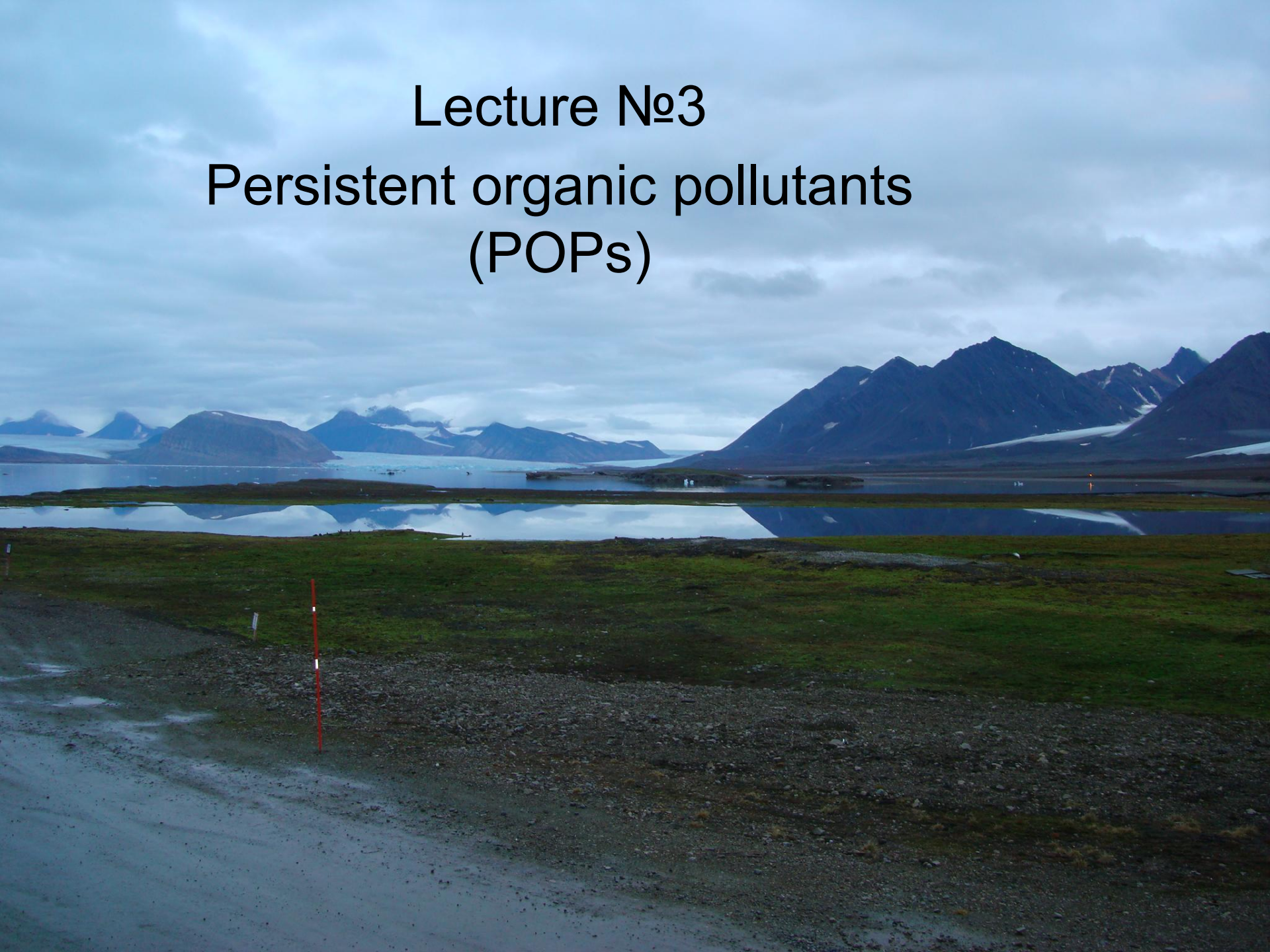
Lecture №3

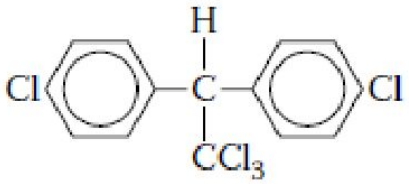
Persistent organic pollutants (POPs)



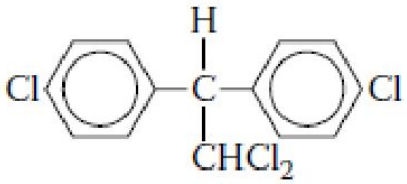
Persistent organic pollutants

- Persistent organic pollutants (POPs) are organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation. POPs are often halogenated and characterised by low water solubility and high lipid solubility, leading to their bioaccumulation in fatty tissues.
- They are also semi-volatile, enabling them to move long distances in the atmosphere before deposition occurs.

