Analytical chemistry
-Monitoring and sampling strategies I

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

Outline – monitoring of POPs

- Why?

  History, control, time trends, new and emerging compounds

  How?

  EMEP, NORMAN and CLRTAP

  Sampling devices, time series, air quality

- Where?

  Remote vs sources

History of POPs

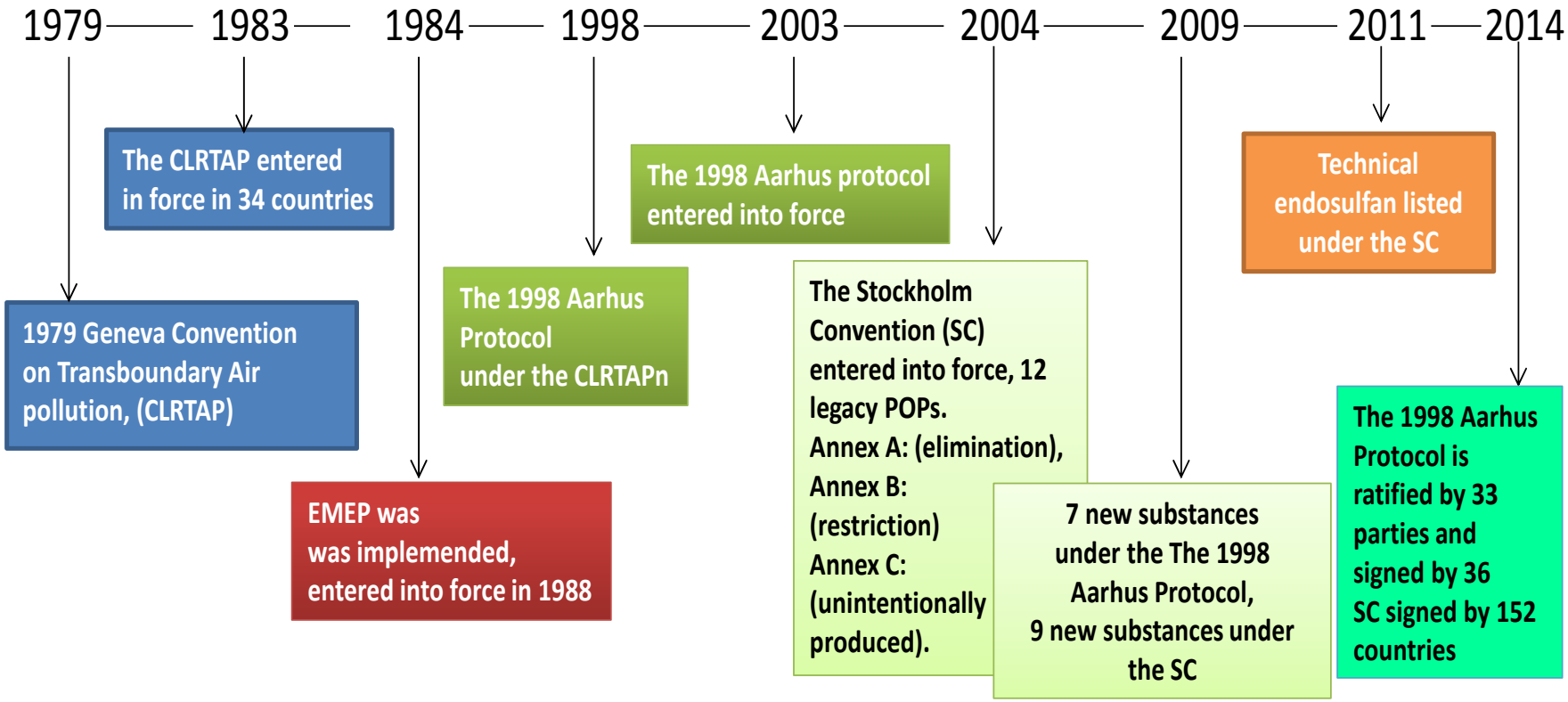


Figure: Kine Halse, NILU/NMBU
PhD thesis 2014

Global Action on POPs

- International Treaty on POPs: Stockholm Convention on Persistent Organic Pollutants (www.pops.int)
- Stockholm Convention aims at eliminating these chemicals from 2004
- Outlawed nine of the “dirty dozen”

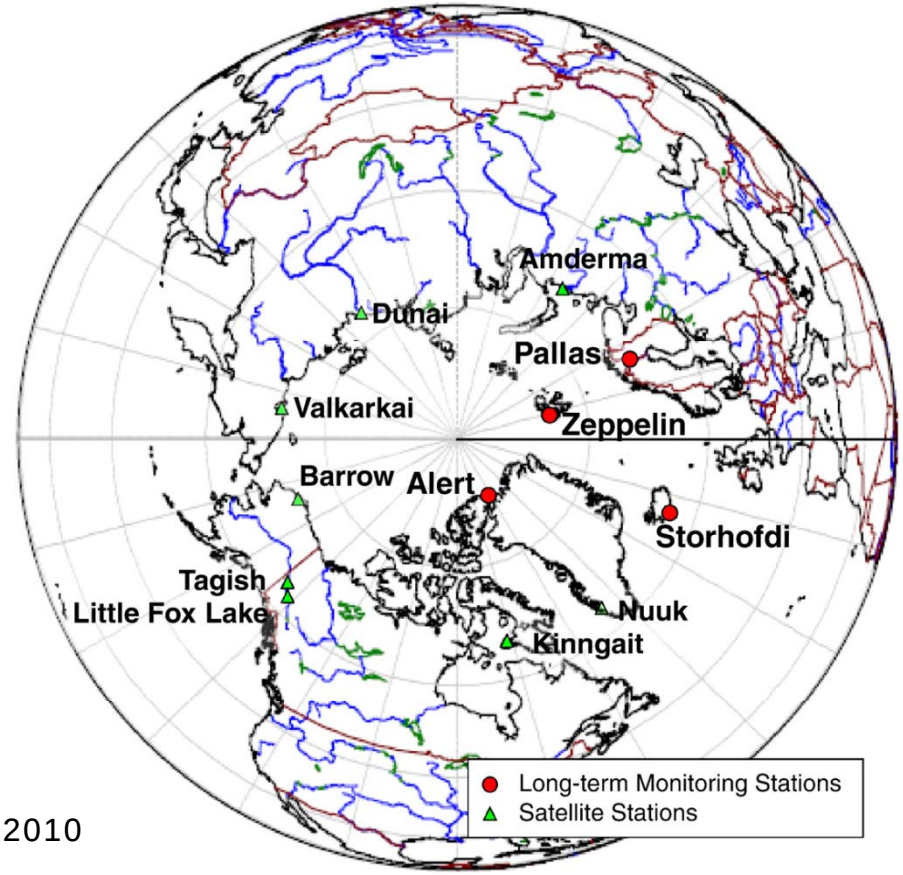
Persistent, bioaccumulative, toxic; PBT

- P: $T_{halflife}$ $\geq$ 6months in soil and sediment, $\geq$ 2 months in water
- B: log Kow >5. Kow =partitioning coefficient for octanol:water
- T: toxic –most often chronic effects for POPs

•POPs: Can also undergo long-range transport (LRT)

•$T_{halflife}$ $\geq$ 2 days in air and/or monitoring in remote areas

•Several atmospheric monitoring stations in the Arctic!



Hung et al., 2010

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?

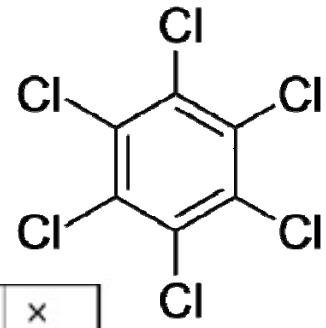
Why monitoring?

