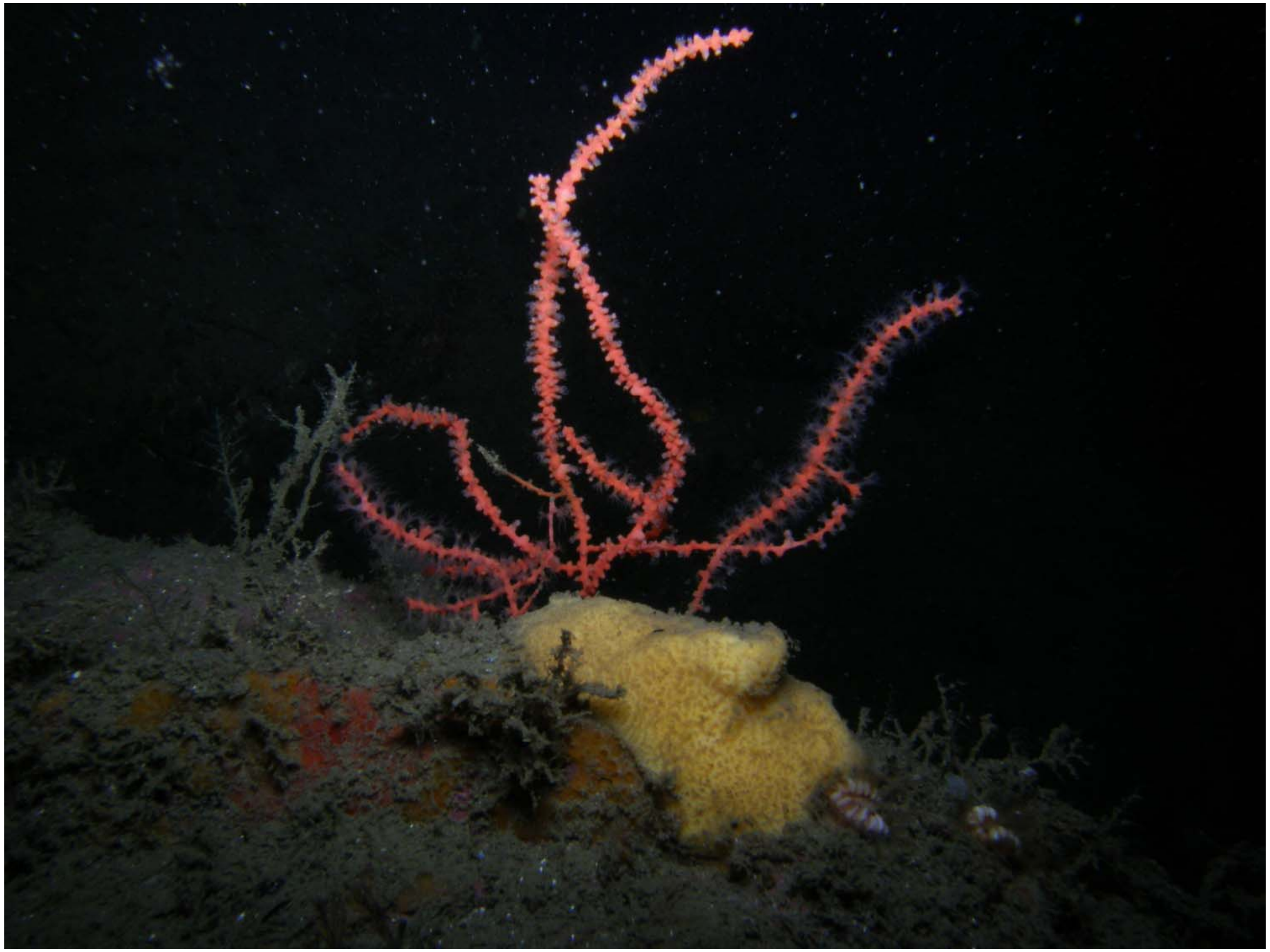
Analytical chemistry
-sampling strategies



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Pernilla Carlsson, RECETOX, Masaryk university, AMAP, Akvaplan-niva

Outline

- Why monitoring POPs?
- 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

Some abbreviations

- Persistent organic pollutants: POP. Group of banned/regulated organic contaminants
- Decabromodiphenyl ethane: DBDPE. Flame retardant
- Perfluorinated alkylated substances: PFAS. GoreTex, Teflon, Ski wax...
- Polybrominated diphenyl ethers: PBDE. Flame retardants.
- Polychlorinated biphenyls: PCB. Banned since ~1970s. Used in electrical equipment, flame retardants, additives in paintings...
- Short- and medium-chained chlorinated paraffins: SCCPs and MCCPs. Lubricants, flame retardants, plastizisers..
- Polyuretan foam: PUF. Sampling material (air).

Why monitoring?

- Control of decisions
  => After a legislation; can we see a decreasing trend?
  Or; do we see unlegal usage of compounds, and where do they then come from?

Why monitoring?

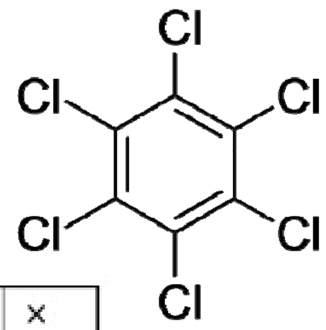
- Trends and timelines
- Trajectories –sources
- New compounds and screening

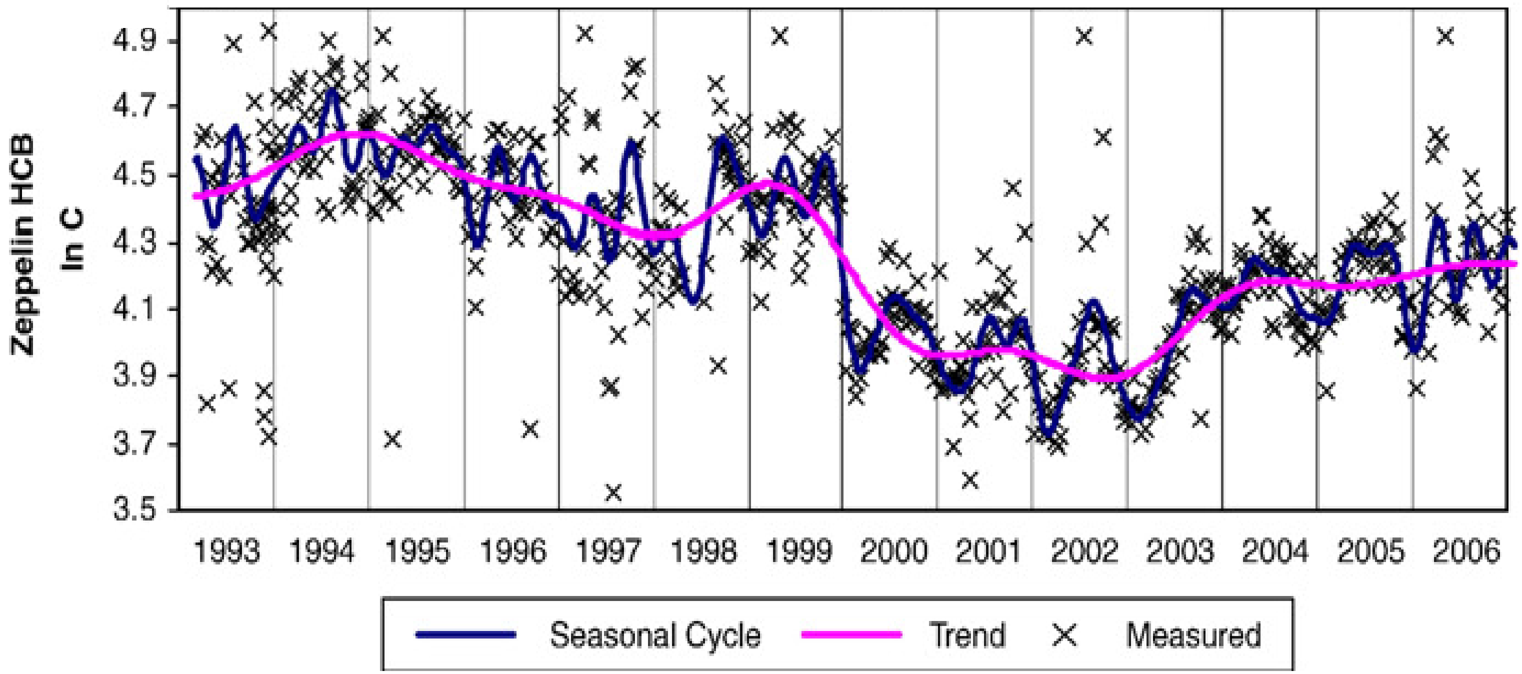
Why monitoring?

- Understaning of transport pathways
- Air: most important transport pathway for POPs



Trends and timelines

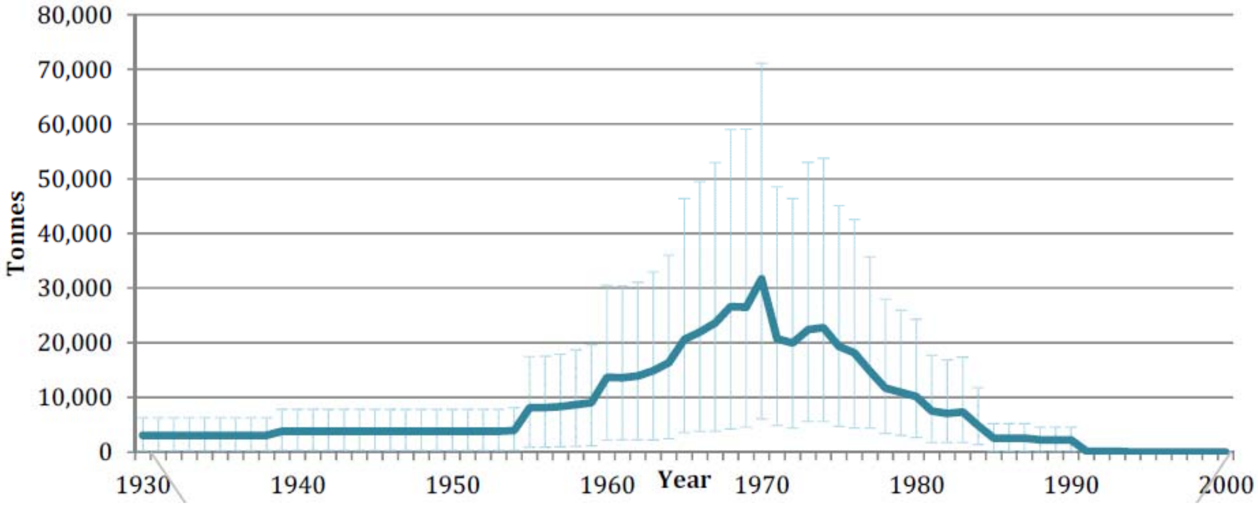




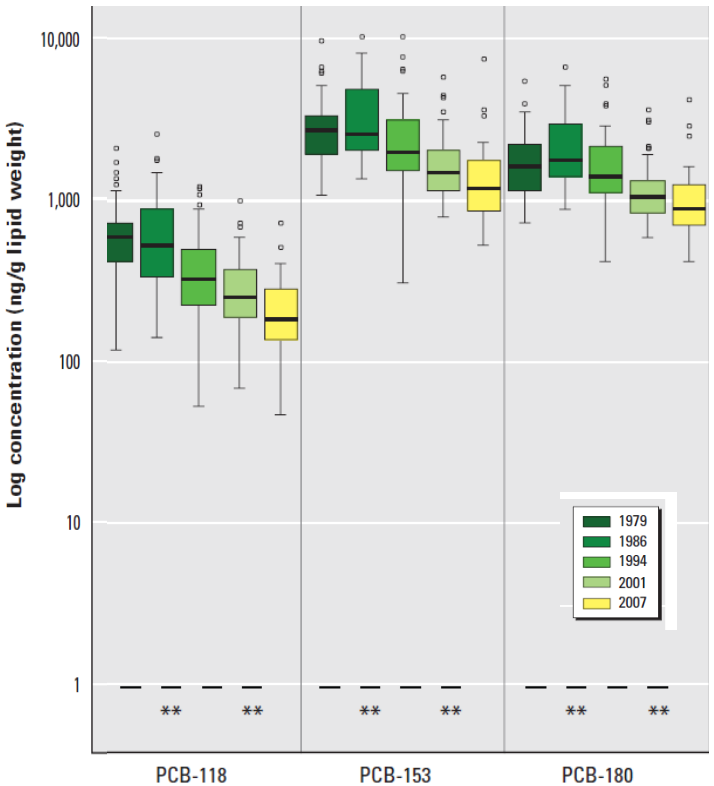
Reasons for increase: Under discussion –ice free ocean, hexachlorobenzene (HCB) as byproduct during pesticide production…