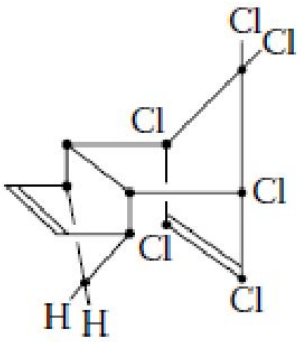
Persistent organic pollutants



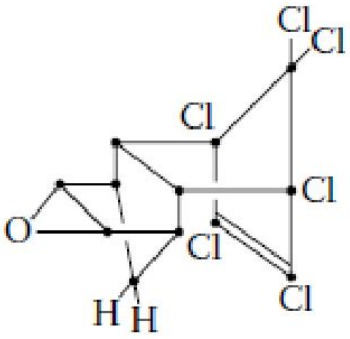
p,p′-DDT



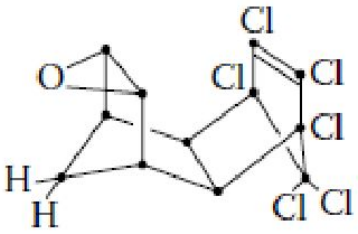
p,p′-DDD



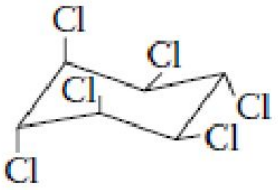
Aldrin



Dieldrin



Endrin



γ-HCH (lindane)

Persistent organic pollutants have four key characteristics in common:

1. Persistent organic pollutants are TOXIC,
2. POPs are ENVIRONMENTALLY PERSISTENT.
3. POPs resist breakdown in water but they are soluble in fatty tissue, which makes them bioavailable to mammals.
4. POPs are semi-volatile and thus are capable of TRAVELLING GREAT DISTANCES through cycles of evaporation and atmospheric cycling and deposition (referred to as the "grasshopper effect").
5. POPs are volatile at warm temperatures and condense at cooler temperatures, reaching their highest concentrations in the cooler regions of the world (northern latitudes and high altitudes).
6. Synthetic (man-made) organic chemicals

POPs have been found on every continent on the planet, and in every major climatic zone, including the world's most remote regions, such as the open ocean and deserts, and in every wildlife species and human being.

Persistence time for some selected pesticides

Sl.No	Pesticide	Persistence time
1	BHC	11 yrs
2	DDT	10 yrs
3	2,4-D	2-8 weeks
4	Aldrin	9 yrs
5	Diuron	16 months
6	Atrazine	18 months
7	Siwazine	17 months
8	Chlordane	12 yrs
9	2,3 6-Trichlorobenzene (TBA)	2-5 yrs

POP	Year of Introduction	Classification
Aldrin	1949	Insecticide
Chlordane	1945	Insecticide
DDT	1942	Insecticide
Dieldrin	1948	Insecticide
Endrin	1951	Insecticide and rodenticide
Heptachlor	1948	Insecticide
Hexachlorobenzene	1945	Fungicide
Mirex	1959	Insecticide
Toxaphene	1948	Insecticide and acaricide
PCBs	1929	Various industrial uses
Dioxins	1920s	By-products of combustion, for example, of plastics, PCBs
Furans	1920s	By-products of PCB manufacture

The POPs are:

- Lipophilic – they have a tendency to remain in fat-rich tissues.
- Highest levels found in marine mammals – immune dysfunction is considered as a plausible cause for increased mortality among marine mammals.
- Acute, high-level toxicity is well characterized – acute effects after high-level exposure have been described for some of the organochlorine pesticides (e.g. aldrin, dieldrin and toxaphene). PCBs have caused welldocumented episodes of mass poisoning called "Yusho" and "Yu Cheng“, that occurred in China, Province of Taiwan, and in Japan.

Groups of POPs

POPs are generally divided into two groups according to their sources:

- they are either intentionally produced for one or more purposes
- or they are accidentally formed in production or combustion processes

1. Intentionally produced chemicals

The group of intentionally produced chemicals can further be divided into two groups:

- **Organochlorine pesticides**.

The organochlorine pesticides were developed in the 1940s and 1950s and widely used until the 1970s and 1980s, where most of them where restricted or banned and they are now to a large extent replaced with less persistent products.

- **Industrial compounds**

The group of chlorinated industrial compounds includes the polychlorinated biphenyls (PCBs), consisting of 209 different congeners with different degree of chlorination.

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Aldrin	1949	Insecticide
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2. Accidentally formed chemicals

The main classes of unintentionally by-products are:

- **the polychlorinated dibenzo–p–dioxins** (PCDDs),
- **the polychlorinated dibenzofurans (PCDFs)**

The PCDD/Fs consist of 75 and 115 different congeners respectively, which are formed as by-products during chlorination processes and combustion.