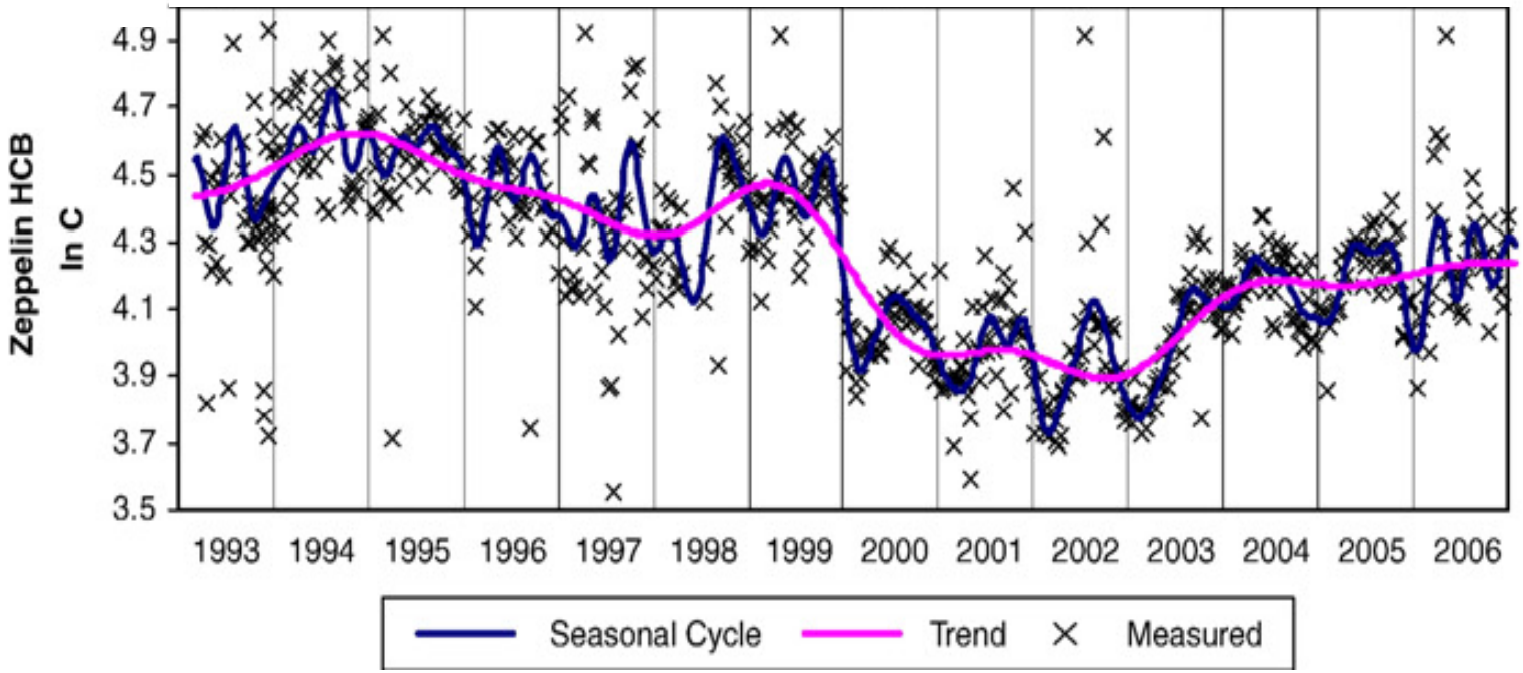
- Trends and timelines
- Trajectories –sources
- New compounds and screening

Why monitoring?

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

Trends and timelines



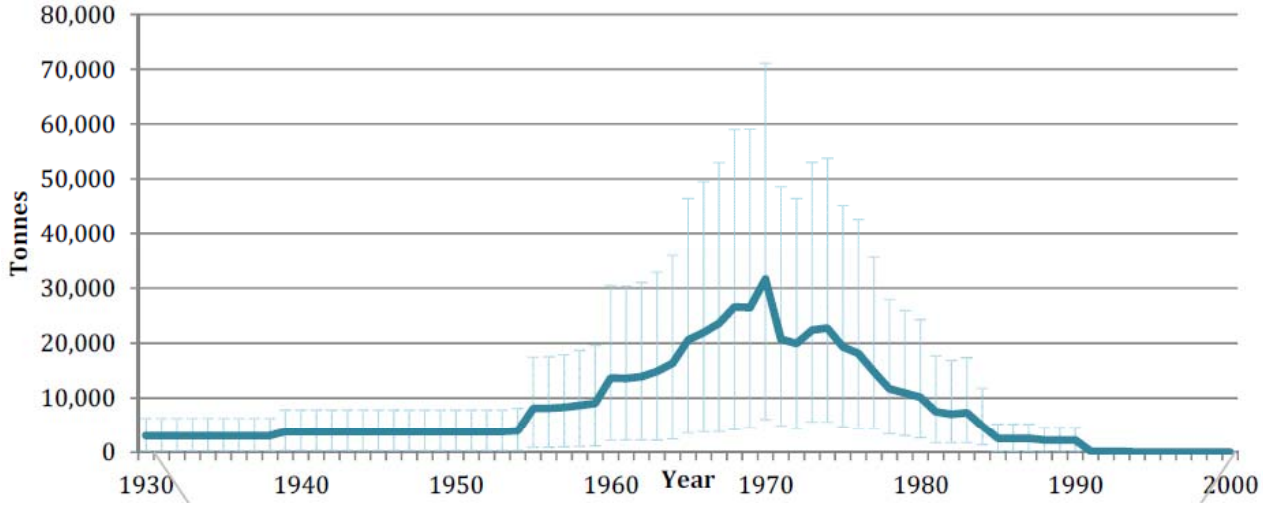


Increased concentrations of HCB in air at Zeppelin station.

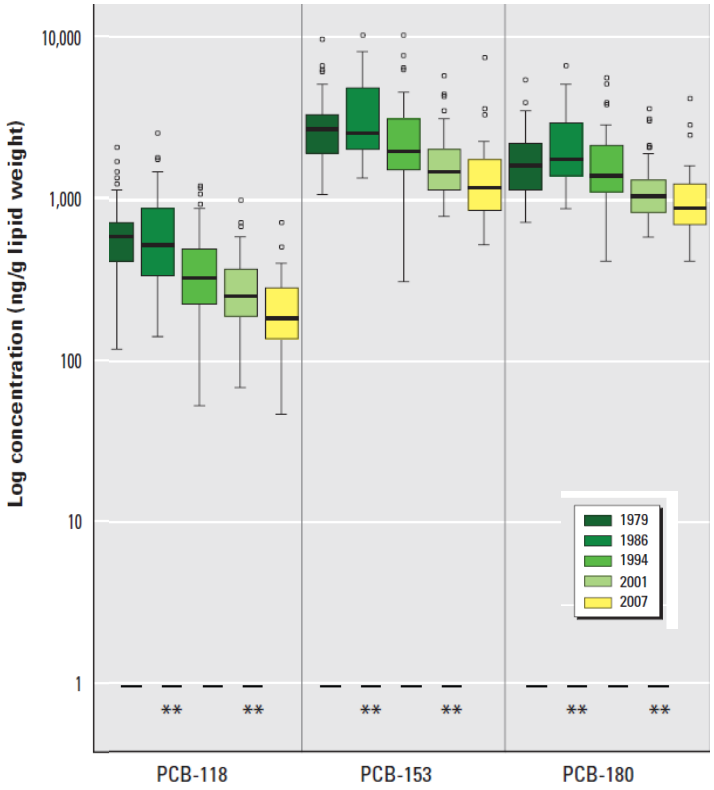
Reasons: Under discussion –ice free ocean, HCB as byproduct during pesticide production…