Ma et al. (2011), Hung et al. (2010), Kallenborn et al. (2012)

Estimates of global emissions of PCBs

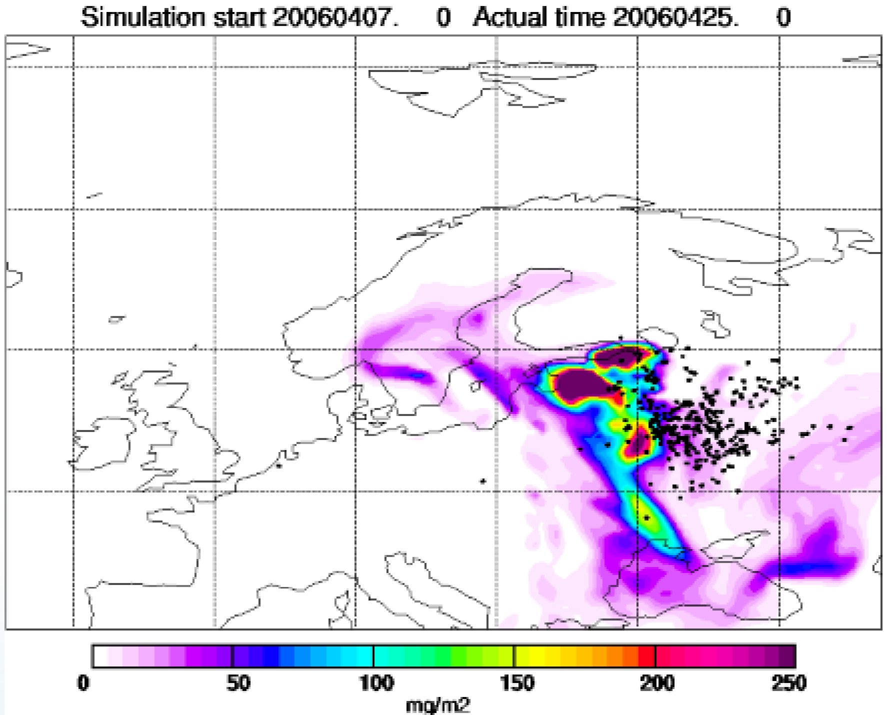


Concentrations (ng/g lw) of PCB in repeated serum samples from Norwegian men



Figures from Therese H. Nøst (Ph.D. thesis; UiT/NILU 2014) and Nøst et al, 2013: http://dx.doi.org/10.1289/ehp.1206317

Trajectories -sources



◆Transport of polluted air (forest/grass fires) to the Arctic

Illustration slide from Torkjel Sandanger, UiT

New compounds -screenings

- Long-range transport vs. local sources
- Establish baseline for future time- and spatial trends
- Assess biomagnification

New compounds -screenings

- Norway and Arctic, 2013: Screening of air, water, terrestrial and marine biota

⇒Few PFAS detected

⇒DBDPE >BDE-47 in several samples

⇒Short- and medium-chained chlorinated paraffins (SCCPs and MCCPs) detected in Arctic biota

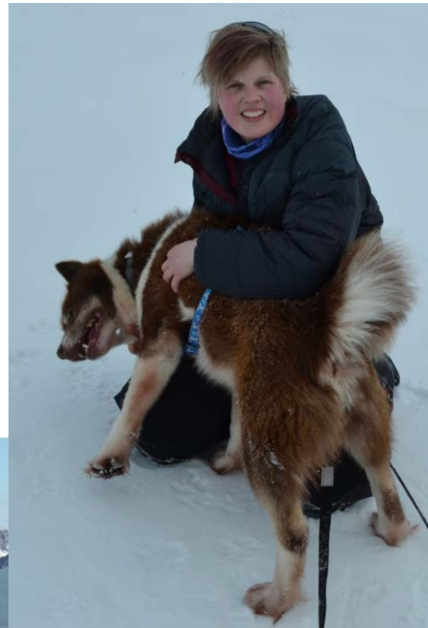
How?

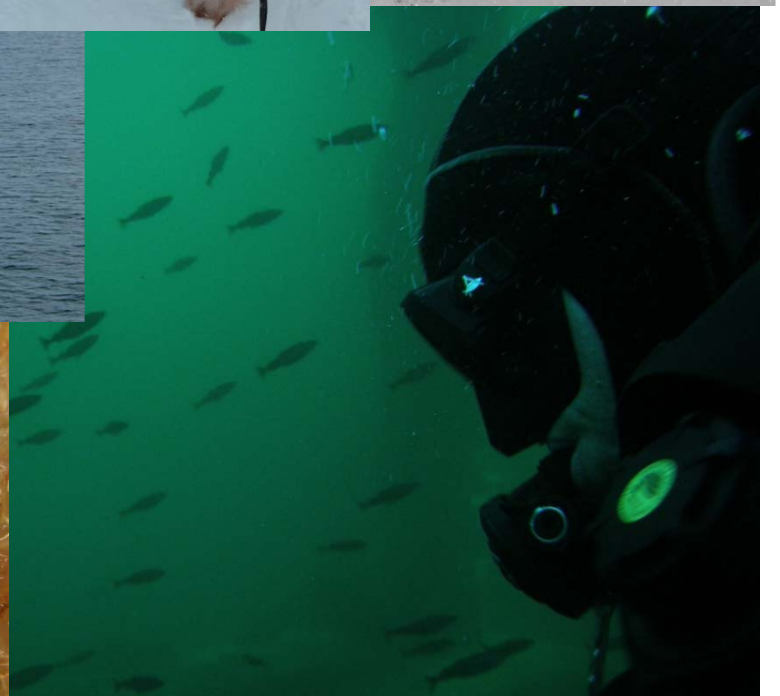
General issues

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

Sampling strategy - biomagnification

Cover the whole food web!

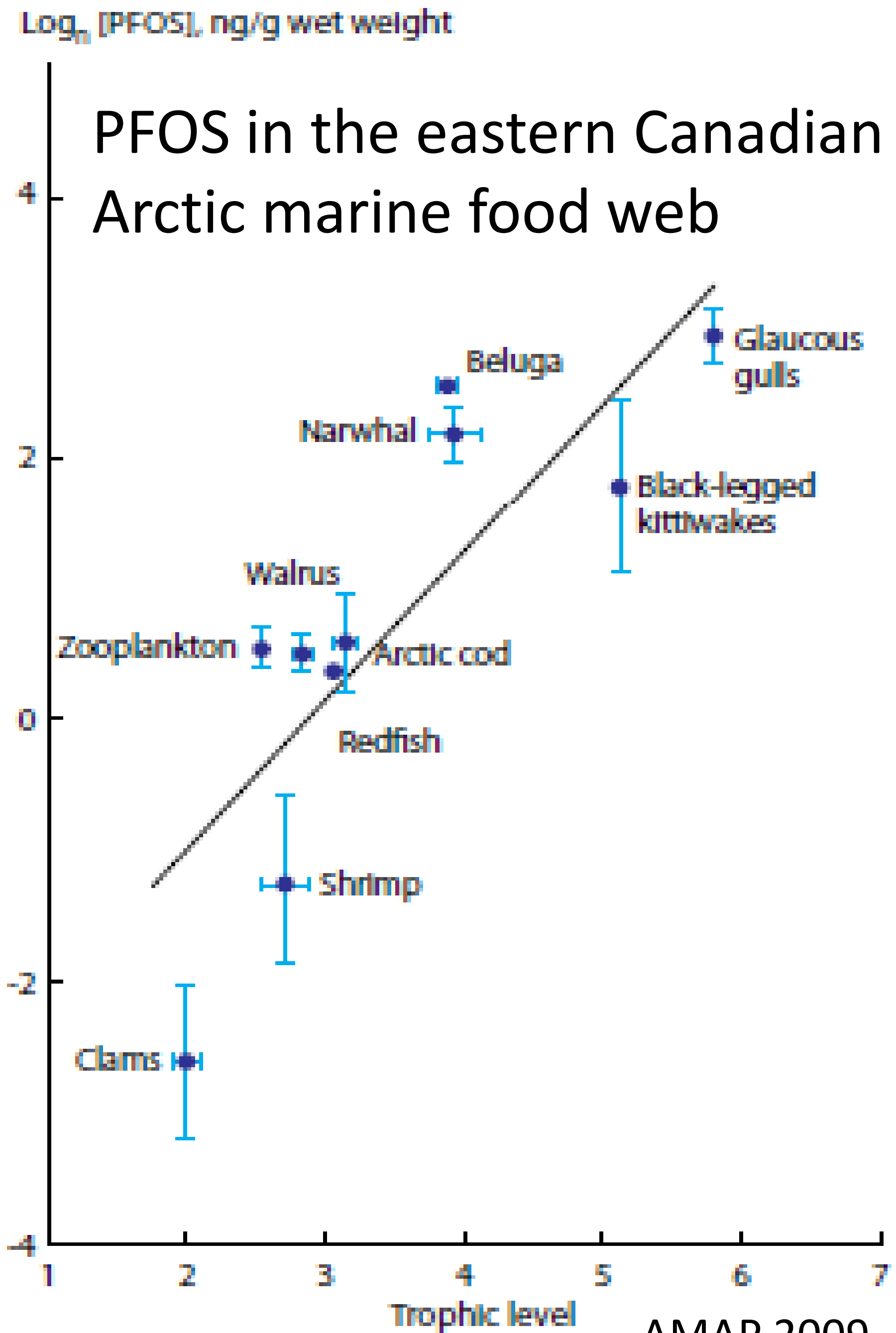




Biomagnification

- Who eats who?
- Benthic/pelagic couplings?