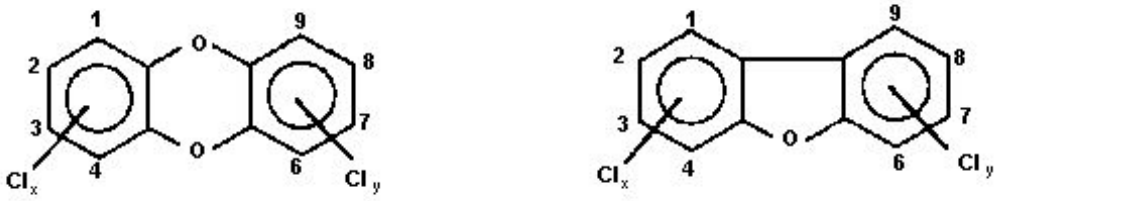
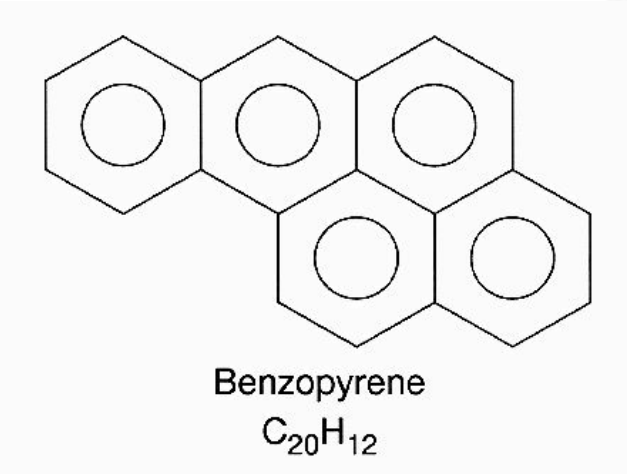
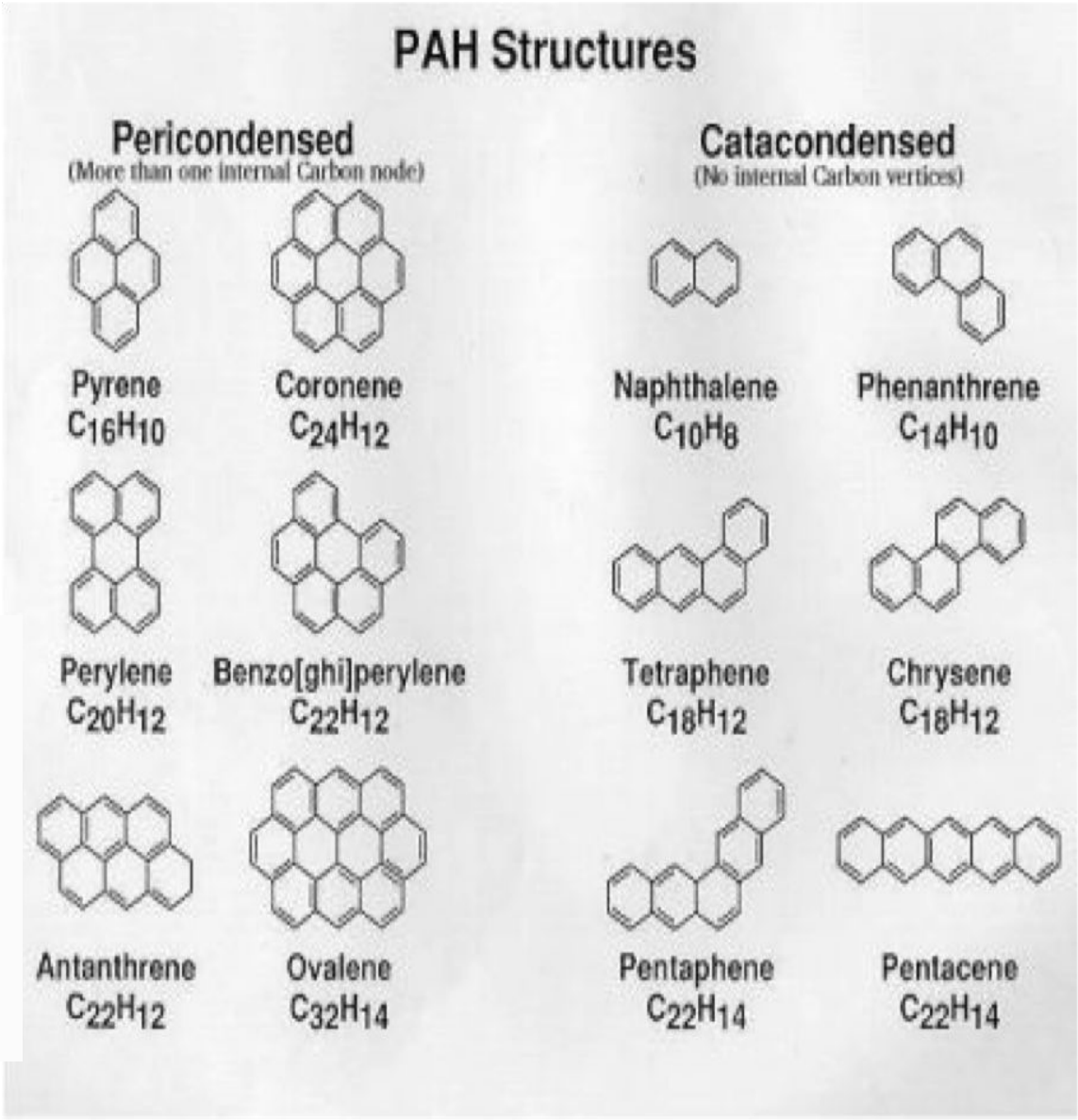


Fig. 1. Structural formulae of PCDDs and PCDFs.

2. Accidentally formed chemicals

- and **the polycyclic aromatic hydrocarbons** (PAHs).





PERSISTENT ORGANIC POLLUTANTS (POPs)

PESTICIDES

Aldrin
Dieldrin
Chlordane
DDT
Endrin
Heptachlor
Mirex
Toxaphene

INDUSTRIAL CHEMICALS

PCBs
HCB

UNINTENDED BYPRODUCTS

Dibenzodioxins
Dibenzofurans

Stockholm Convention: a global treaty ratified by the international community lead by UNEP – calls for the elimination and/or phasing out of 12 POPs

www.chem.unep.ch/pops/default.html

These are the persistent organic pollutants – grouped according to their use and origin:
-8 pesticides – Introduced in 1940-1950, banned later on but still in use in some countries.
-2 industrial chemicals – One of these, HCB, was used as a fungicide in the past.
-2 unintended industrial by-products.