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

Estimates of global emissions of PCBs

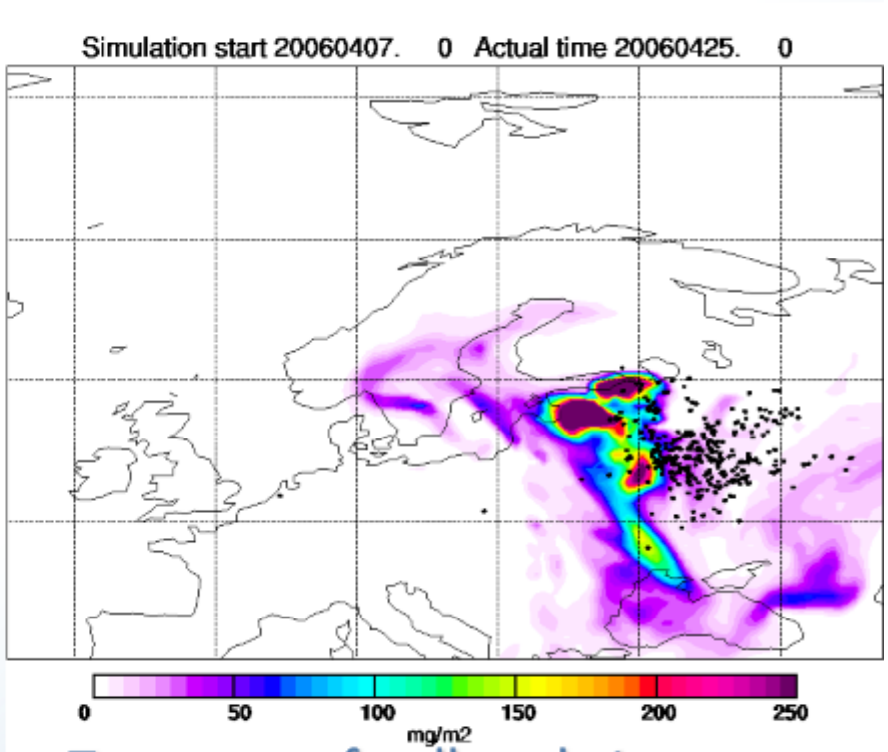


Concentrations (ng/g lw) of PCB in repeated serum samples from Norwegian men



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

$\Rightarrow$Few PFAS detected

$\Rightarrow$DBDPE >BDE-47 in several samples

$\Rightarrow$Short- and medium-chained chlorinated paraffins (SCCPs and MCCPs) detected in Arctic biota

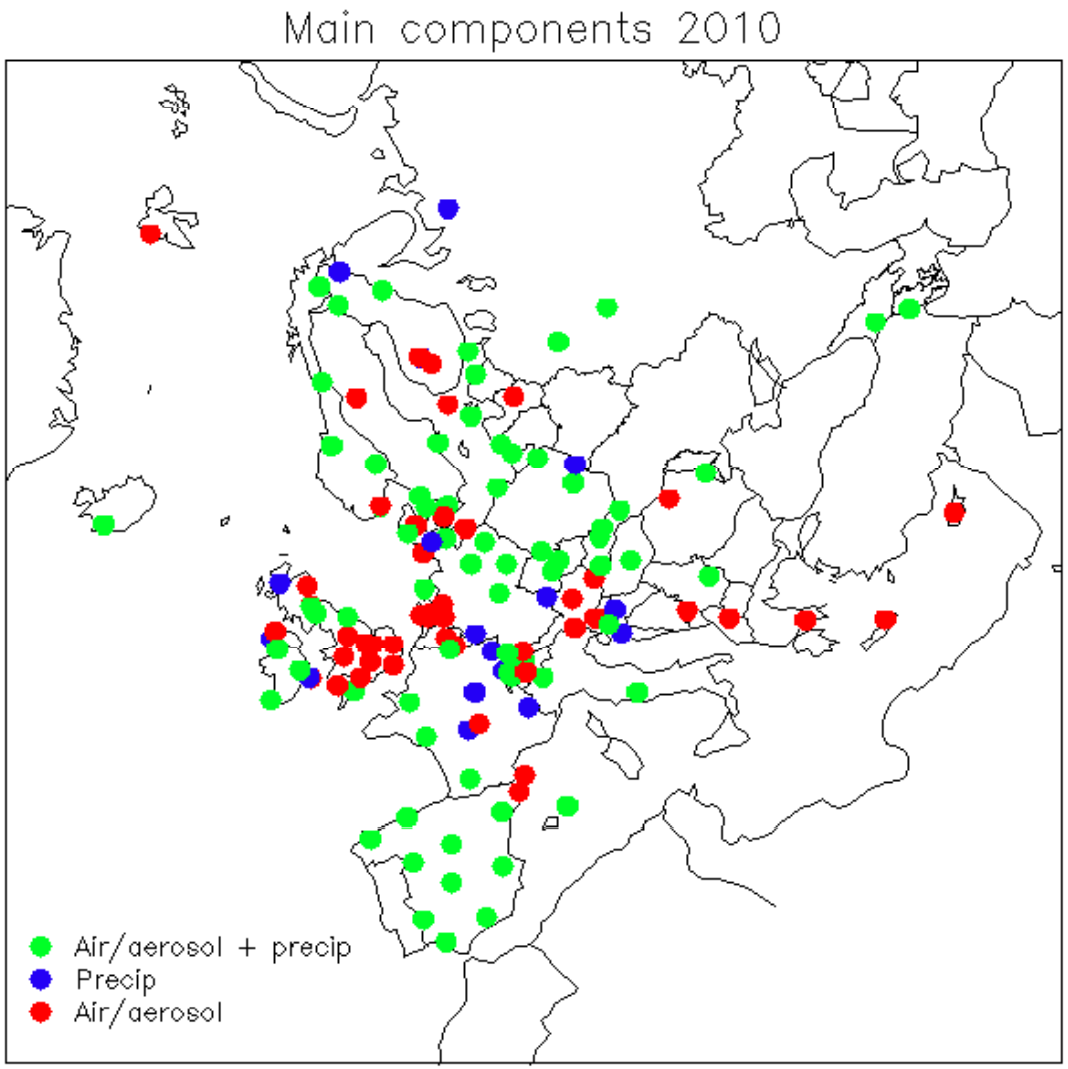
How?

CLRTAP, EMEP, NORMAN,

- Convention on Long-range Transboundary Air Pollution: CLRTAP
- European Monitoring and Evaluation Programme: EMEP
- NORMAN: Scientific network for investigations of emerging compounds

CLRTAP, EMEP, NORMAN

Monitoring network



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

CLRTAP, EMEP, NORMAN

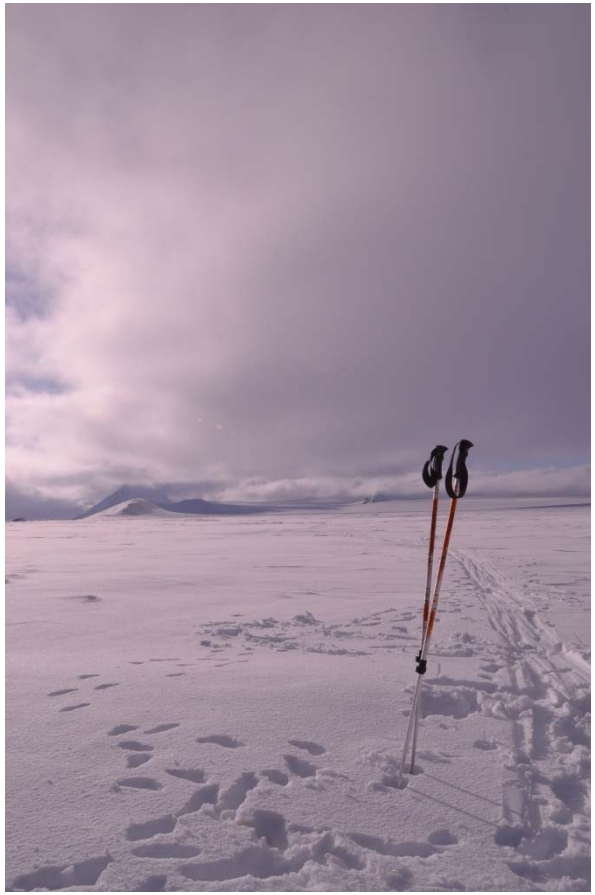
- EMEP is a scientifically based and policy driven program and provides support to the CLRTAP on:
  - ¤ Atmospheric monitoring and modelling;
  - ¤ Emission inventories and emission projections;
  - ¤ Integrated assessment modelling;
  - ¤ Hemispheric transport of air pollution