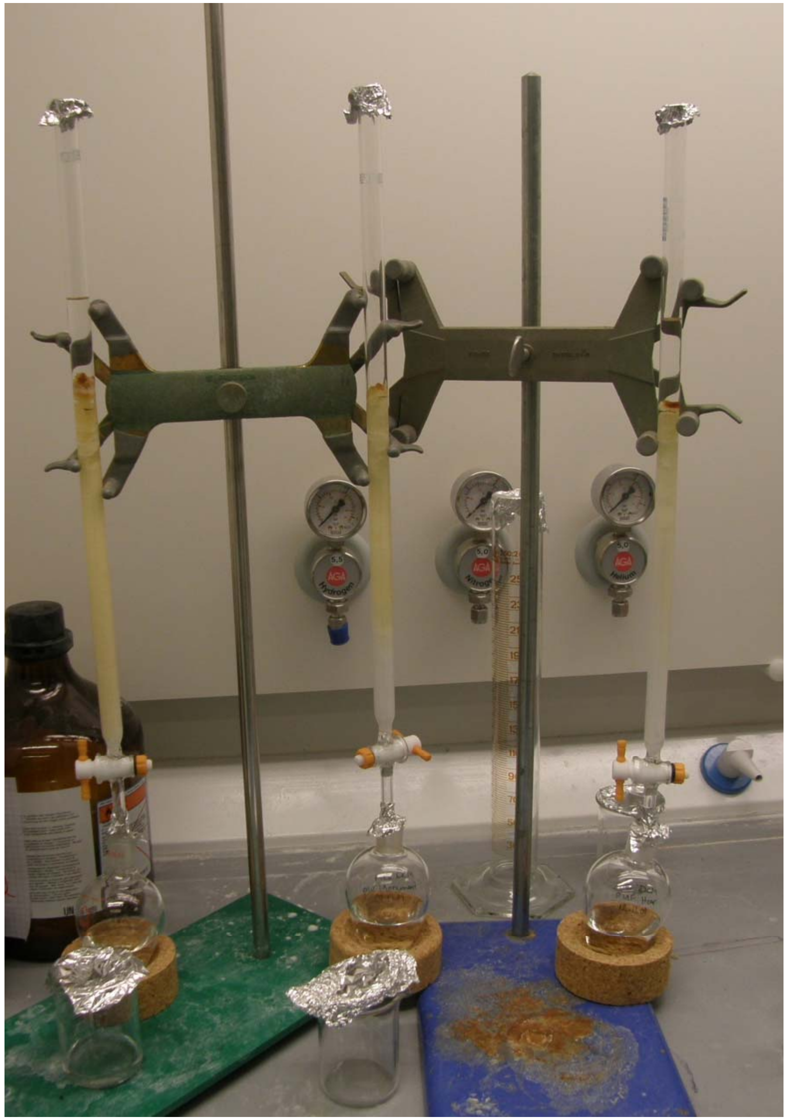
PFOS in the eastern Canadian Arctic marine food web



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

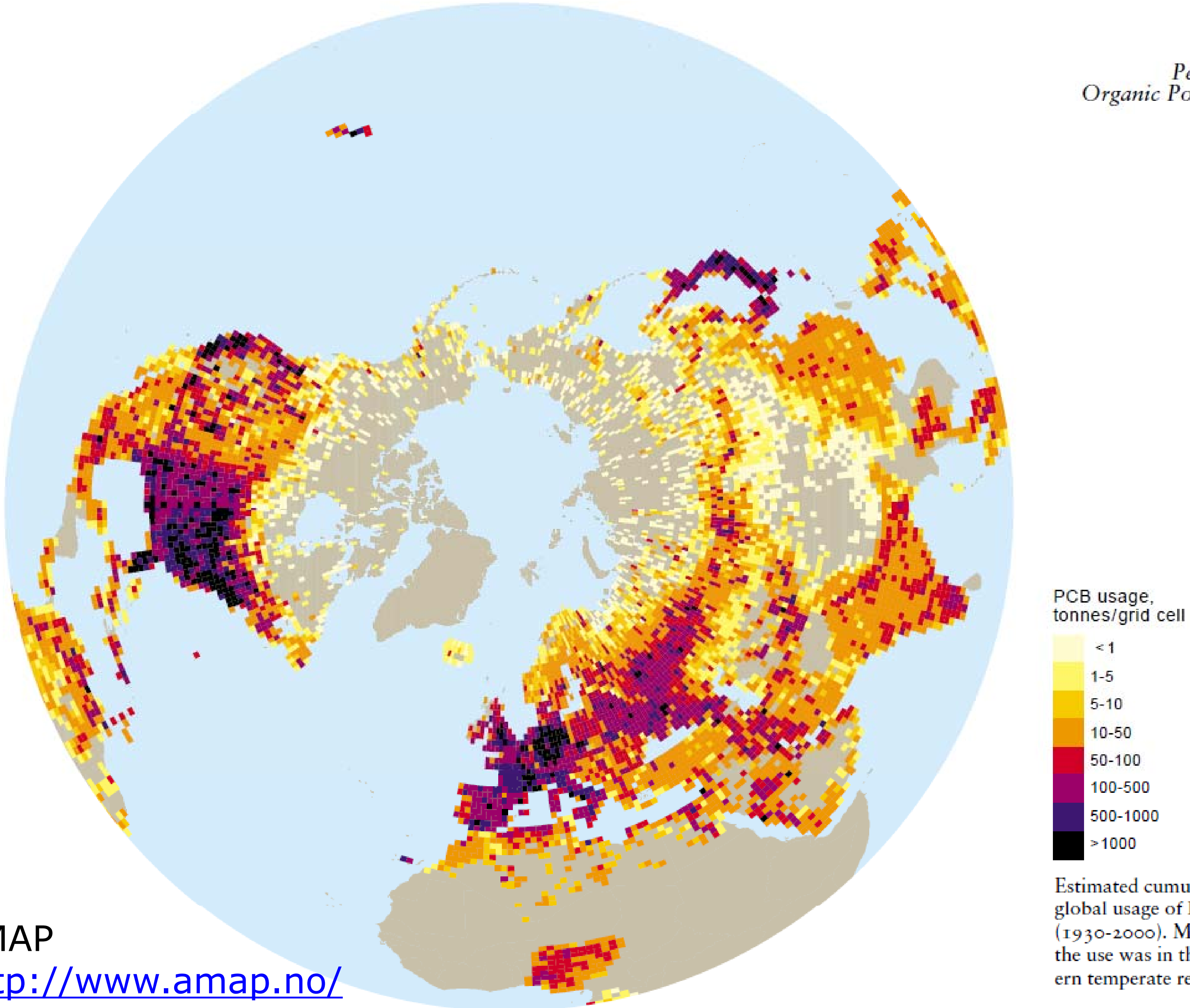
- Study design:
- Fish –species
- Sampling: fishing or buying?
- Transport
- Analyses
- Data interpretation
- Literature comparison

Chemical ”tools”

- Relative distribution
- Degradation and metabolites
- Chirality
- Isotopes

Relative distribution

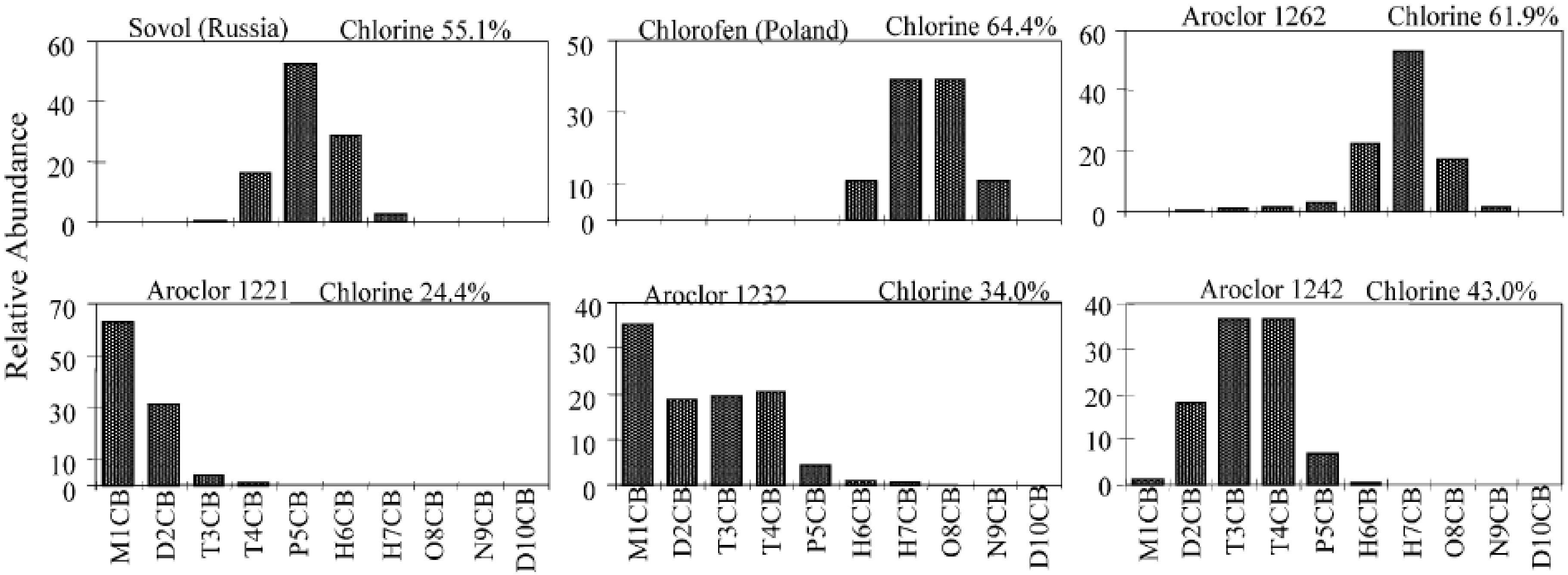
- PCBs: different mixtures had different ratio between congeners
- Low-chlorinated PCBs: Easily undergo long-range transport.



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



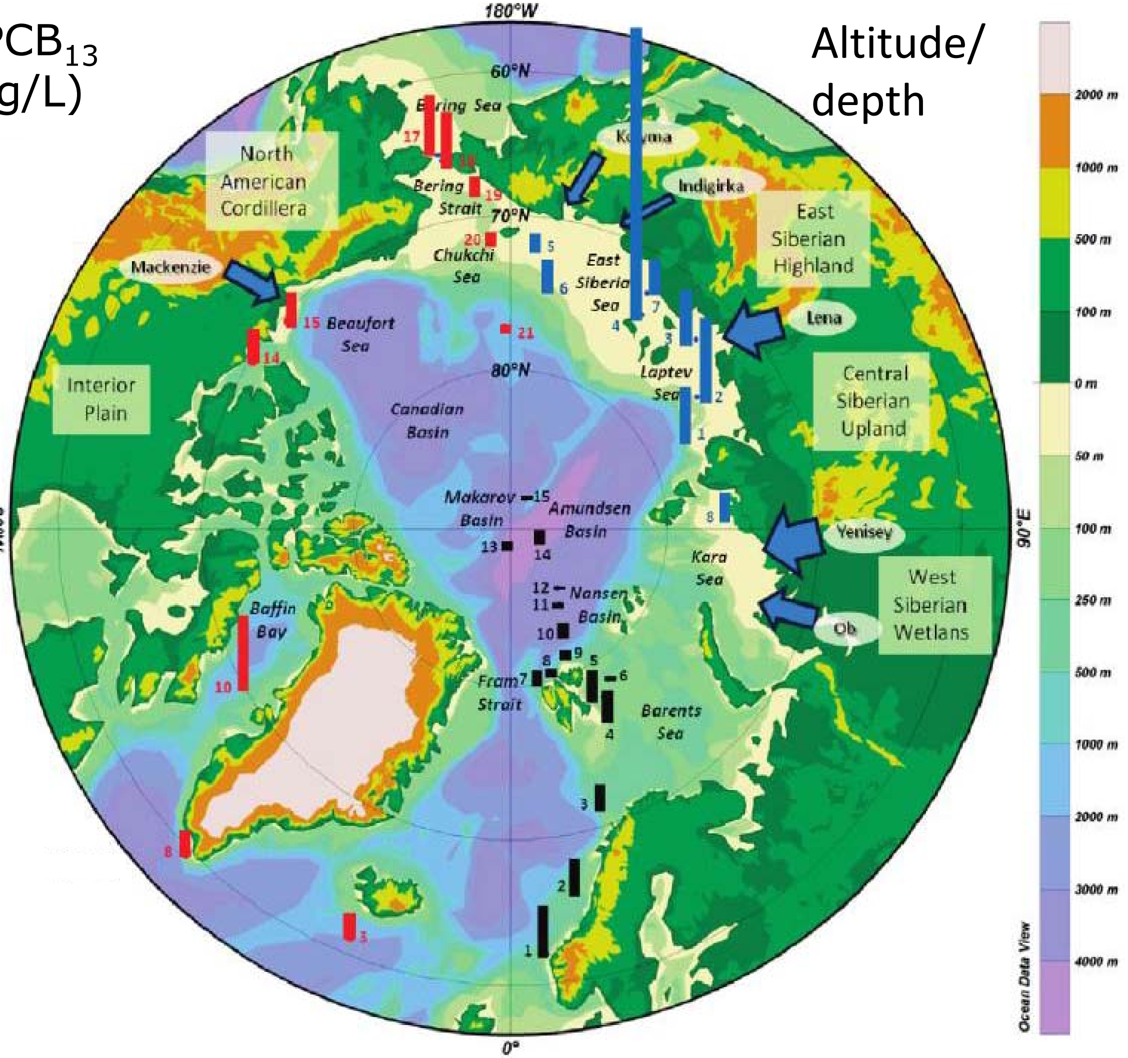
Arochlor: USA

Takasuga et al., 2006

PCB flux to the Arctic

ΣPCB_{13} (pg/L)