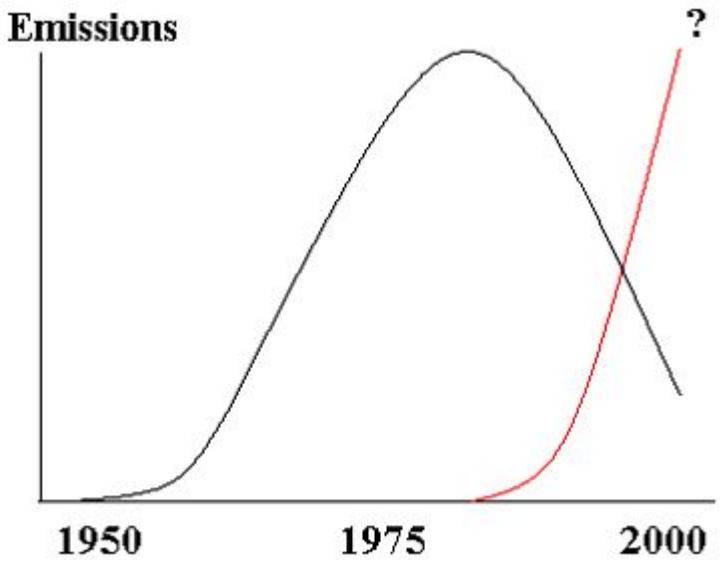
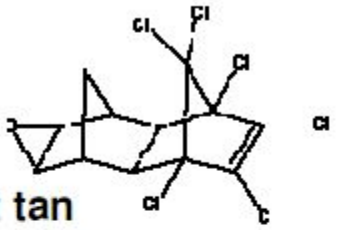
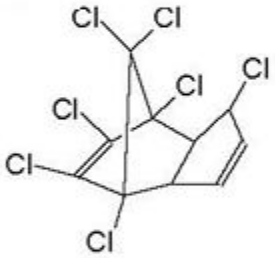


Figure: Typical usage and environmental emission history of POPs.
The black line corresponds to the 'classic' POPs now under restrictions, such as the HCHs and the PCBs, while the red line corresponds to compounds of more recent concern, such as the PBDEs. Modified from Jones and de Voogt [1999].

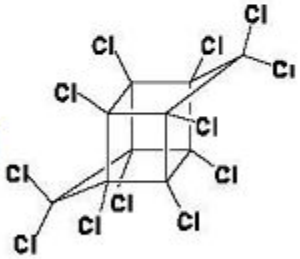
POPs - PESTICIDES



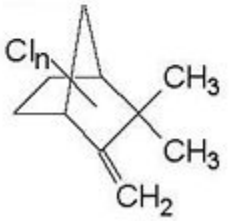
Endrin: White, odourless, crystalline solid (pure); light tan colour with faint chemical odour for technical grade



Heptachlor: White to light tan, waxy solid or crystals with a camphor-like odour



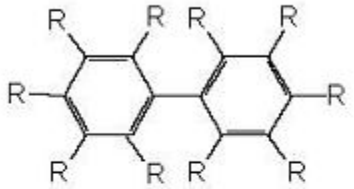
Mirex: White crystalline, odourless solid



Toxaphene: Yellow, waxy solid w/ chlorine/terpene-like odour

UNEP

POPs – INDUSTRIAL CHEMICALS



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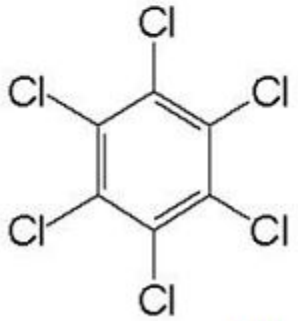
PCBs: Polychlorinated biphenyls

Trade Names for different mixtures (partial list): Aroclor, Pyranol, Pyroclor, Phenochlor, Pyralene, Clophen, Elaol, Kanechlor, Santotherm, Fenchlor, Apirolio, Sovol

HCB: Hexachlorobenzene

White monoclinic crystals or crystalline solid

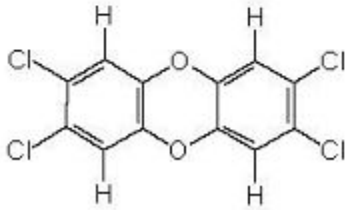


UNEP

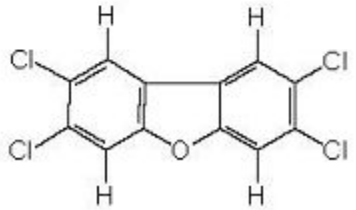
POPs – UNINTENDED BYPRODUCTS

Dibenzodioxins and dibenzofurans

- Byproducts of production of other chemicals
- Detected in incineration of coal, peat, wood, hospital waste, hazardous waste, municipal waste, car emissions
- Of 210 dioxins and furans, 17 are in toxic mixtures