CLRTAP, EMEP, NORMAN

- 2005: The NORMAN Network started with support from EU
- 2009: NORMAN lives on!
  The network includes reference laboratories and research centers related to monitoring and biomonitoring of emerging environmental substances
- RECETOX is part of NORMAN

CLRTAP, EMEP, NORMAN

- The NORMAN mission:
- Enhance exchange information
- Encourage validation of analytical methods and monitoring tools
- Ensure that knowledge of emerging pollutants is maintained and developed



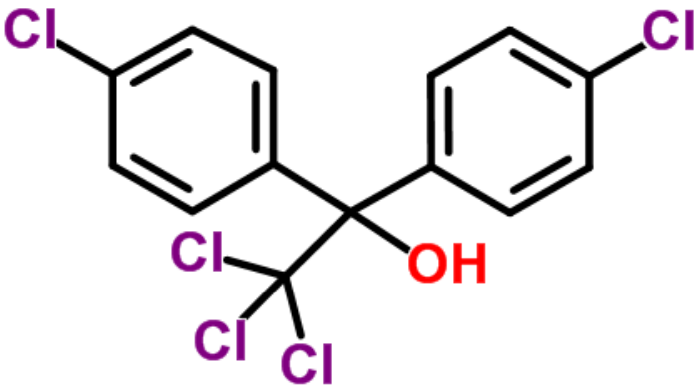
CLRTAP, EMEP, NORMAN

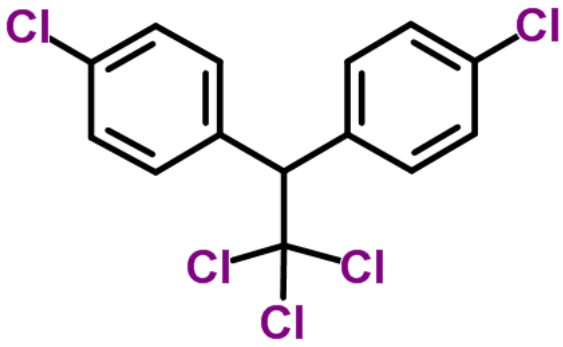
- Emerging substances: Not always new!

- **Emerging substances**
  Have been detected in the environment, but are currently not included in routine monitoring programmes at EU level. The fate, behaviour and (eco)toxicological effects of the substances are not well understood.

CLRTAP, EMEP, NORMAN

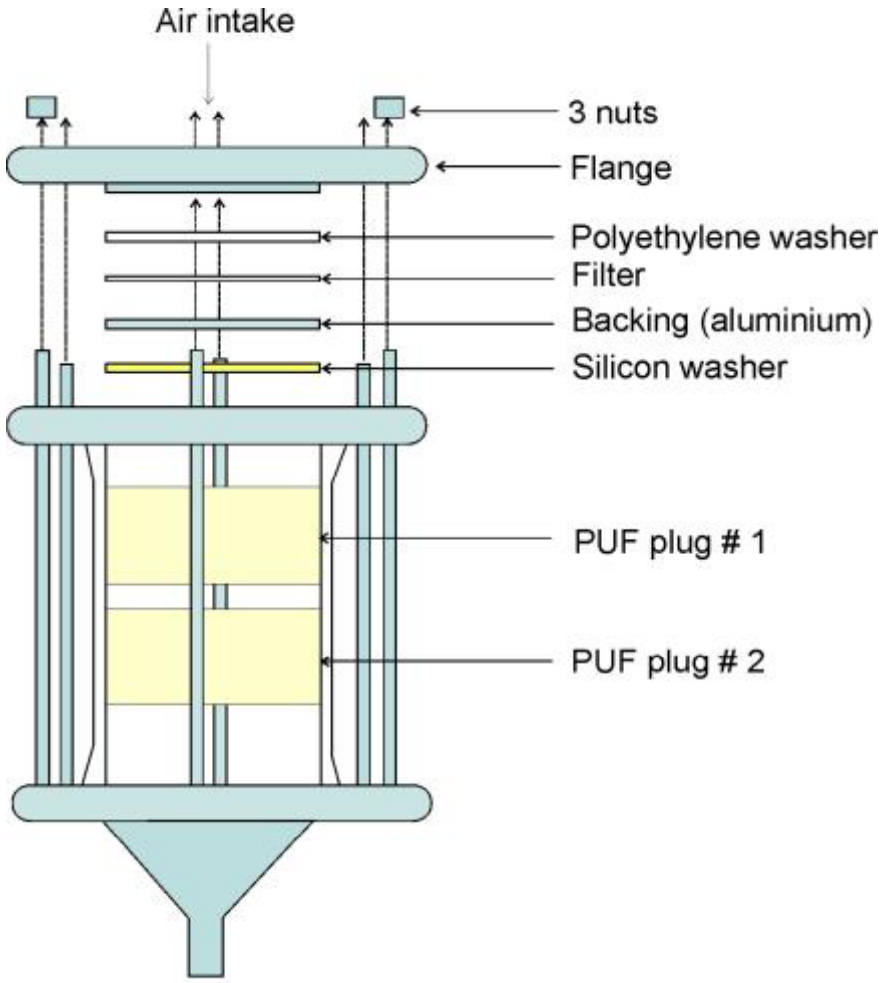
- Examples of emerging substances: Non-regulated PFAS (although PFOS is on the list), **dicofol** (replacement for **DDT**), pharmaceuticals, siloxanes (in your deodorant), «unknown» compounds