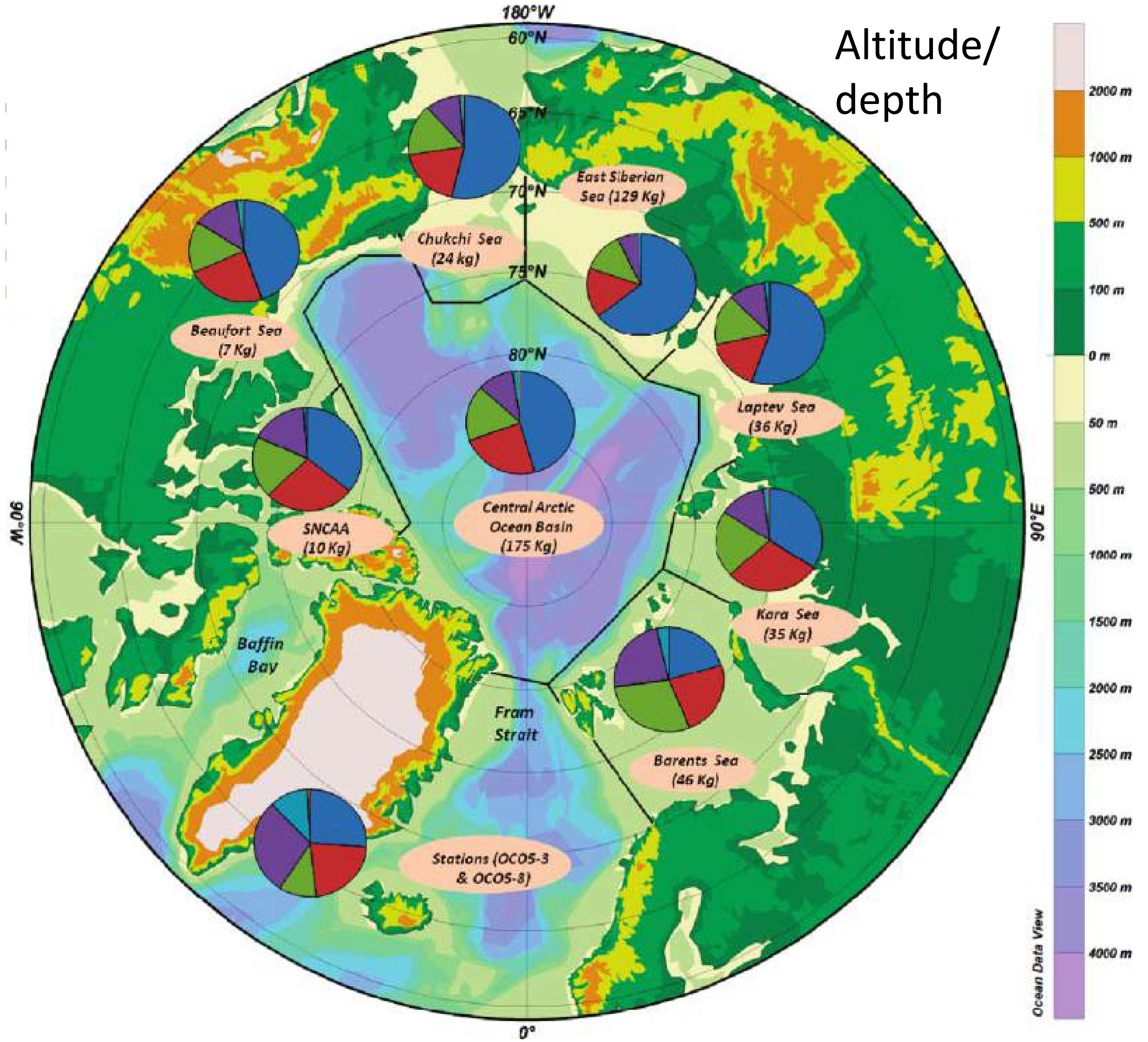
Altitude/ depth



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



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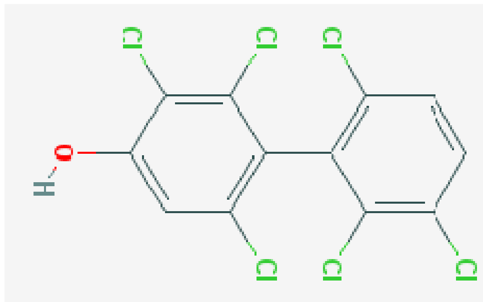
Carrizo, D.; Gustafsson, O. Pan-Arctic River Fluxes of Polychlorinated Biphenyls. *ES&T* 2011

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



Isotopes

Who eats who?

Trophic positions: “place in the food web”

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

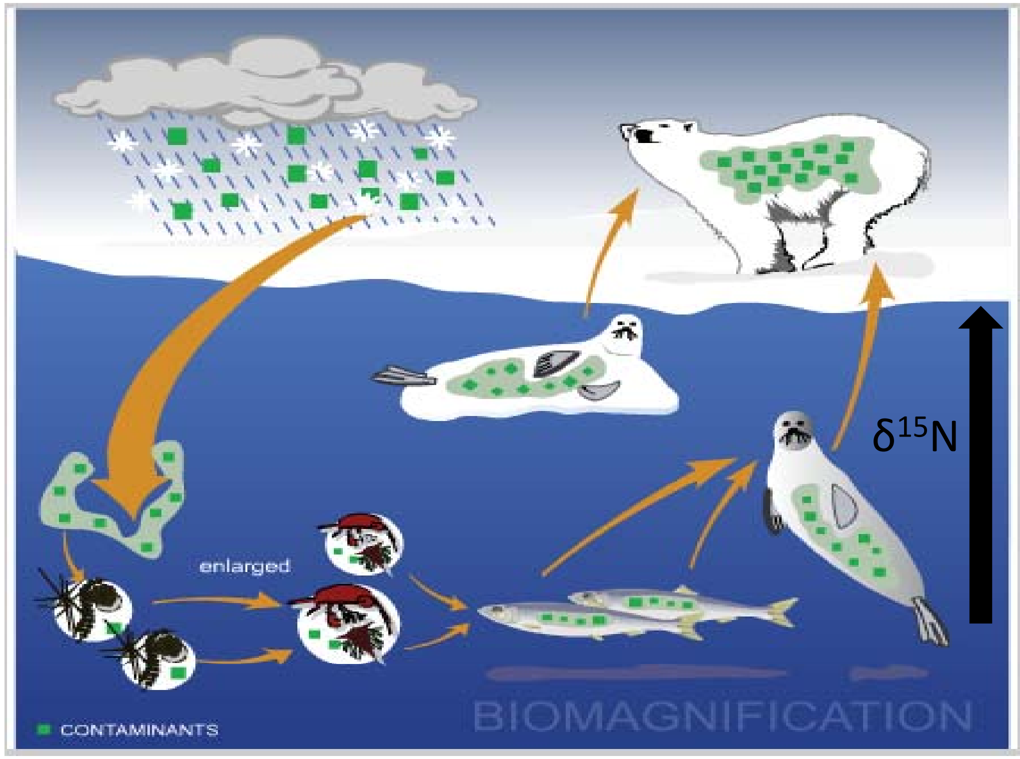
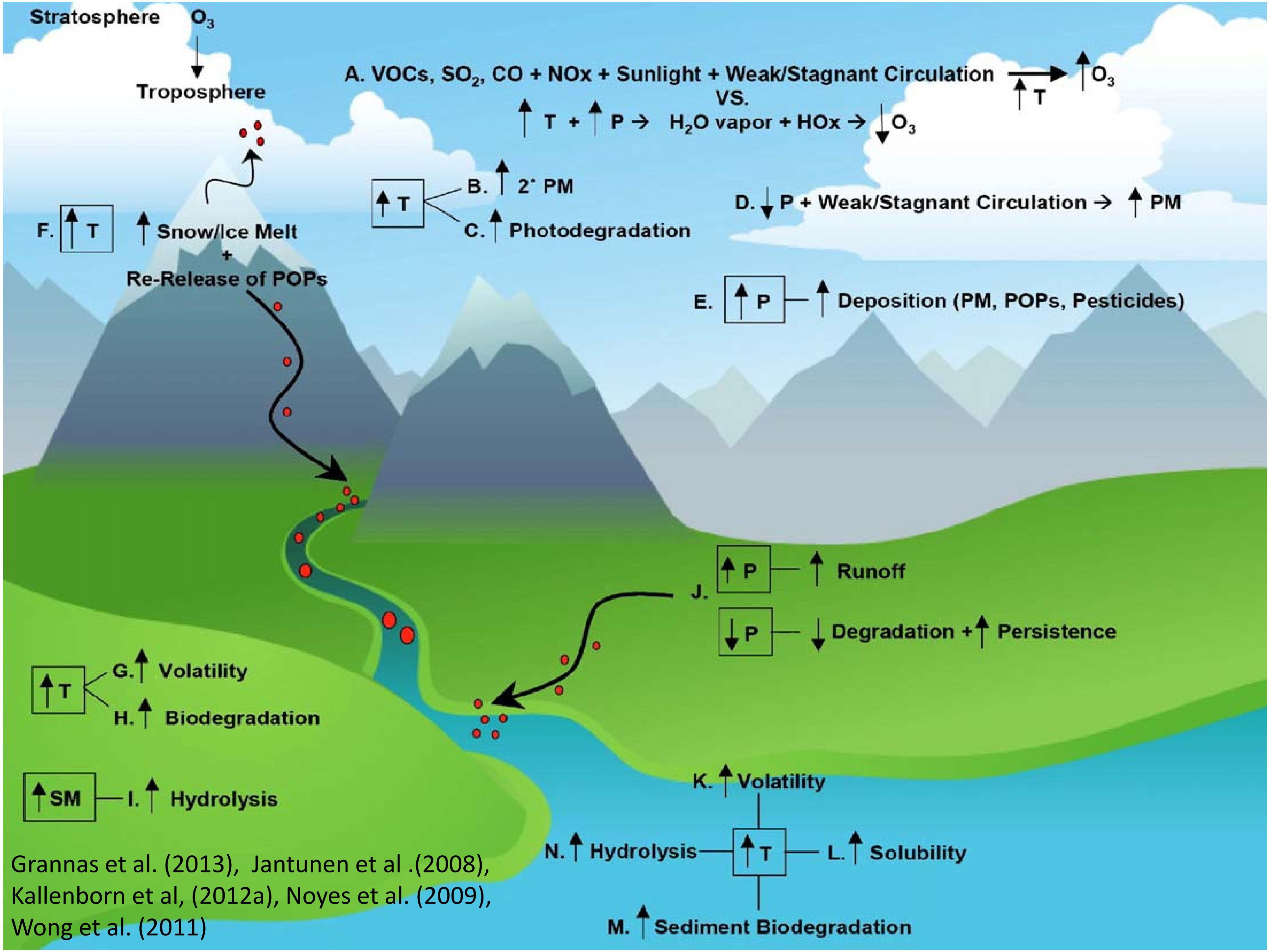