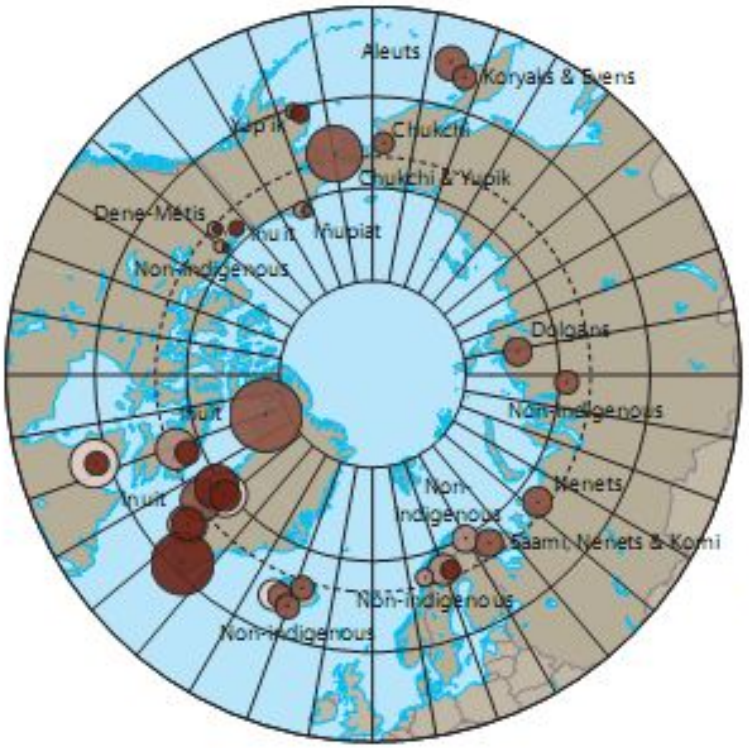
2,3,7,8-TCDD

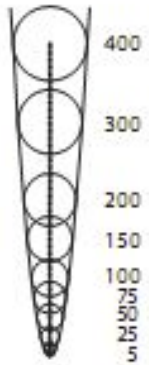


2,3,7,8-TCDF

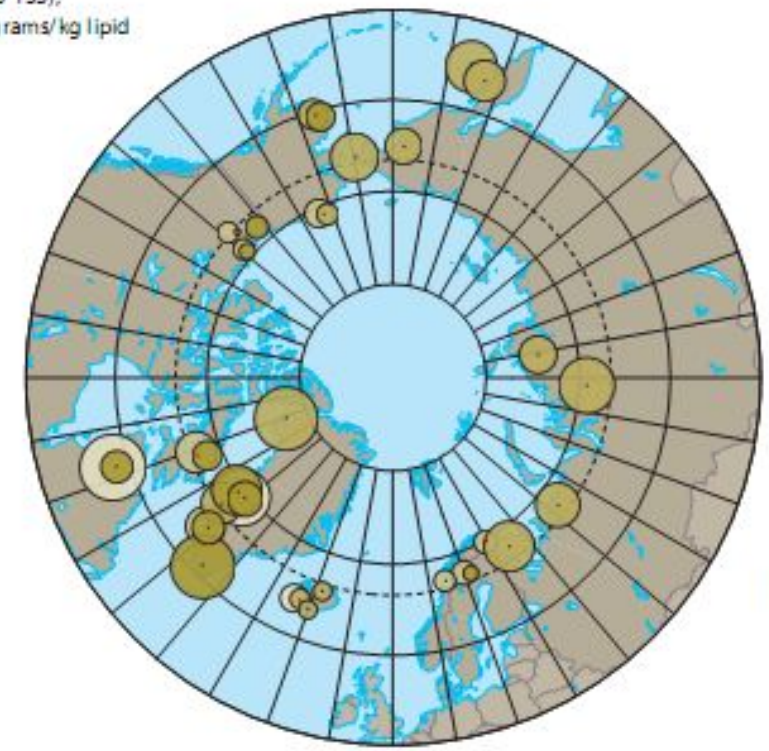
UNEP

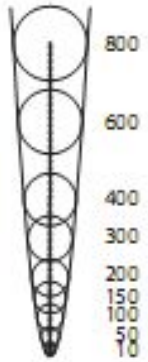
PCB and DDE in blood plasma of mothers pregnant