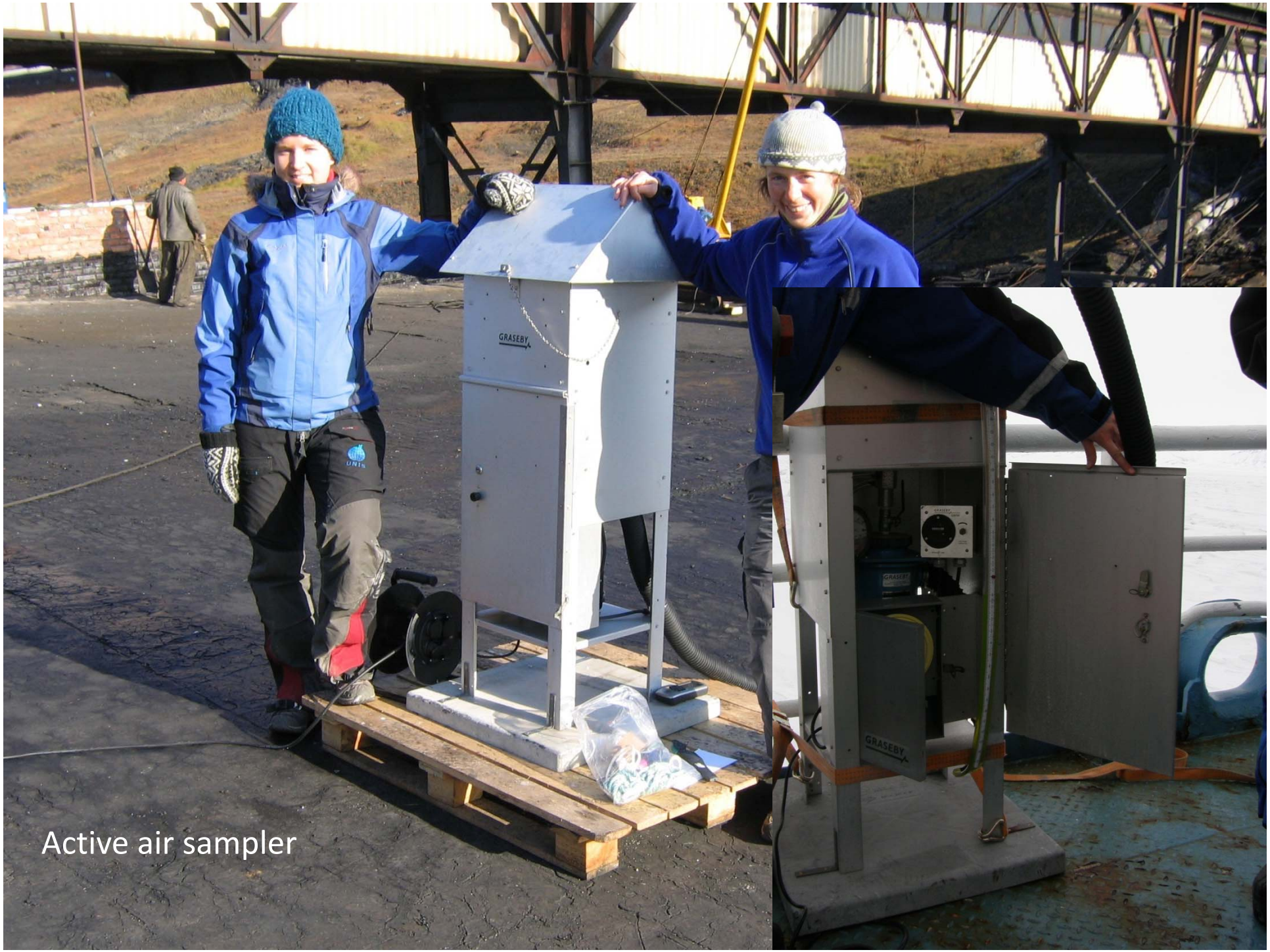


How? –Air sampling

- **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



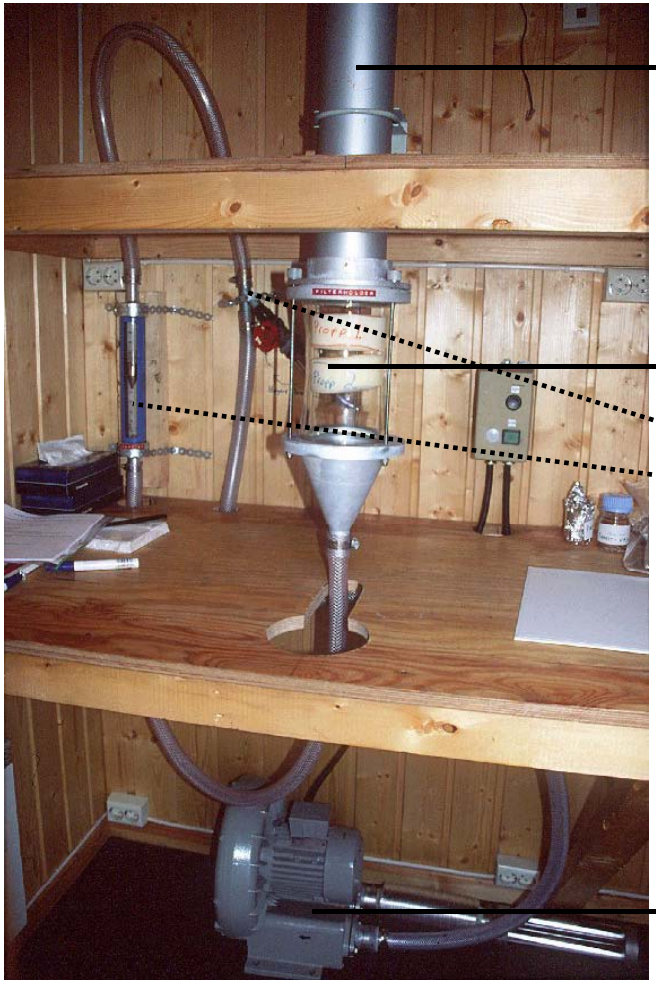
Active air sampler

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



Aluminum tube (3 m long)

