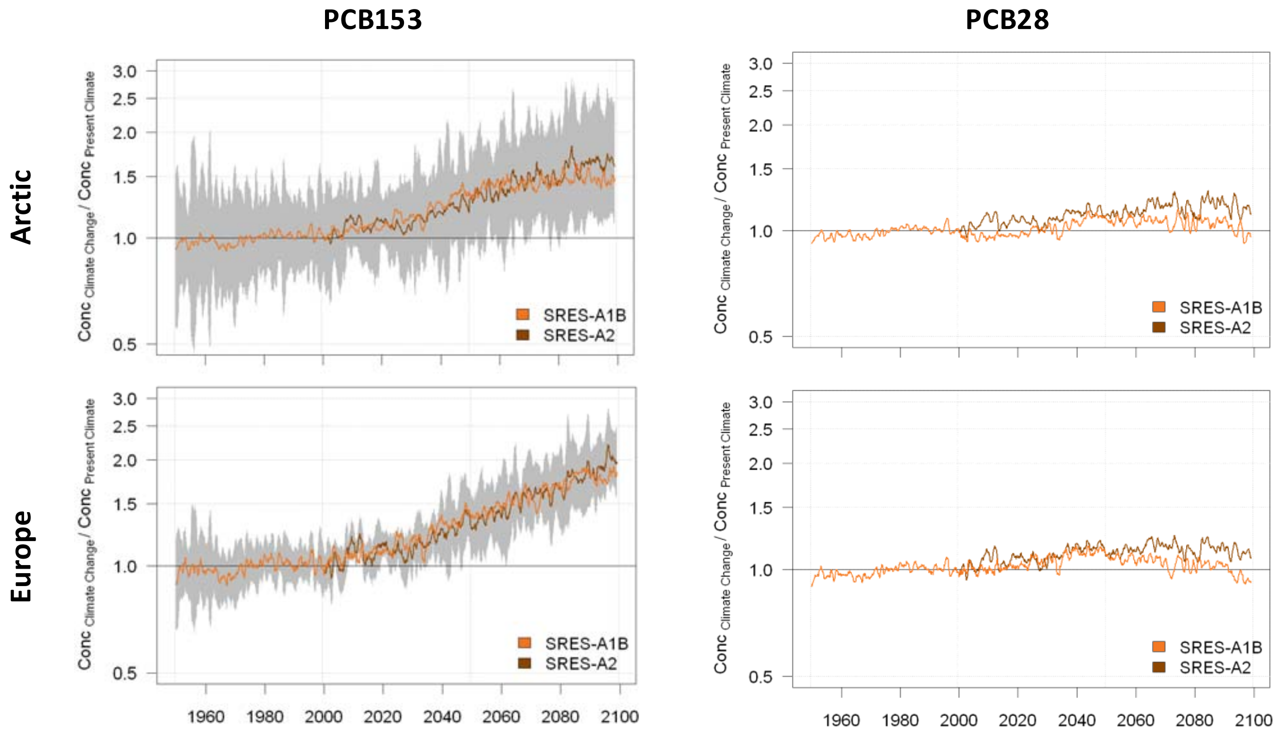
What will happen when the climate changes?

- Model results: relative increases in PCB concentrations in the Arctic atmosphere and ocean. Mainly due to the temperature effect on volatilisation.
- The absolute concentrations by 2090 are forecasted to be several orders of magnitude below present levels in all scenarios.
- Atmospheric PCB concentrations in the Arctic have shown a continuous decreasing trend over the past decades.

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

What will happen when the climate changes?

Modeled relative change of PCB-153 and PCB-28 concentrations in the Arctic and European atmosphere.