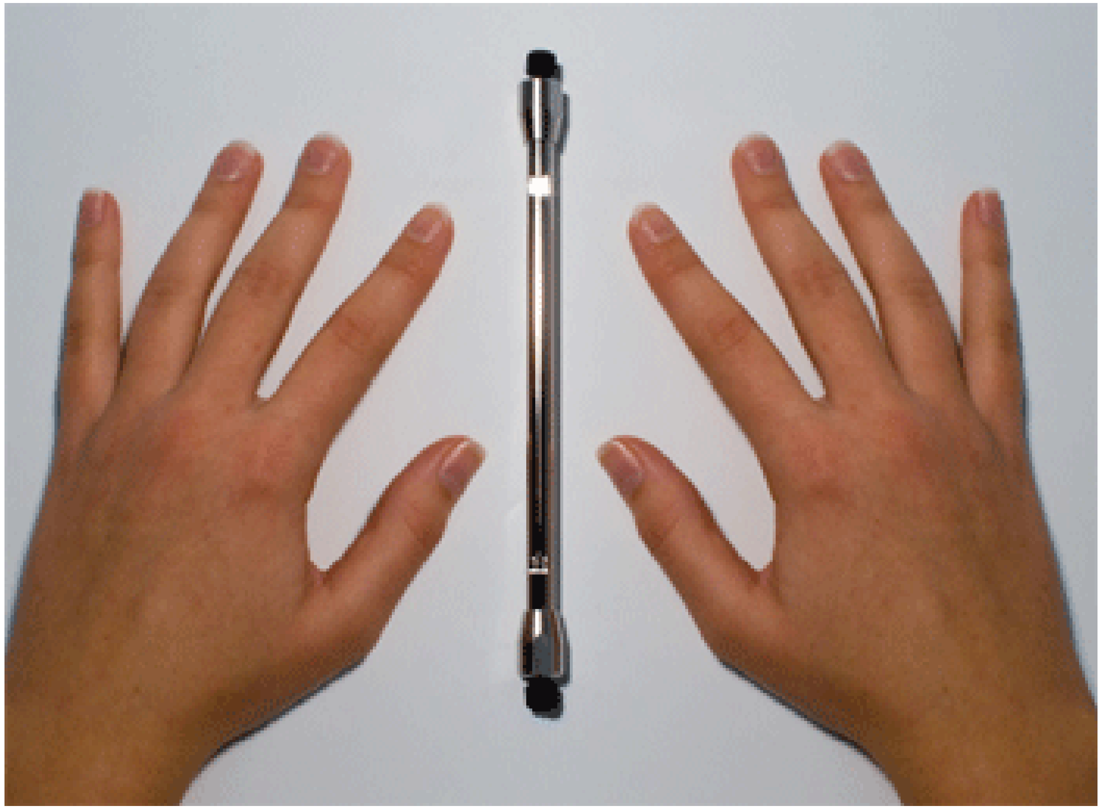
Illustration: Eldbjørg Heimstad


Transport processes
-tracking sources

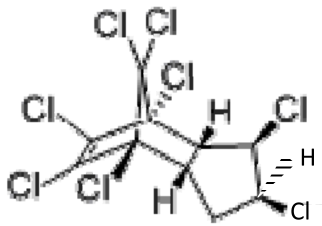


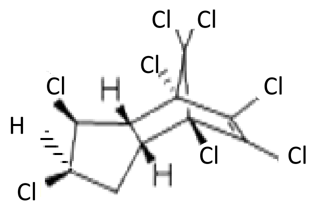
Grannas et al. (2013), Jantunen et al .(2008), Kallenborn et al, (2012a), Noyes et al. (2009), Wong et al. (2011)

Chirality
–tracing environmental processes and sources



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

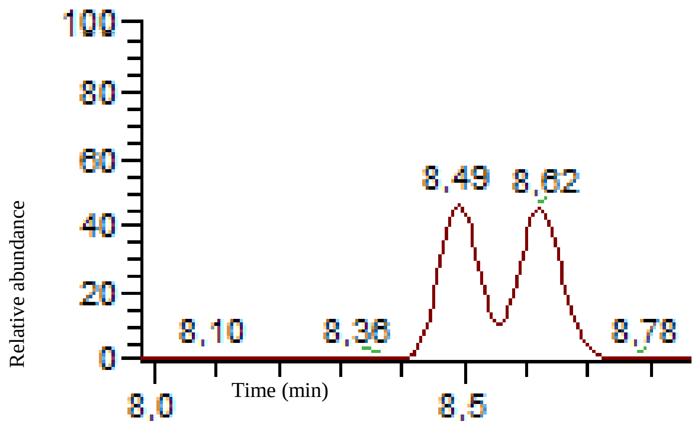




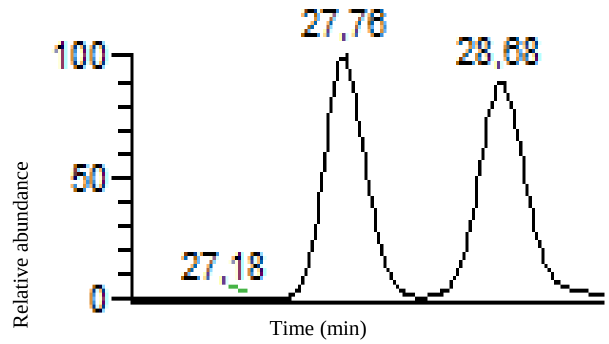
Enantiomer selective analyses

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

α-Hexachlorocyclohexane (α-HCH): (-)-α-HCH, (+)-α-HCH



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



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

Carlsson et al, 2014

Chiral pesticides

⇒ non-racemic EFs: indicate biological transformation processes

Plankton

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

Chiral pesticides and water masses

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

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

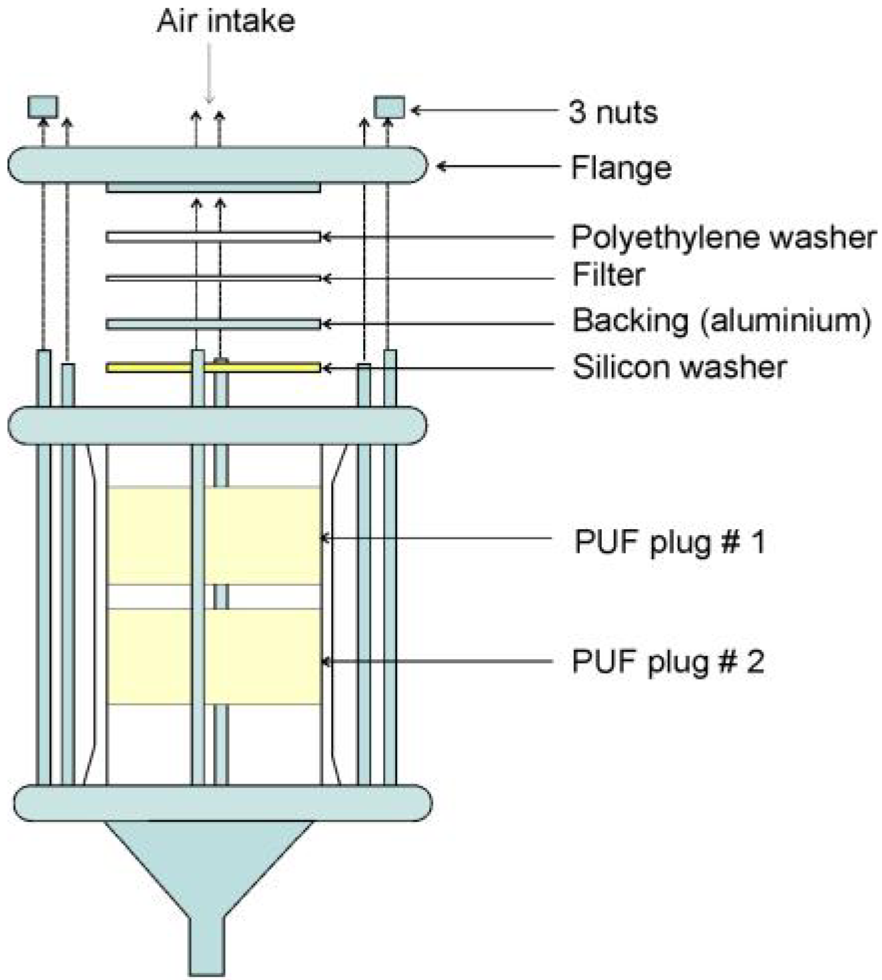
•Water masses and ice cover are important for the EF distribution

•Impact from benthic-pelagic processes not completely understood yet

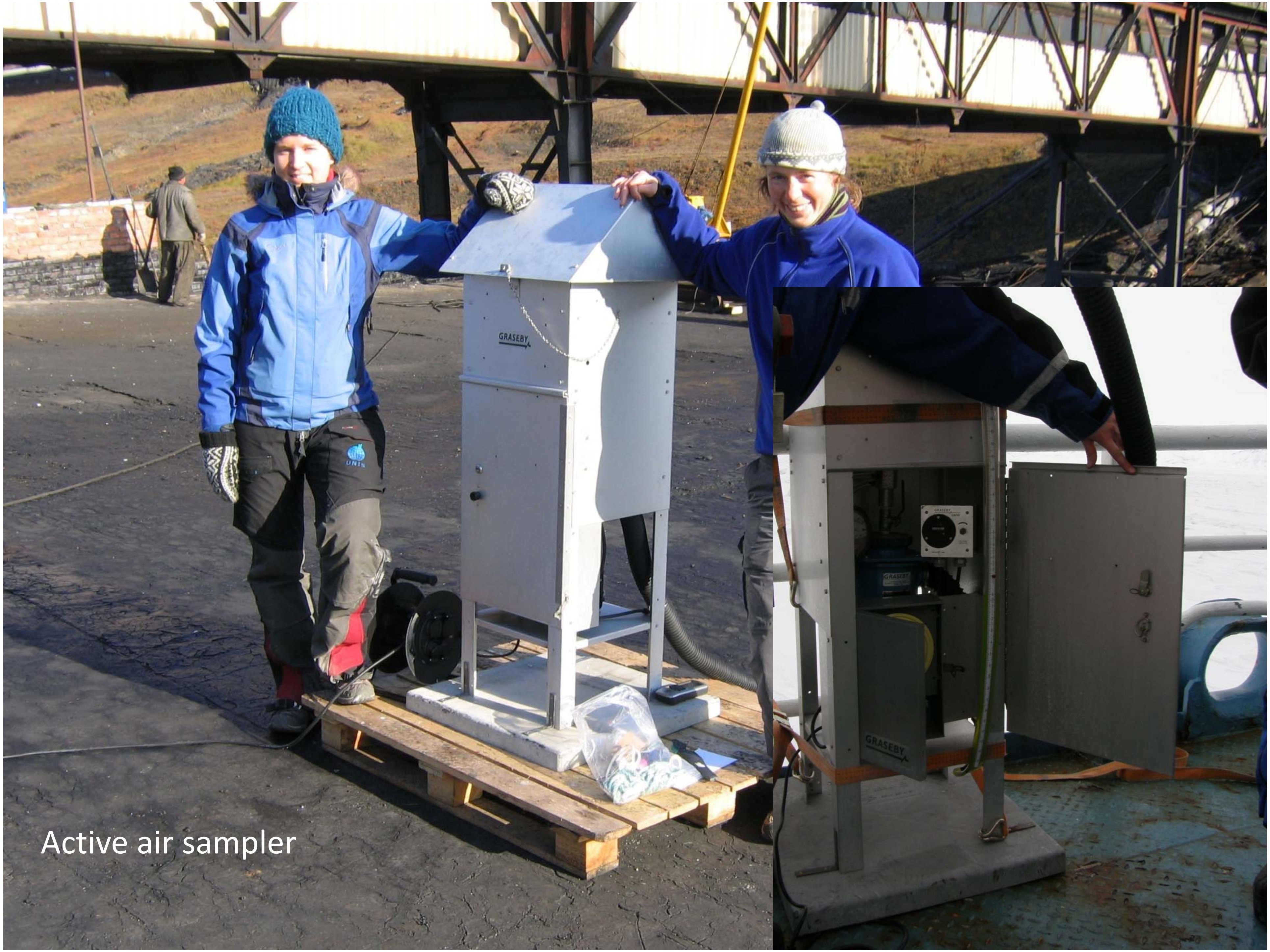
Case studies of environmental pollution

How? –Air sampling

- **Active air sampler** ~vaccum cleaner!
- PUF: Polyurethane foam (sampling media for gaseous compounds)
- Filter: particle associated compounds
- Easy to measure amount of air filtrated
- Sampling time: ~Hours-days
- Need electricity
- Higher cost compared to passive air samplers