Sample holder

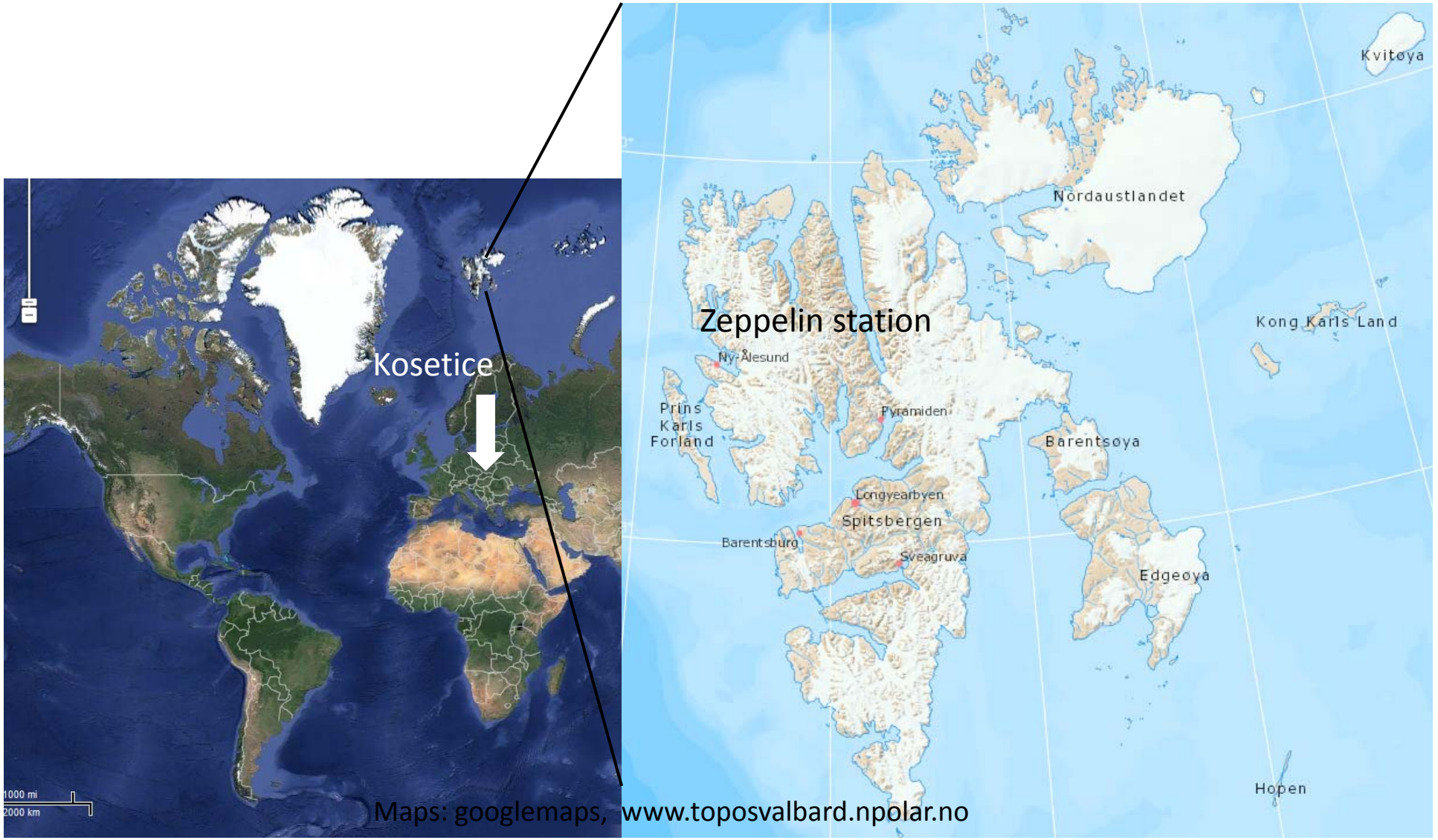
Air Flow control

High volume pump

Pictures from Roland Kallenborn, NMBU

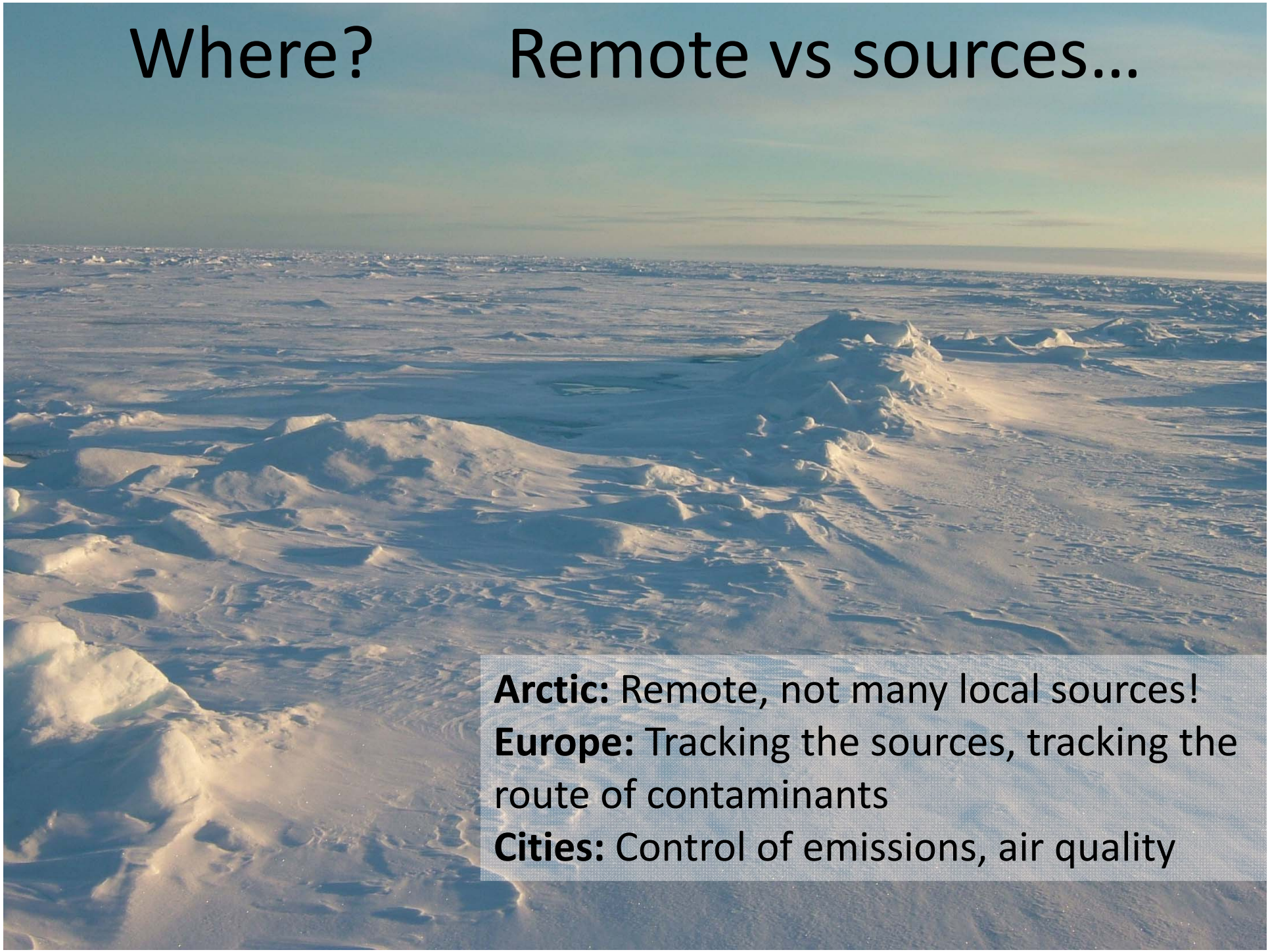

Where?
PEPSI
LITEACE
UAL 781N
Bata

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

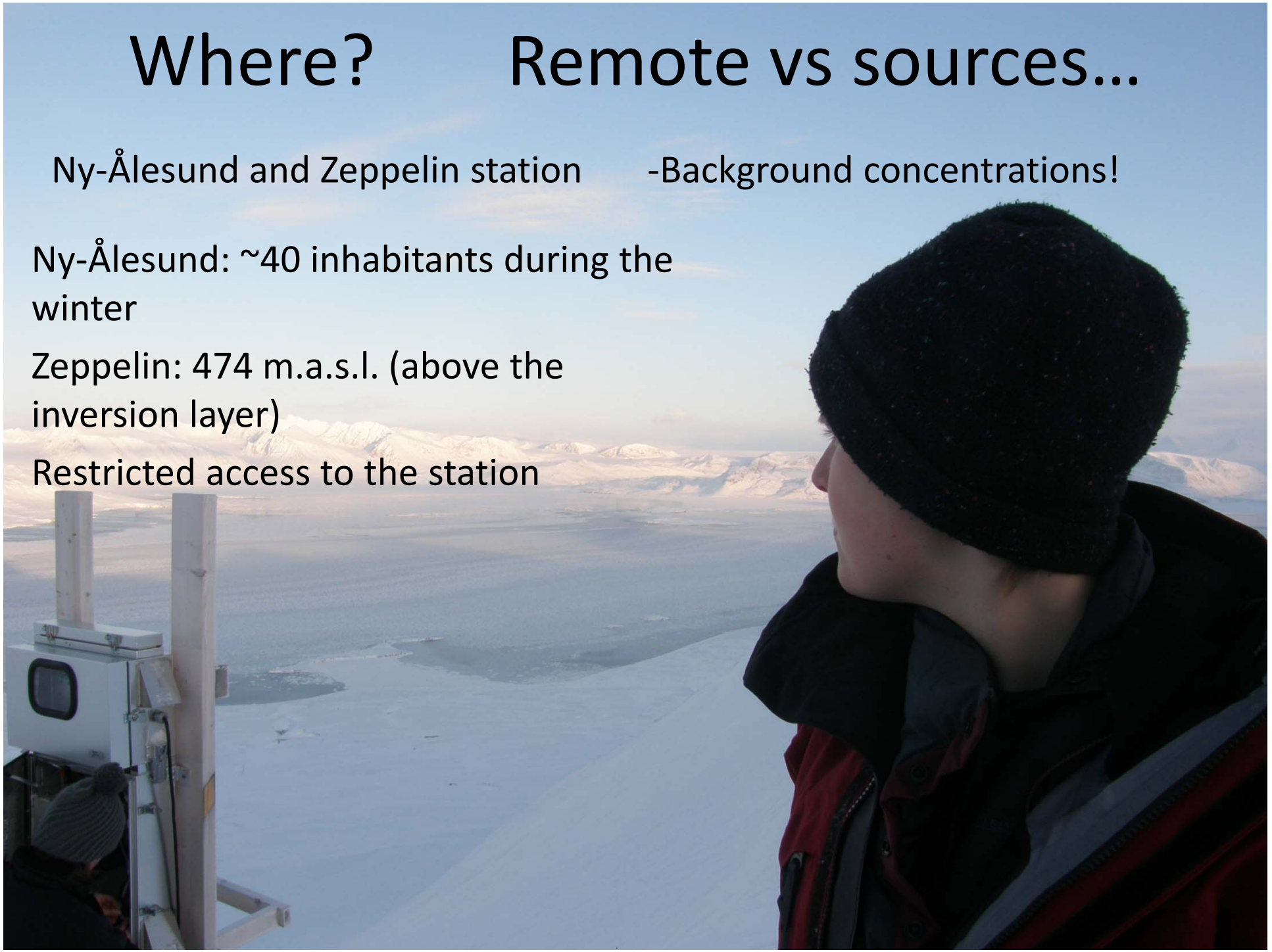
Where? Remote vs sources…

Ny-Ålesund and Zeppelin station -Background concentrations!