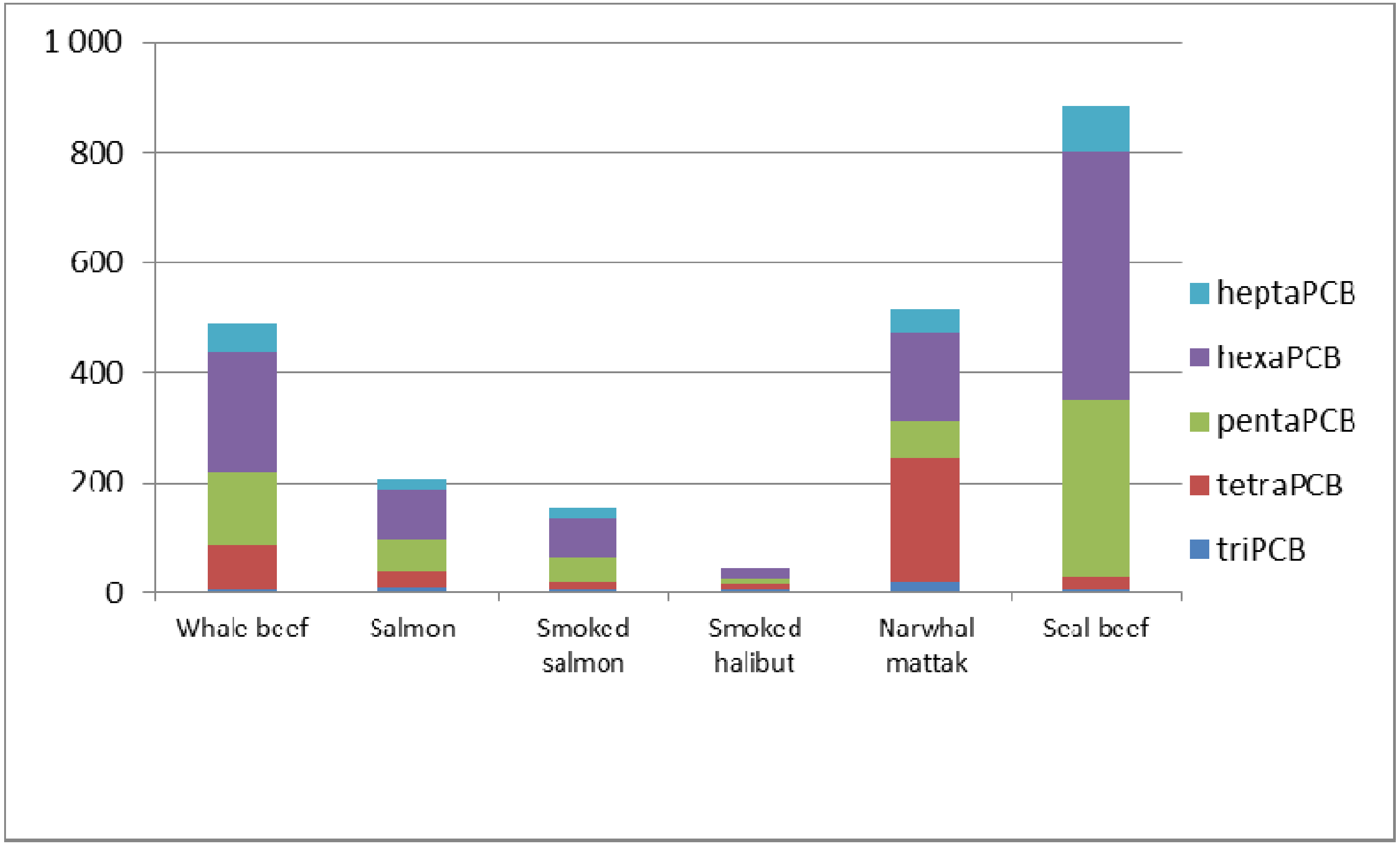


PCB-153 in the Arctic: relative increase of ~1.5.
PCB-153 in Europe:relative increase of 2.

PCB-28: less sensitive to climate change, the effect is within the parameter uncertainties.

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Concentrations of PCBs in biota (food items)