Picture: http://www.nilu.no/projects/ccc/manual/index.html



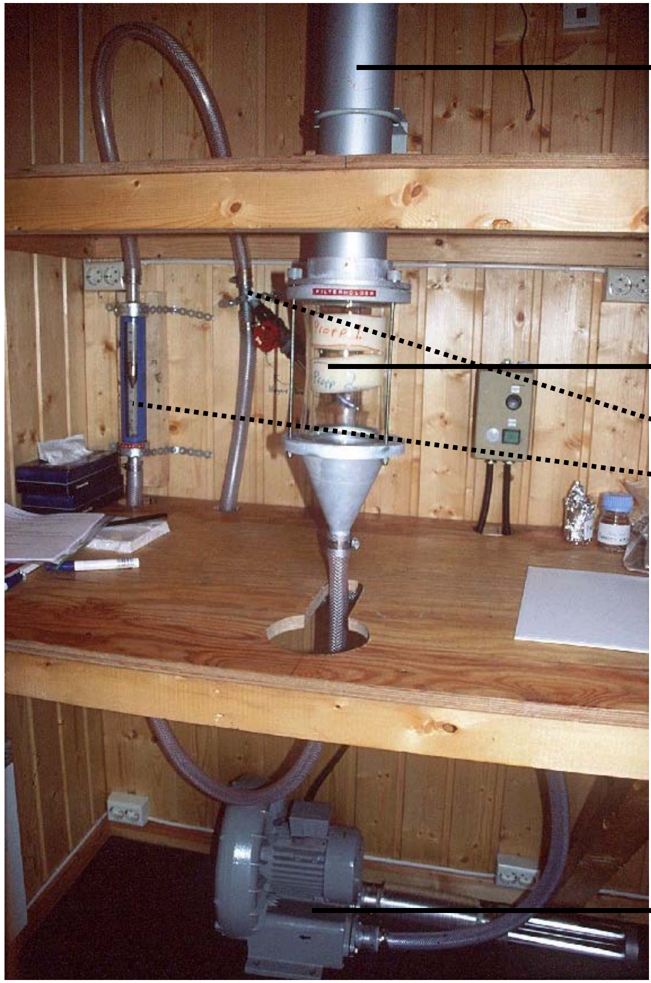
Active air sampler

How? –Air sampling

- **Passive air sampler:**
- Calibration: requires extra experiments and calculations.
- Long exposure time to reach equilibrium (Air-PUF). Sampling time: ~Months.

- Same media (PUF) as active sampler.
- Cheap, easy to run.
- No need for electricity.

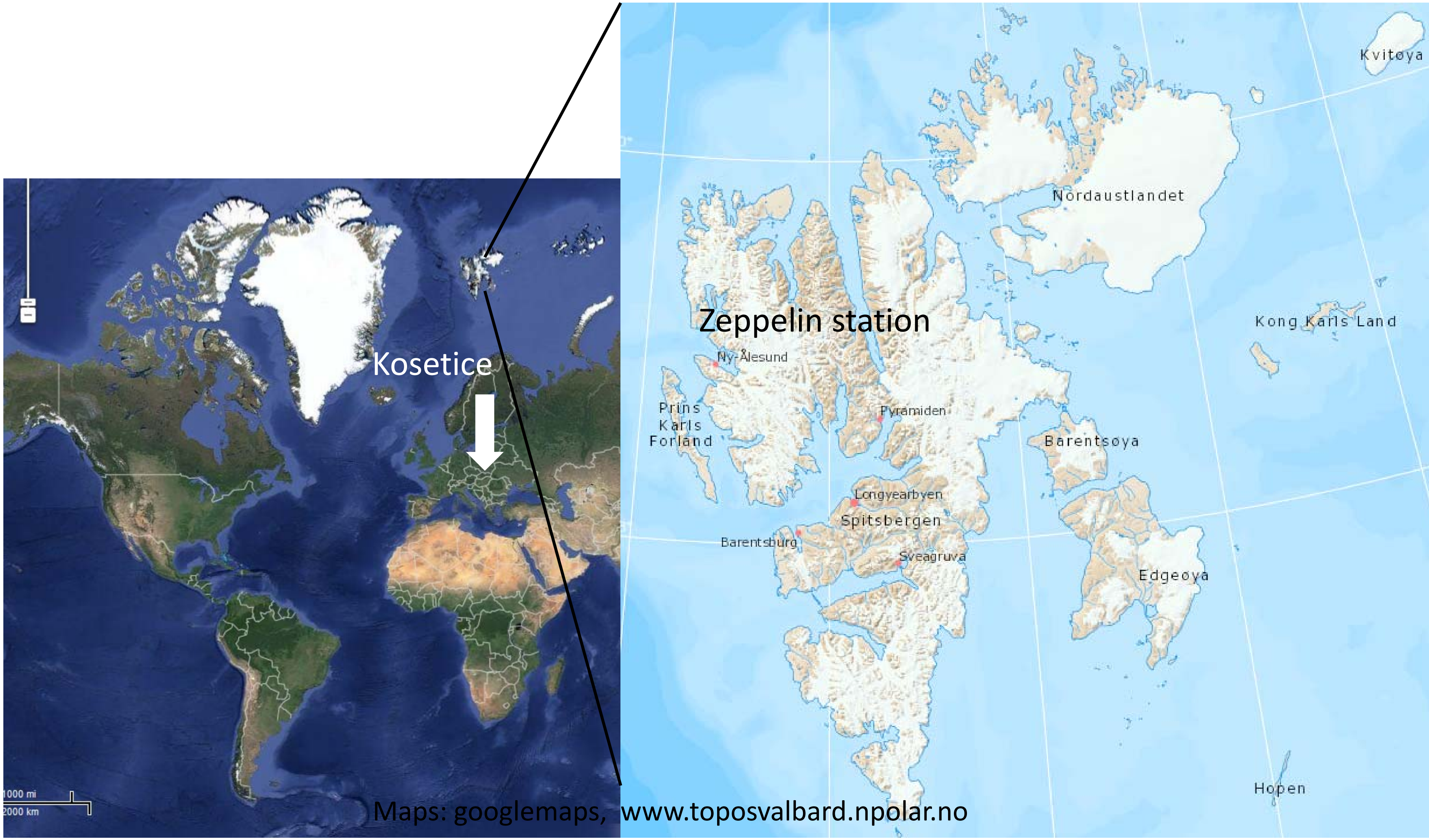
Active and passive air sampler



Pictures from Roland Kallenborn, NMBU

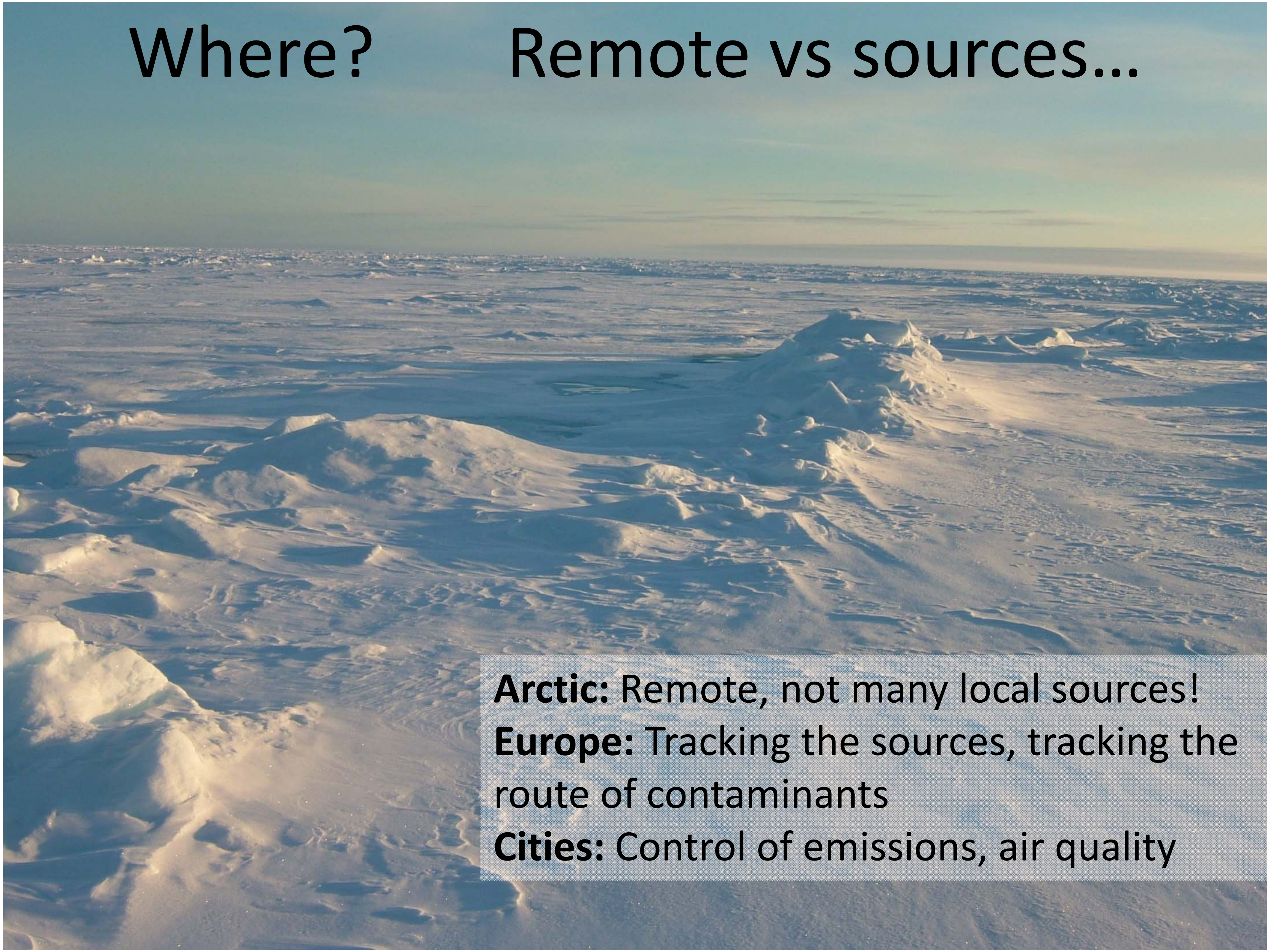
Where?

Where? Remote vs sources...