PCB (CB-153),
micrograms/kg lipid





*p,p'*DDE,
micrograms/kg lipid

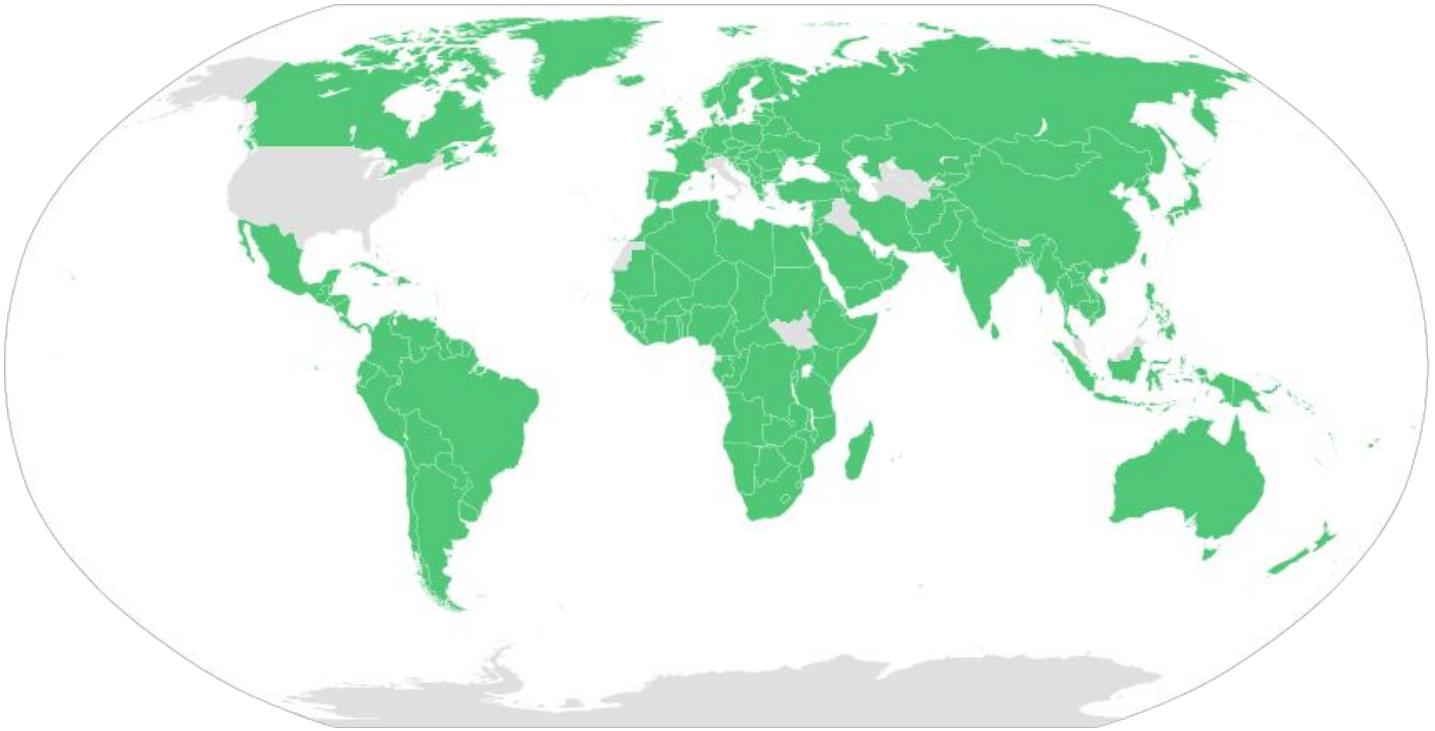
Time period

1990-1994
1995-1999
2000-2004
2005-2007

Persistent organic pollutants

- The Stockholm Convention on Persistent Organic Pollutants (May 2001) focuses on reducing and eliminating releases of 12 POPs (coined the "Dirty Dozen” by the United Nations environment Programme (UNEP)
- http://chm.pops.int/default.aspx

State parties to the Stockholm Convention on Persistent Organic Pollutants



The twelve priority persistent organic pollutants listed under the Stockholm Convention.

Category	Chemical	CAS#	Stockholm Convention Annex[a]	Use[b]	Soil Half-life (in years)
Pesticides	Aldrin	309-00-2	A	insecticide	N/A
	Chlordane	57-74-9	A	insecticide, termiticide	1
	DDT	50-29-3	B	insecticide	10-15
	Dieldrin	60-57-1	A	insecticide	5
	Endrin	72-20-8	A	insecticide, rodenticide	Up to 12
	Heptachlor	76-44-8	A	insecticide, termiticide	Up to 2
	Hexachlorobenzene	118-74-1	A	fungicide	2.7-22.9
	Mirex	2385-85-5	A	insecticide, termiticide	Up to 10
	Toxaphene	8001-35-2	A	insecticide	100 days up to 12 years
Category	**Chemical**	**CAS#**	**Stockholm Convention Annex**	**By-product (typical formation)**	**Soil Half-life (in years)**
Industrial Chemicals	Hexachlorobenzene	118-74-1	A	by-product of manufacture (chlorinated solvents, pesticides), application of pesticides, incineration of HCB-containing wastes	2.7-22.9
	Polychlorinated biphenyls	1336-36-3	A	Industry manufacture; co-planar PCBs are a by-product of combustion	10 days to 1.5 years
Unintended By-Products	Dioxins	Several	C	by-product	10-12
	Furans	Several	C	by-product	10-12

Sources: The Stockholm Convention on Persistent Organic Pollutants, the International Program on Chemical Safety, Persistent Organic Pollutants: *An Assessment Report on DDT, Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, Polychlorinated Biphenyls, Dioxins, and Furans*, L. Ritter, et al., submitted to the Second Meeting of the ISG, Intergovernmental Forum on Chemical Safety, ISG/96.5B, Dec. 1995.

[a] Annex A substances: slated for "elimination" in the Stockholm Convention. Annex B substances: slated for "restriction" for which there is a specified "acceptable purpose"; Annex C substances: continuing minimization and, where feasible, ultimate elimination of the total releases derived from anthropogenic sources.

[b] Typical uses; not to be confused with use exemptions listed in the Convention, which are noted in Table 4.