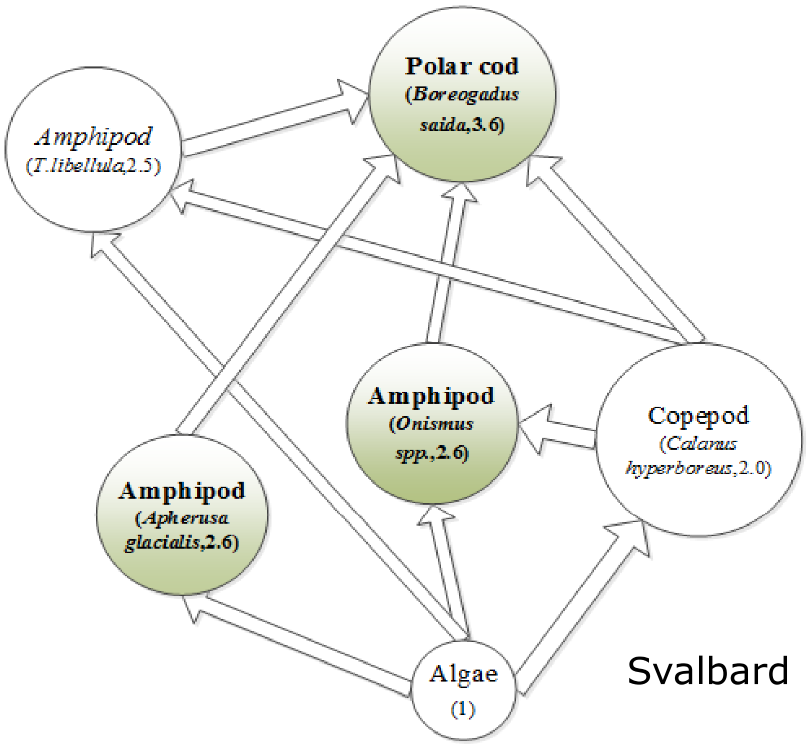
Median (ng/g lw). Samples from Nuuk, Greenland (2010).

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Bioavailability, food web transfer of PCBs

Bioavailability

Major climate change impact on bioavailability: distribution changes in matrices, changed partitioning of PCBs in water due to increased temperatures.



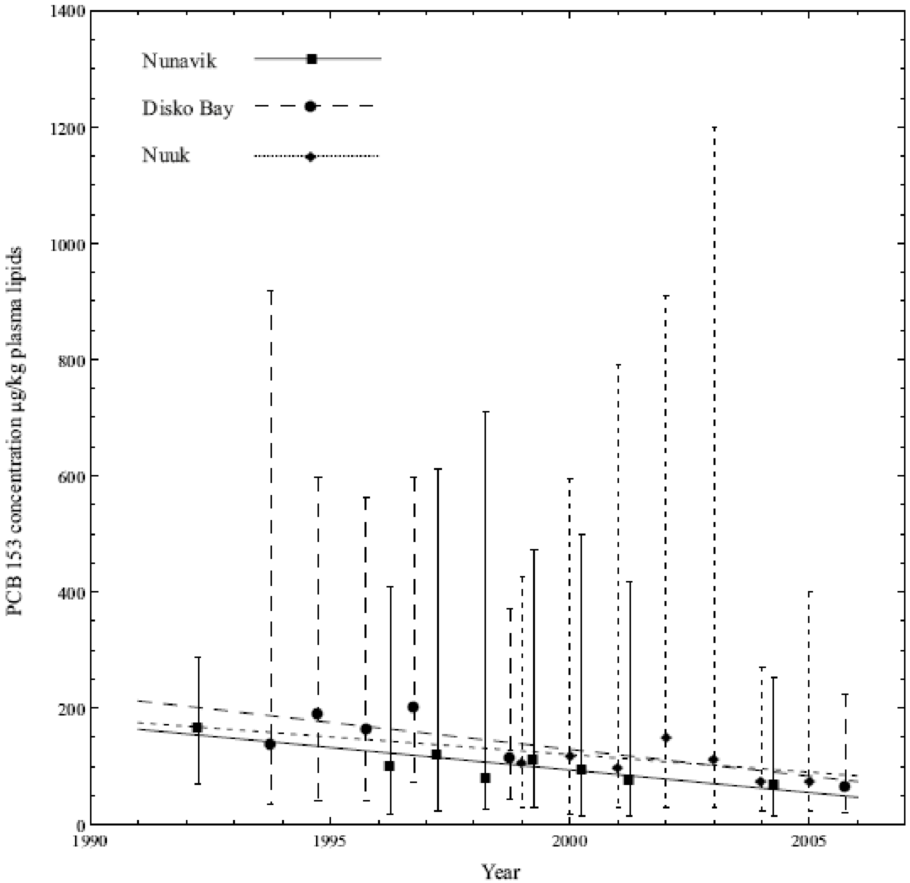
Svalbard marine food web

Food web transfer acts as a link between the abiotic environment and human exposure

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Health effects: Human exposure of PCBs

PCB-153 TREND DATA IN PLASMA LIPIDS (µg/kg), IN PREGNANT WOMEN LIVING IN DISKO BAY (GREENLAND), NUUK (GREENLAND), AND NUNAVIK (QUEBEC, CANADA) DURING YEARS 1992 – 2007.