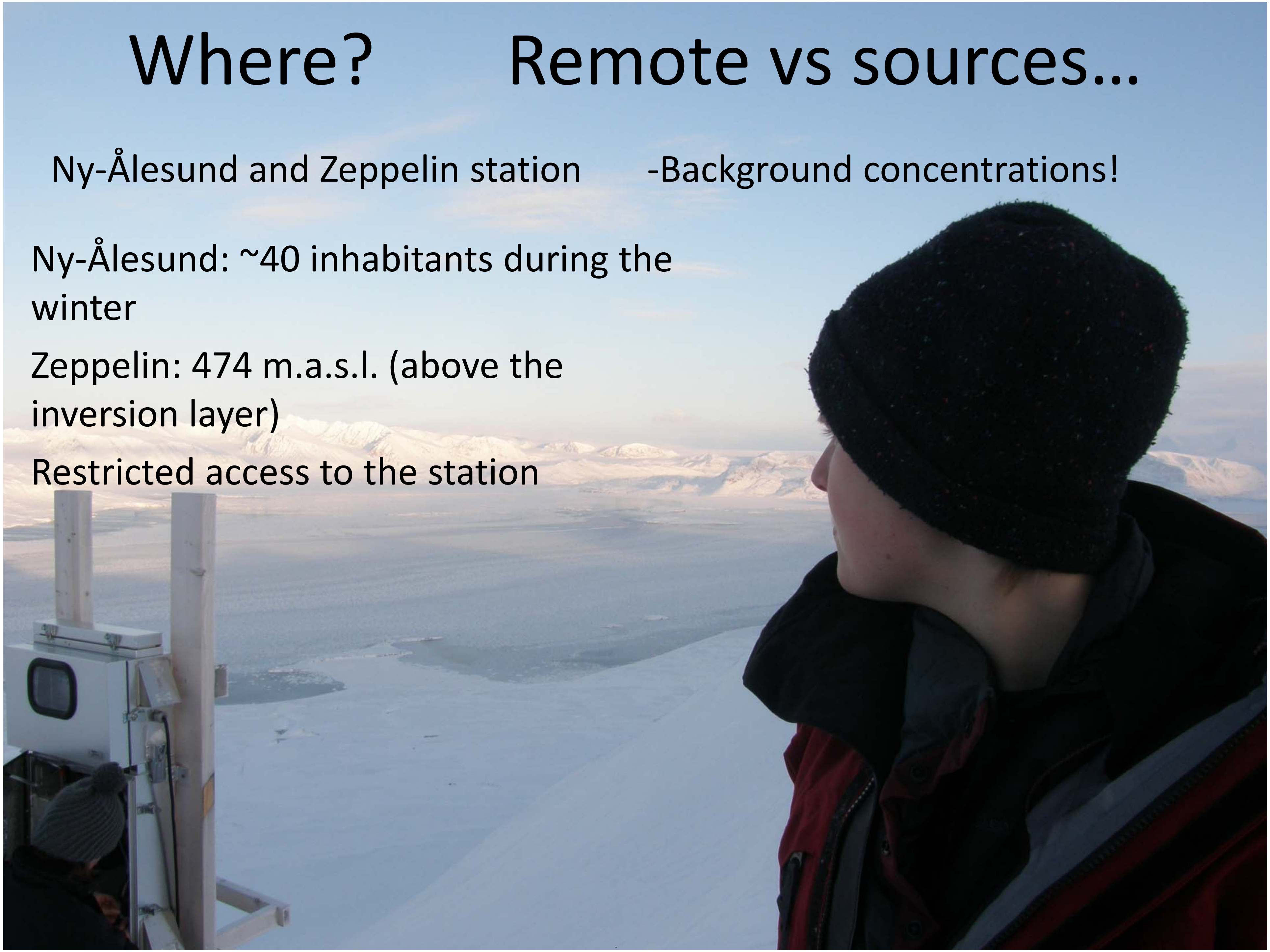


Maps: googlemaps, www.toposvalbard.npolar.no

Where? Remote vs sources…

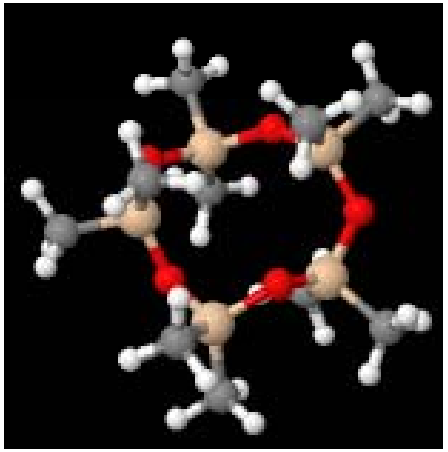


Arctic: Remote, not many local sources!
Europe: Tracking the sources, tracking the route of contaminants
Cities: Control of emissions, air quality


Where? Remote vs sources…
Ny-Ålesund and Zeppelin station
-Background concentrations!
Ny-Ålesund: ~40 inhabitants during the winter
Zeppelin: 474 m.a.s.l. (above the inversion layer)
Restricted access to the station

Where? Remote vs sources…

- Zeppelin: Detection of cyclic volatile methyl siloxanes (cVMS) in the air.
- Active air sampling for decamethylcyclopentasiloxane (D5), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), and dodecamethylcyclohexasiloxane (D6).
- Measured D5 were in agreement with modelled predictions.



Krogseth et al., 2013.

Where? Remote vs sources…

Environmental Science & Technology Article

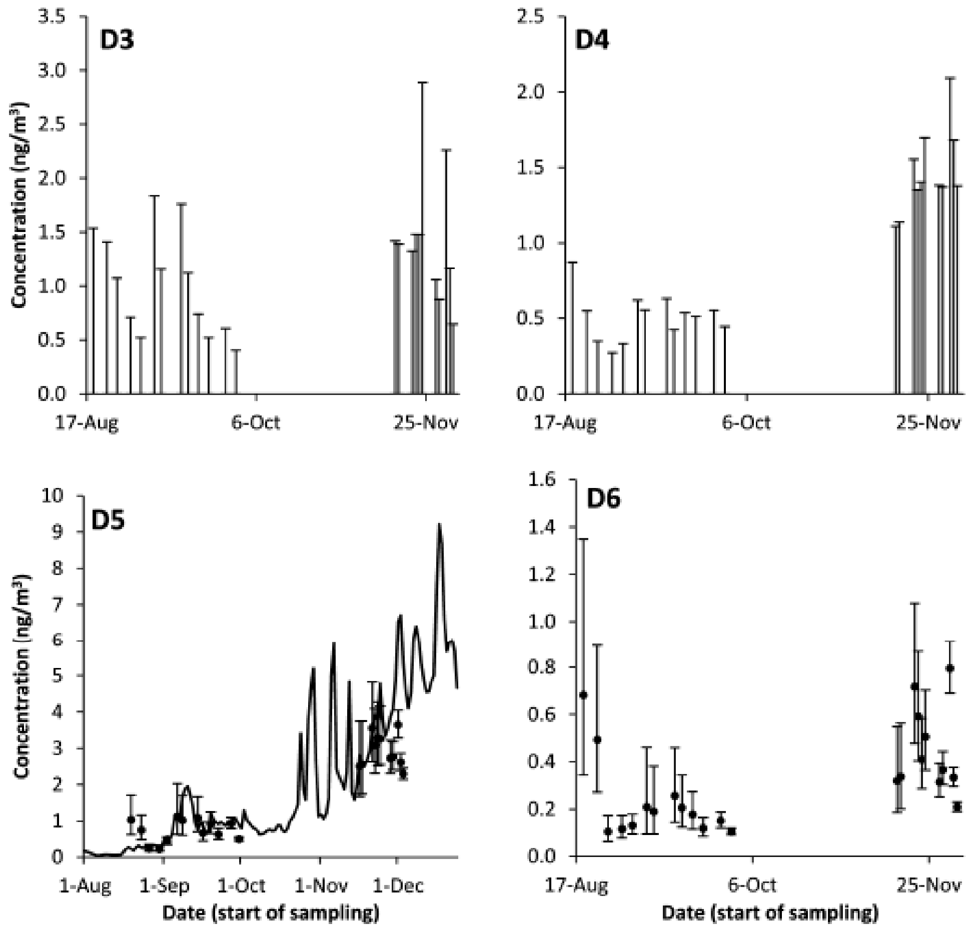


Figure 1. Concentrations of D3, D4, D5, and D6 in air for all samples at Zeppelin in 2011. The concentrations are shown as ranges for D3 and D4, taking into account both possible under- and overestimation due to the storage artifacts. The concentrations for D5 and D6 are the storage-corrected concentrations with the uncertainties as error bars. The DEHM-model estimate for D5 concentrations in Arctic air from August to December 2011 is displayed as a line. Note the different scales on the *y*-axes.

Krogseth et al., 2013.

Monitoring and management
-a case study from Svalbard

Case study from Svalbard

Can background contamination still be an issue? …..

Picture: Guttorm Christensen, Akvaplan-niva

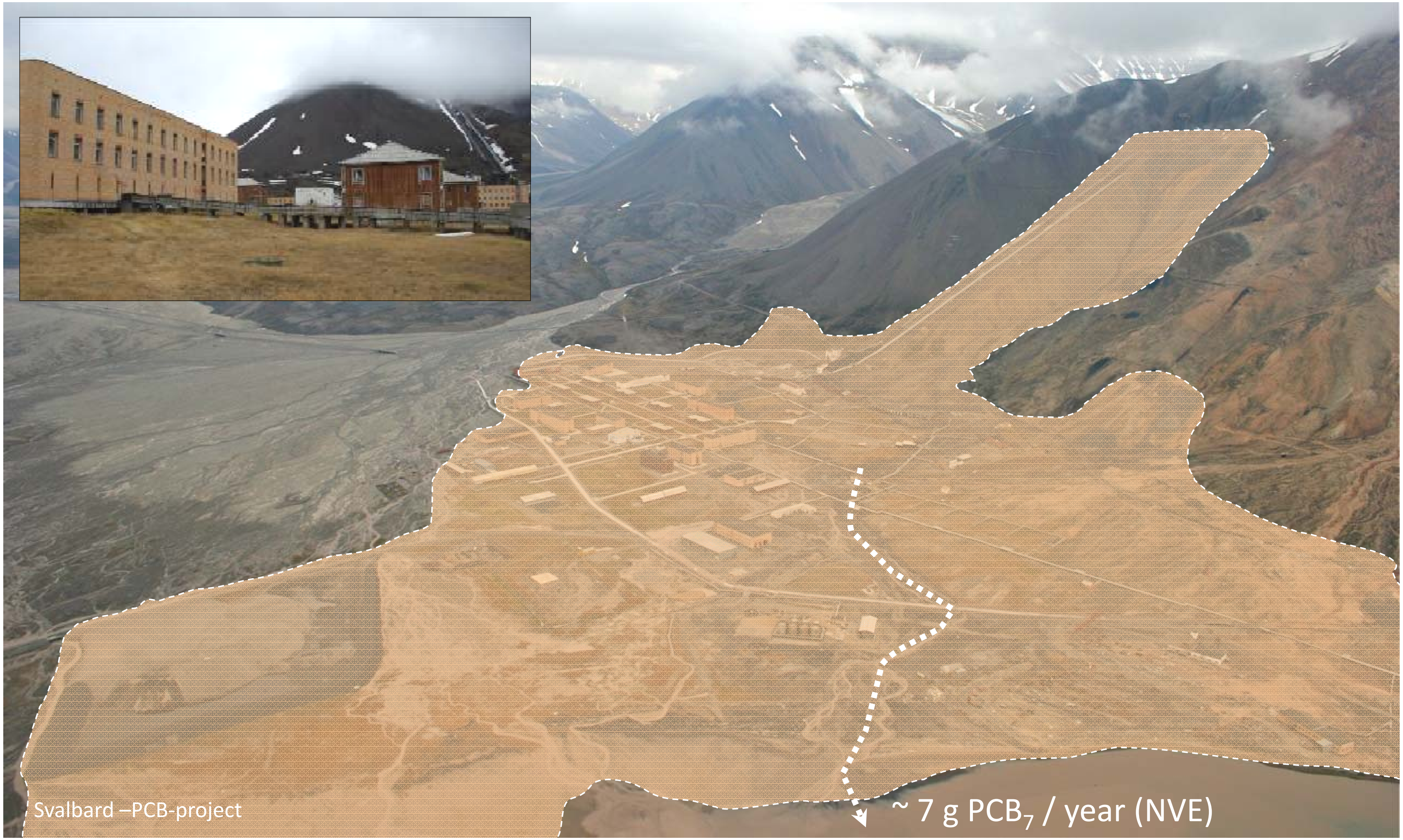
Case study from Svalbard

- Extensive usage of PCB in Barentsburg => local sources are present.
- Similar atmospheric contribution of PCB in Ny-Ålesund and Barenstburg (short distances)

=> Clean-up Svalbard from PCBs!