Ny-Ålesund: ~40 inhabitants during the winter

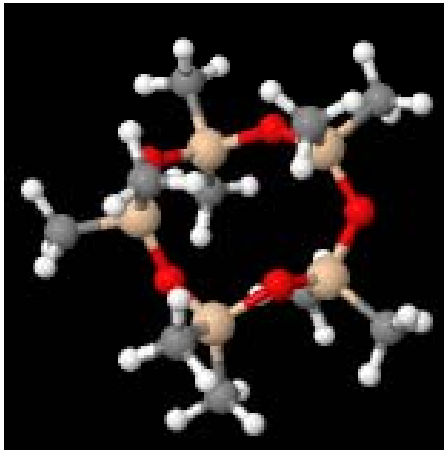
Zeppelin: 474 m.a.s.l. (above the inversion layer)

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

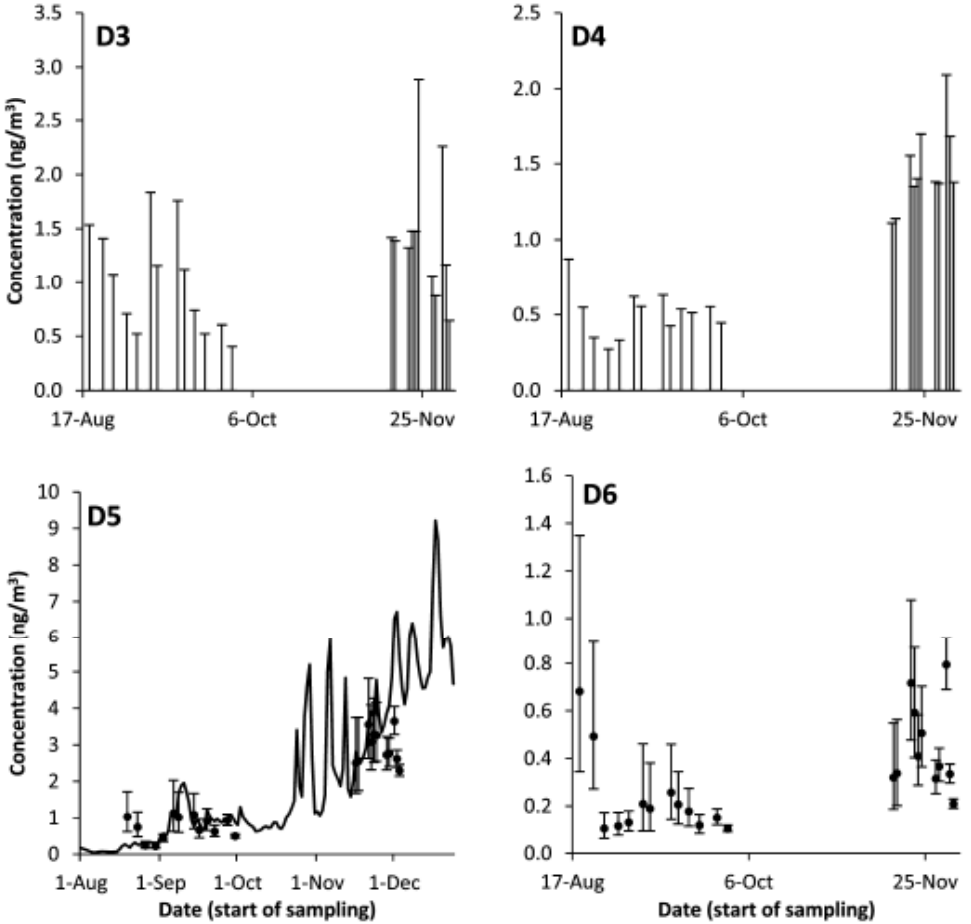


Figure 1. Concentrations of D3, D4, D5, and D6 in air for all samples at Zeppelin in 2011. The concentrations are shown as ranges for D3 and D4, taking into account both possible under- and overestimation due to the storage artifacts. The concentrations for D5 and D6 are the storage-corrected concentrations 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