Criteria for identification of 'new' POPs under the Stockholm Convention (2001)

Chemical identity	Structure, including specification of isomers where applicable, and the structure of the chemical class
Persistence	1. The half-life of the chemical in water is greater than two months, or the half-life in soil is greater than six months, or the half-life in sediment is greater than six months. 2. Other evidence that the chemical is sufficiently persistent to justify its consideration.
Bioaccumulation	1. Evidence that the bioconcentration factor or bioaccumulation factor in aquatic species is greater than 5000. 2. The logarithm of the octanol-water partition coefficient (log K_{ow}) is greater than 5. 3. Evidence that a chemical presents other reasons for concern, such as high bioaccumulation in other species, high toxicity or ecotoxicity. 4. Monitoring data in biota indicating that the bioaccumulation potential of the chemical is sufficient to justify its consideration.
Potential for long-range environmental transport	1. Measured levels of the chemical in locations distant from the sources of its release that are of potential concern. 2. Monitoring data showing that long-range environmental transport of the chemical, with the potential for transfer to a receiving environment, may have occurred via air, water, or migratory species. 3. Environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water or migratory species. 4. The half-life in air is greater than two days.
Adverse effects	1. Evidence of adverse effects to human health or to the environment that justifies consideration. 2. Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

Characteristics of POPs

- The definition of **persistence** is that the half-life in water is greater than two months or the half-life in soil or sediments is greater than six months or that there is other evidence that the chemical is sufficiently persistent to be of concern.
- A compound **bioaccumulates** if the logarithm of the octanol-water partition coeffcient ($\log K_{ow}$) is greater than 5 or if the bioconcentration factor (BCF) or the bioaccumulation factor (BAF) is greater than 5000 or if there is other evidence that the chemical bioaccumulates.

Characteristics of POPs

- There is potential **for long-range transport** if the half-life of a compound in air is greater than two days or if it is detected in remote regions.
- If there is evidence of adverse effects or indications of potential damage to human health or the environment a compound is said to be **toxic**. Observed adverse effects are e.g. effects on the reproduction, development and the immune system and the promotion of tumors.

Characteristics of Arctic ecosystems related to POP accumulation.

1. Cold
2. Conspicuous species and humans at high trophic levels

Arctic food chains, in general, are neither longer nor shorter than natural food chains in temperate regions. There are many species of first-level carnivores in both

3. Low species diversity
4. Low productivity
5. Cyclic annual productivity

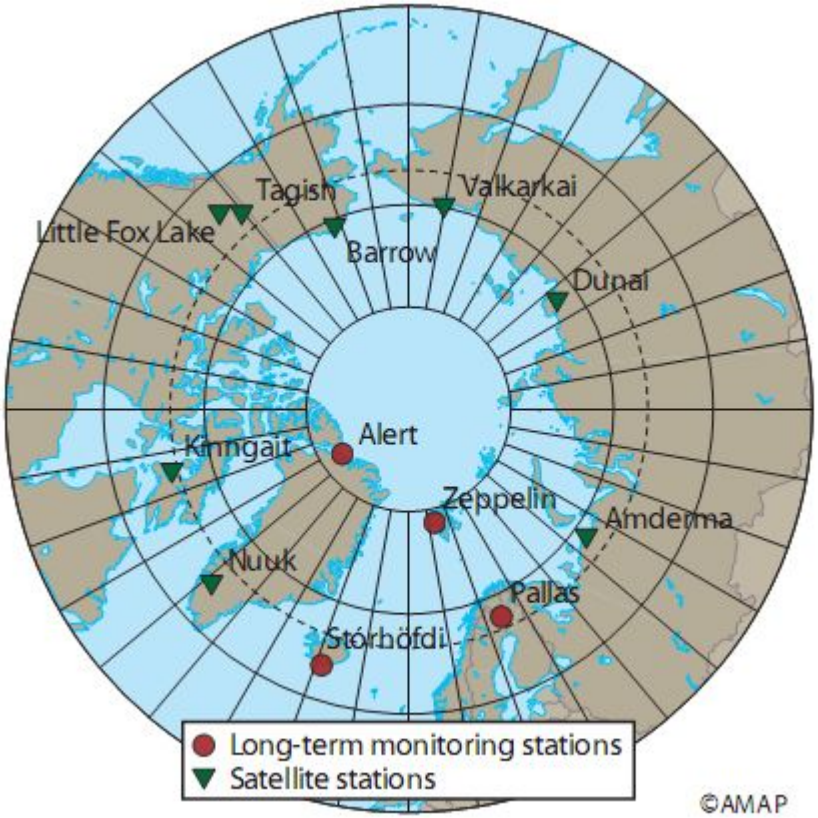
- Arctic ecosystems are highly pulsed due to fluctuations in light levels, nutrient input, and temperature. OCs and nutrients deposited on

6. Physical stressors in the Arctic

Transport of POPs in the environmental compartments

- The **atmosphere is the fastest environmental transport path**, and most POPs are believed to enter the Arctic **through the air**. It can take a few days or weeks for the air from source regions to reach into the Arctic.
- Pollutants are also transported **in the oceans by the ocean currents**. Although the transport is slow, it can be important depending on the partitioning into water compared to the partitioning into air.
- Soil is a stagnant medium, so there is no horizontal transport of POPs in soil. Partitioning into the water within the soil and subsequent run-through can though lead to transport of POPs within the soil. A recent model study has suggested that vertical movement of chemicals sorbed to soil particles, by e.g. bioturbation, cryoturbation and erosion into cracks in dry soil is of importance for the environmental fate of POPs
- Fresh water transport through major rivers is considered to be an important sourceof contamination of the Arctic Ocean. Sea ice may also be a mean of POPs re-distribution. POPs sorbed to particles bound to sea ice can be transported out of the Arctic Ocean to melt regions in the Fram Strait.
- Another transport pathway that may be of importance for the transport into the Arctic is through migratory animals, e.g. seabirds, cetaceans, salmons, and Arctic cods.