Pyramiden

Roughly 430 kg PCB_7/km^2 in the soil (0-20 cm)



Barentsburg
Roughly 300 kg PCB_7/km^2 in the soil (0-20 cm)

Longyearbyen

Roughly 3,3 kg PCB_7/km^2 in the soil (0-20 cm)

Remote areas of Svalbard

Roughly 1,1 kg PCB_7/km^2 in the soil (0-20 cm)

Case study from Svalbard

- Routine monitoring => higher concentrations of PCB detected
- High levels of PCB => management measurements –clean-up
- Prevention for future => education, information, monitoring

Where? -A case study from Iceland

- FUNI: Small incineration plant in Isafjördur, NW Iceland
- Built 1995, small throughput (~3000 tons waste/year)
- Dispensation from EU regulations on dioxins in fly ash
- 2010: Too high levels of dioxins in sheep milk (1 sample) from the area

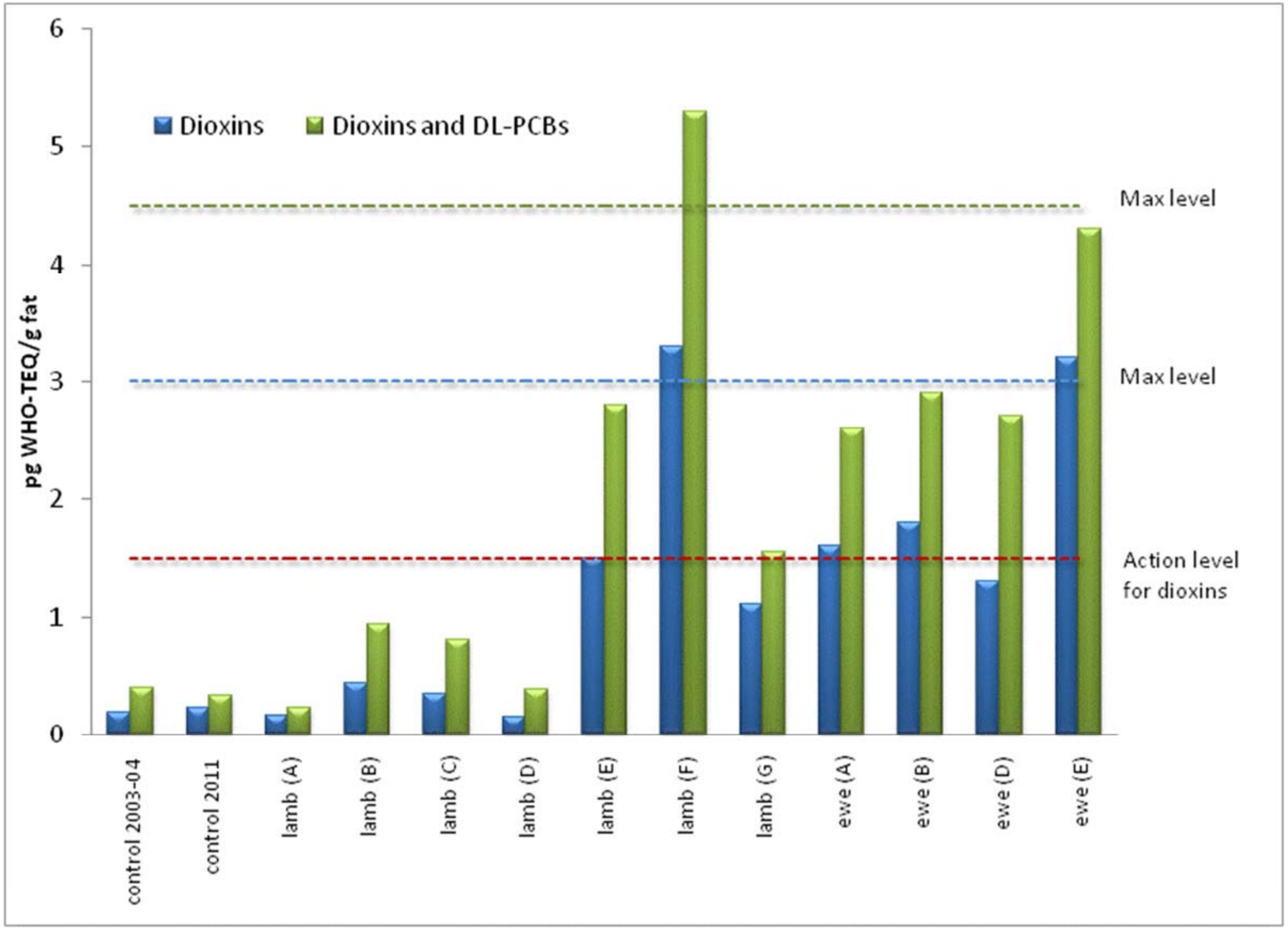
Map: www.maps.google.com

Case study from Iceland

- Lamb meat: elevated concentrations
- Concentration in hay of PCDD/Fs: 0.85 pg WHO-TEQ/g
- Slightly above the EU maximum limit of 0.75 pg WHO-TEQ/g

Picture: Wikipedia

Case study from Iceland



Ewe =female, adult sheep

Case study from Iceland

- Why did it happen?
- Small incinerator and too little maintainance

=> bad combustion process =>dioxins

Case study from Iceland

- Prevention for the future: maintenance of incinerators, regular surveys of PCBs, dioxins, public awareness.
- This incinerator is not used anymore.

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 limitations in literature

References

AMAP, 2011. Snow, Water, Ice and Permafrost in the Arctic (SWIPA): Climate Change and the Cryosphere. in: AMAP (Ed.), Oslo, Norway, p. xii +538.
Becker, S., Halsall, C.J., Tych, W., Kallenborn, R., Schlabach, M., Manø, S., 2012. Changing sources and environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic atmosphere. Atmospheric Chemistry and Physics 12, 4033- 4044.
Borgå, K., Saloranta, T.M., Ruus, A., 2010. Simulating climate change-induced alterations in bioaccumulation of organic contaminants in an arctic marine food web. Environ. Toxicol. Chem. 29, 1349-1357.
Gouin, T., Armitage, J.M., Cousins, I.T., Muir, D.C.G., Ng, C.A., Reid, L., Tao, S., 2013. Influence of global climate change on chemical fate and bioaccumulation: The role of multimedia models. Environ. Toxicol. Chem. 32, 20-31.
Grannas, A.M., Bogdal, C., Hageman, K.J., Halsall, C., Harner, T., Hung, H., Kallenborn, R., Klan, P., Klanova, J., Macdonald, R.W., Meyer, T., Wania, F., 2013. The role of the global cryosphere in the fate of organic contaminants. Atmospheric Chemistry and Physics 13, 3271-3305.
Hung, H., Chi Lee, S., Wania, F., Blanchard, P., Brice, K., 2005. Measuring and simulating atmospheric concentration trends of polychlorinated biphenyls in the Northern Hemisphere. Atmos. Environ. 39, 6502-6512.
Hung, H., Kallenborn, R., Breivik, K., Su, Y.S., Brorstrom-Lunden, E., Olafsdottir, K., Thorlacius, J.M., Leppanen, S., Bossi, R., Skov, H., Mano, S., Patton, G.W., Stern, G., Sverko, E., Fellin, P., 2010. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993-2006. Sci. Total Environ. 408, 2854-2873.
IPCC, 2013. Fifth Assessment Report (AR5). in: Intergovermental Panel on Climate Change, W., UNEP (Ed.).
Jantunen, L.M., Helm, P.A., Kylin, H., Bidleman, T.F., 2008. Hexachlorocyclohexanes (HCHs) In the Canadian Archipelago. 2. Air−Water Gas Exchange of α- and γ-HCH. Environ. Sci. Technol. 42, 465-470.
Kallenborn, R., Halsall, C., Dellong, M., Carlsson, P., 2012a. The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants. Journal of Environmental Monitoring 14, 2854-2869.

References

Kallenborn, R., Reiersen, L.O., Olseng, C.D., 2012b. Long–term atmospheric monitoring of persistent organic pollutants (POPs) in the Arctic: a versatile tool for regulators and environmental science studies. Atmospheric Pollution Research 3, 485-493.

Macdonald, R.W., Harner, T., Fyfe, J., 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Sci. Total Environ. 342, 5-86.

Malanichev, A., Mantseva, E., Shatalov, V., Strukov, B., Vulykh, N., 2004. Numerical evaluation of the PCBs transport over the Northern Hemisphere. Environmental Pollution 128, 279-289.

Noyes, P.D., McElwee, M.K., Miller, H.D., Clark, B.W., Van Tiem, L.A., Walcott, K.C., Erwin, K.N., Levin, E.D., 2009. The toxicology of climate change: Environmental contaminants in a warming world. Environment International 35, 971-986.

Toose, L., Woodfine, D.G., MacLeod, M., Mackay, D., Gouin, J., 2004. BETR-World: a geographically explicit model of chemical fate: application to transport of α-HCH to the Arctic. Environmental Pollution 128, 223-240.

UNEP/AMAP, 2011. Climate Change and POPs: Predicting the Impacts. in: UNEP/AMAP (Ed.).

Wong, F., Jantunen, L.M., Pucko, M., Papakyriakou, T., Staebler, R.M., Stern, G.A., Bidleman, T.F., 2011. Air-Water Exchange of Anthropogenic and Natural Organohalogens on International Polar Year (IPY) Expeditions in the Canadian Arctic. Environ. Sci. Technol. 45, 876-881.

Wöhrnschimmel, H., MacLeod, M., Hungerbuhler, K., 2012a. Global multimedia source–receptor relationships for persistent organic pollutants during use and after phase–out. Atmospheric Pollution Research 3, 392-398.

Wöhrnschimmel, H., MacLeod, M., Hungerbuhler, K., 2013. Emissions, Fate and Transport of Persistent Organic Pollutants to the Arctic in a Changing Global Climate. Environ. Sci. Technol. 47, 2323-2330.

Wöhrnschimmel, H., Tay, P., von Waldow, H., Hung, H., Li, Y.F., MacLeod, M., Hungerbuhler, K., 2012b. Comparative Assessment of the Global Fate of alpha- and beta-Hexachlorocyclohexane before and after Phase-Out. Environ. Sci. Technol. 46, 2047-2054.

References

Halldorsson T, Audunsson G, Guicharnaud R, Dyrmundsson O, Hansson S, Hreinsson K. 2012. Contamination of livestock due to the operation of a small waste incinerator: A case incident in skutulsfjordur, iceland, in 2010. Acta Veterinaria Scandinavica 54:S4.

Hung, H., Kallenborn, R., Breivik, K., Su, Y.S., Brorstrom-Lunden, E., Olafsdottir, K., Thorlacius, J.M., Leppanen, S., Bossi, R., Skov, H., Mano, S., Patton, G.W., Stern, G., Sverko, E., Fellin, P., 2010. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993-2006. Sci. Total Environ. 408, 2854-2873.

Kallenborn, R., Reiersen, L.O., Olseng, C.D., 2012. Long–term atmospheric monitoring of persistent organic pollutants (POPs) in the Arctic: a versatile tool for regulators and environmental science studies. Atmospheric Pollution Research 3, 485-493.

Krogseth, I. S.; Kierkegaard, A.; McLachlan, M. S.; Breivik, K.; Hansen, K. M.; Schlabach, M., Occurrence and Seasonality of Cyclic Volatile Methyl Siloxanes in Arctic Air. *Environ. Sci. Technol.* **2013,** *47*, 502−509.

Ma, J., Hung, H., Tian, C., Kallenborn, R., 2011. "Revolatilization of persistent organic pollutants in the Arctic induced by climate change." Nature Clim. Change 1(5): 255-260.

Nøst T.H, Breivik K, Fuskevag O.M, Nieboer E, Odland JO, Sandanger TM. 2013. Persistent organic pollutants in norwegian men from 1979 to 2007: Intraindividual changes, age-period-cohort effects, and model predictions. Environmental Health Perspectives 121:1292-1298.

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