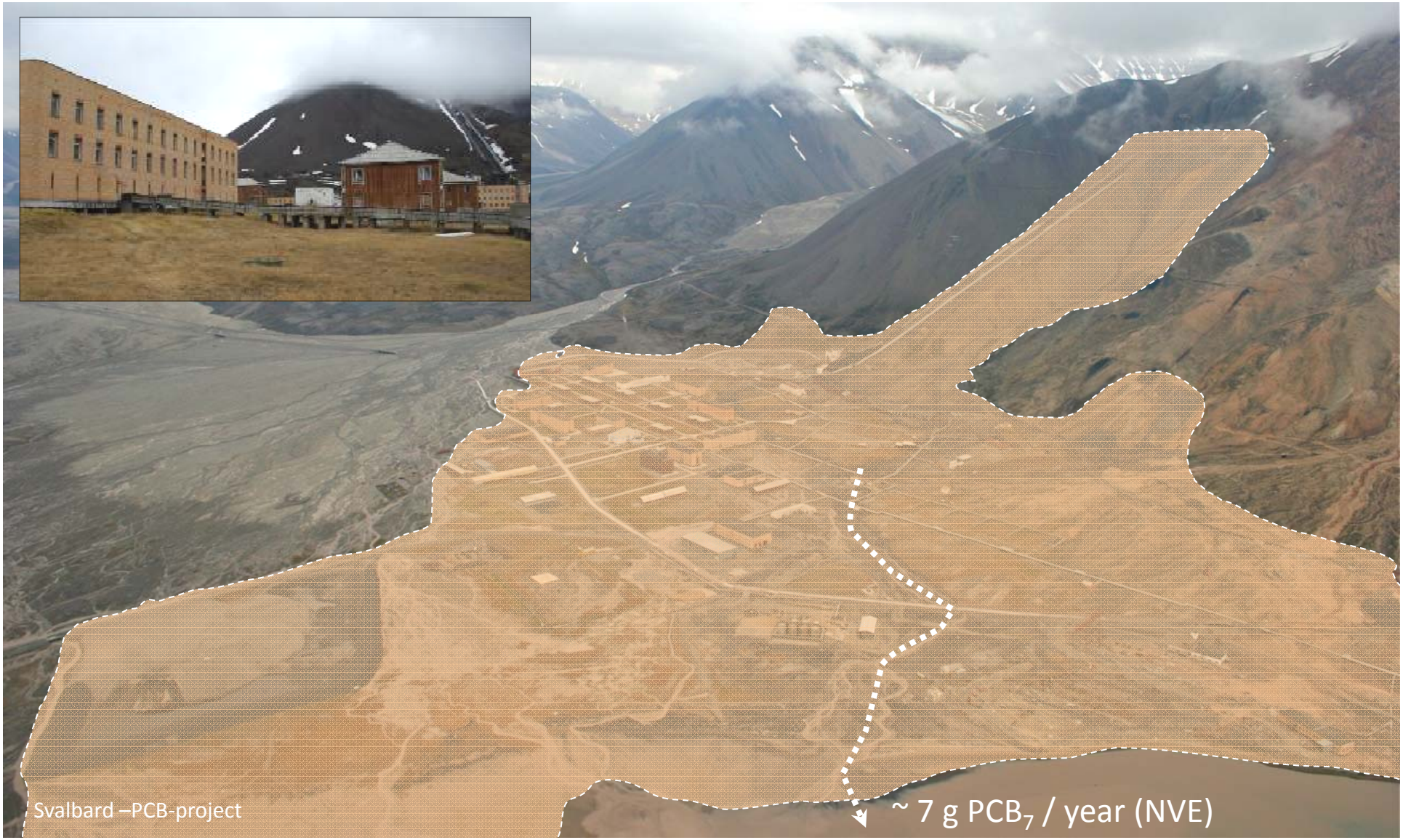
Case study from Svalbard

- 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

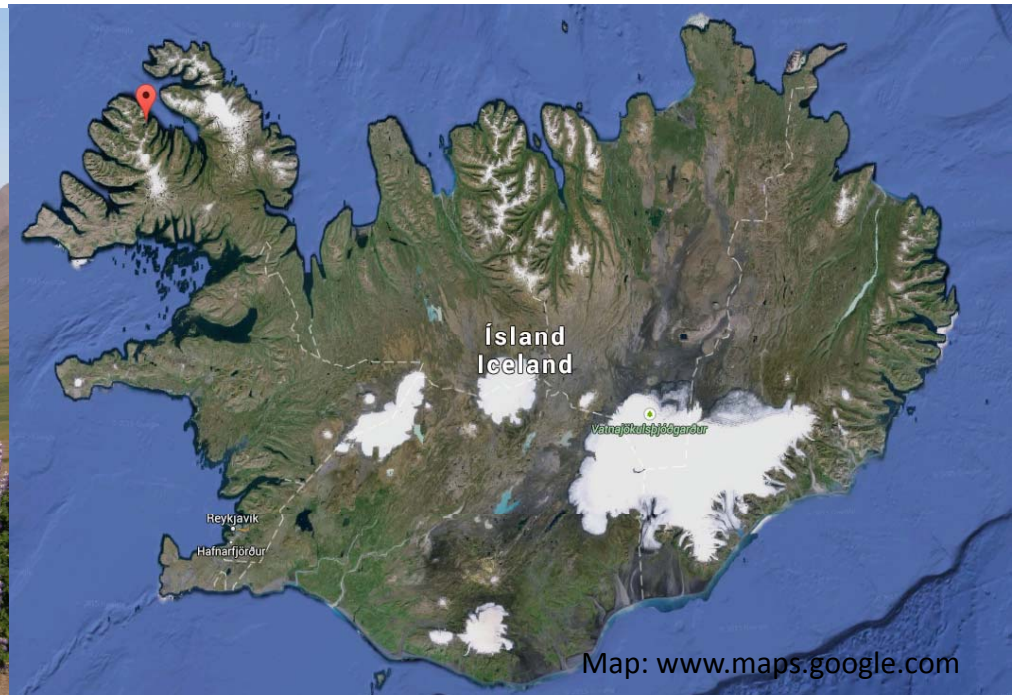
Roughly 1,1 kg PCB_7/km^2 in the soil (0-20 cm)

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

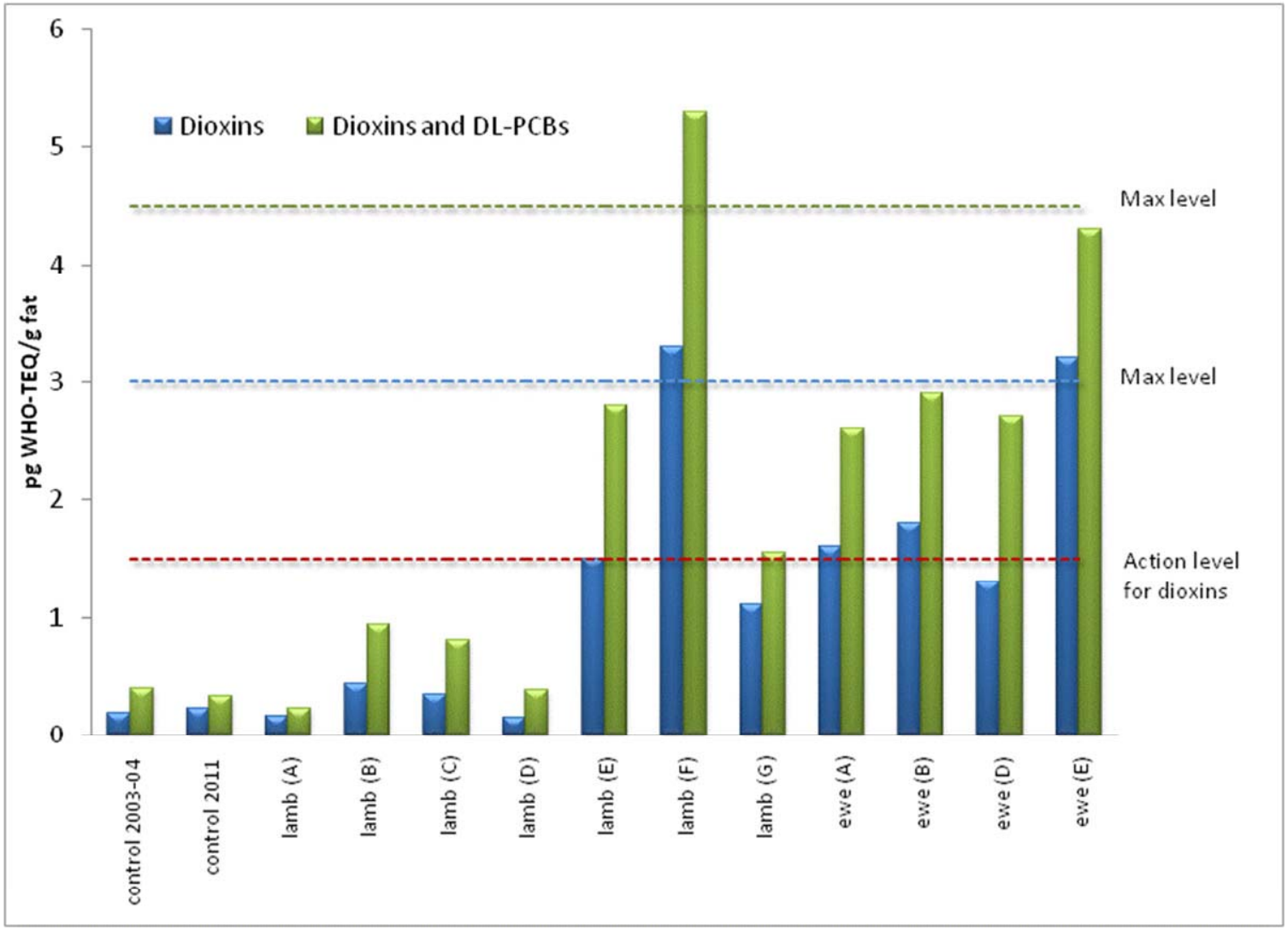


Case study from Iceland

- 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.

Summary monitoring

- Why?
  -Control over emissions
  -Detection of new, emerging substances
- EMEP, NORMAN, CLRTAP
  -Conventions and organisations for air monitoring
- Where?
  -Remote areas =>background information, confirmation of stability-
  -Source areas => Control of emissions, part of the trajectory information
- How?
  -Air monitoring: volatile/semivolatile compounds, particle associated compounds. Active vs passive sampling. Monitoring of biota/human for ecotoxicological reasons.

References

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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.

PCB clean-up project; Governor of Svalbard, www.sysselmannen.no

Additional information –EMEP, NORMAN, CLRTAP

- More info: http://www.unece.org/env/lrtap/welcome.html http://ebas.nilu.no/ (EMEP air monitoring data), www.norman-network.net
- CLRTAP is a convention via United Nations Economic Commission for Europe (UNECE)
- Geneva: 1960s: Sulphur emissions continental Europe –acidification Scandinavian lakes.
- 1972-77: Several studies about transport of air pollutants. => International cooperation
- Ministrial high-level meeting for these acute problems in Geneva nov 1979. => Signature of the Convention on Long-range Transboundary Air Pollution (CLRTAP) by 34 Governments and the European Community (EC). This was the first international legally binding instrument to deal with problems of air pollution on a regional basis
- CLRTAP: In force 1983
- Aarhus protocol: Regional protocol, P not necessary (PAHs on the list).
- Stockholm conv: Global protocol. By September 2014, the SC has been signed by 152 countries and include 179 parties and have a global action monitoring plan (GMP).

Additional information

- EMEP: Scientifically based and policy driven programme under the CLRTAP for international co-operation to solve transboundary air pollution problems.
- Some of the monitored compounds: Surface ozone, particles (PM_{10}; particulate matter <10µm), nitrogen and sulphur compounds, PAHs, dioxins, PCBs, HCH, Hg, Cd, Pb (Mercury, cadmium and lead).

Additional information

- The NORMAN mission:
- Enhance the exchange of information and collection of data on emerging environmental substances.
- Encourage the validation and harmonisation of common measurement methods and monitoring tools so that the demands of risk assessors can be better met.
- Ensure that knowledge of emerging pollutants is maintained and developed by stimulating coordinated, interdisciplinary projects on problem-oriented research and knowledge transfer to address identified needs.