- In general, levels of PCB in humans populations have declined over the past 20-30 years.
- Declining trends of PCB-153 are seen in all these regions in plasma lipids in Inuit women.

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Health effects
-Human exposure of PCBs in a warmer Arctic

- The impact of changes in contaminant concentrations in food will be small relative to the impact of changes in dietary behaviour.
- Consumption and type of fish and other seafood are the most important factors for contaminant exposure, also in the future.

Eva Brorstrøm-Lundén, Swedish Environmental Research Institute, IVL

Summary and conclusions

-PCBs in a changing Arctic

- ArcRisk results provides an overall picture of PCBs in the Arctic.
- Understanding of relationships between sources, transport, bioaccumulation, exposure and health impacts of PCBs in relation to climate change.
- Long term monitoring of PCBs and other POPs in air, sea water and biota is important both for evaluation of time trends and for detection of responses to environmental change.
- Models are useful tools to predict future concentrations of contaminants in environmental media and human exposure.
- Future needs: High quality datasets with simultaneously sampled biotic and abiotic samples, which can be used to evaluate and improve model performance.

ArcRisk

Eva Brorstrøm-Lundén, Swedish Environmental Institute, IVL

Contaminants in farmed versus wild fish

Salmon
Lowering risk of cardiovascular diseases.
Omega-3 fatty acids
=>Salmon farming

Farmed salmon (Hites et al. 2004)
Higher concentrations of POPs compared to wild salmon
Cause: the feed used

Contaminants in farmed versus wild fish

Risk assessment

¤ Only cancer considered as effect
¤ Positive outcome of fish eating not included
¤ PCB and dieldrin concentrations ok according to US Food and Drug Administration
¤ EPA guidlines: Combined concentrations of PCBs, toxaphenes and dieldrin were cause for concern.

¤ =>Eating farmed salmon 0.5-2 meals/month ok.

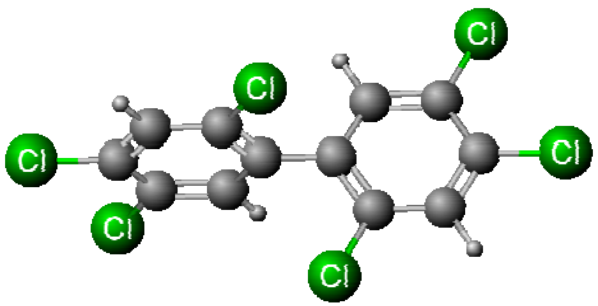
Contaminants in farmed versus wild fish

But…
The combined effect of PCBs, dieldrin and toxaphenes are not well known.
Benefits of omega-3 fatty acids (reducing cardiovascular diseases) are larger compared to the backdraws of POPs

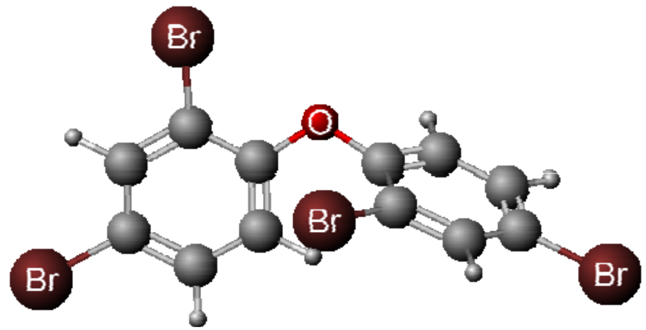
Contaminants in farmed versus wild fish

Salmon feed today (Norway)
More vegetabilic feed =>less POPs compared to fish-based feed.
However, also less fatty acids…

Norwegian farmed salmon in 2004:
ΣPBDE: 2.5 ng/g ww in salmon, BDE-47 and -99: 1.9 ng/g ww.
BDE-47 and -99 in (wild) mackerel and herring: 0.5-1.8 ng/g ww.



PCB-153



BDE-47

Study design of your projects

- Laboratory/field experiment
- Analytical methods
- Interpretation of data –limitations?
- Time limitations?
- Suggestions for larger scale project

Summary -sampling strategies

- Plan your work: clear hypothesis, limitations of data, seasonality, time and financial frames
- Chemical “tools”: stable isotopes, chirality, relative distribution
- Important to link models with empirical data
- Identify limitiations in literature

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