POPs have been monitored at several locations around the-arctic



Contaminant sources can be provisionally separated into three categories:

- **Distant sources**: Located far from receptor sites in the Arctic. Contaminants can reach receptor areas via air currents, riverine flow, and ocean currents. During their transport, contaminants are affected by the combined effects of physical and chemical factors. Persistence in the environment is, therefore, one of the most important characteristic in determining the ability of contaminants to reach the Arctic. In this respect, PTS, due to their low degradation rates, are often considered to be ‘global contaminants’ subject to long-range transportation.

Persistent Organic Pollutants:

- Are transported long distances from the source
- Resist environmental degradation
- Accumulate in biota
- Can produce toxic effects in exposed organisms

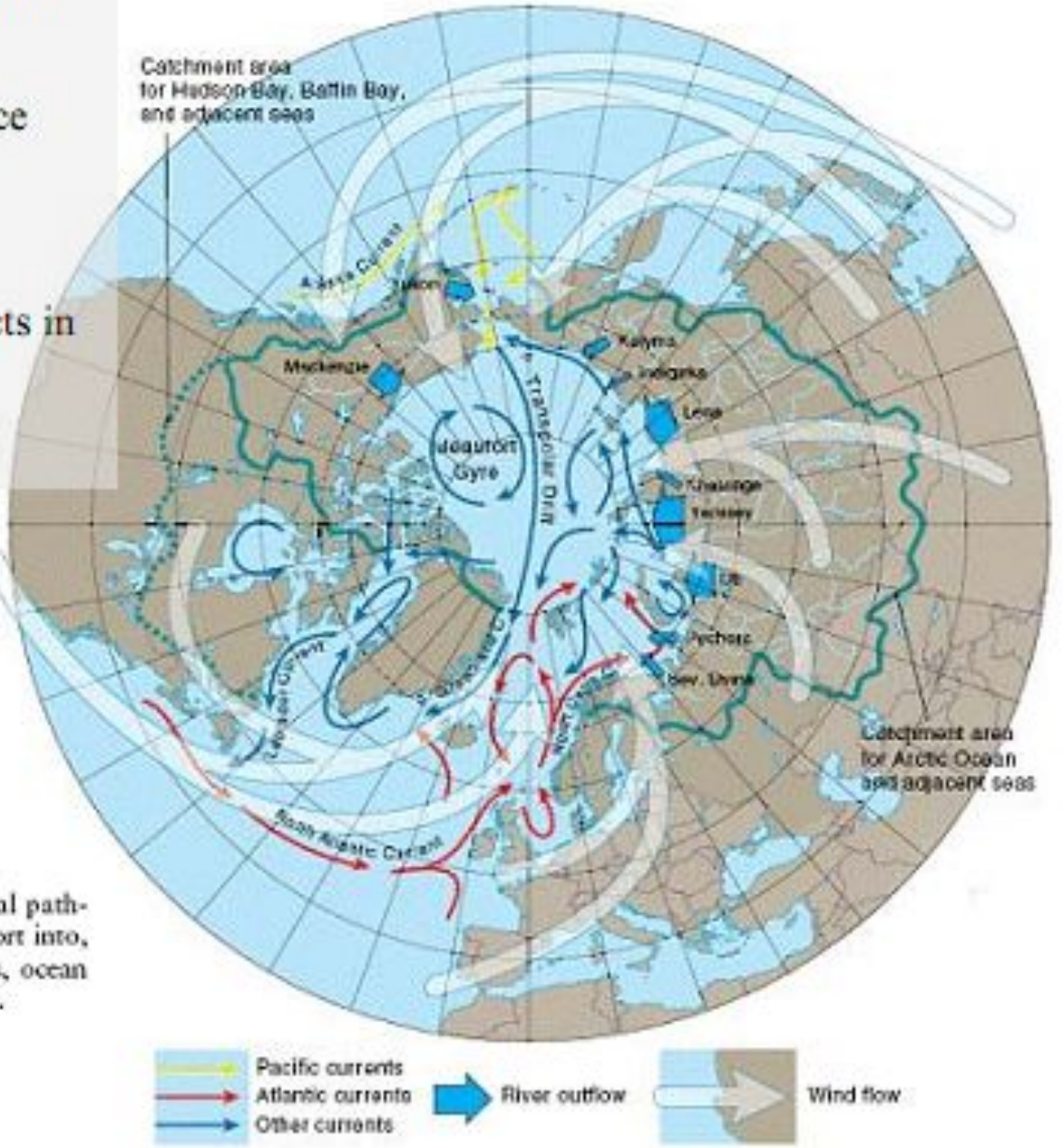


Illustration of the different physical pathways by which POPs enter the Arctic. Transport into, and within, the Arctic occurs via air currents, ocean currents, rivers, and transpolar ice movements.

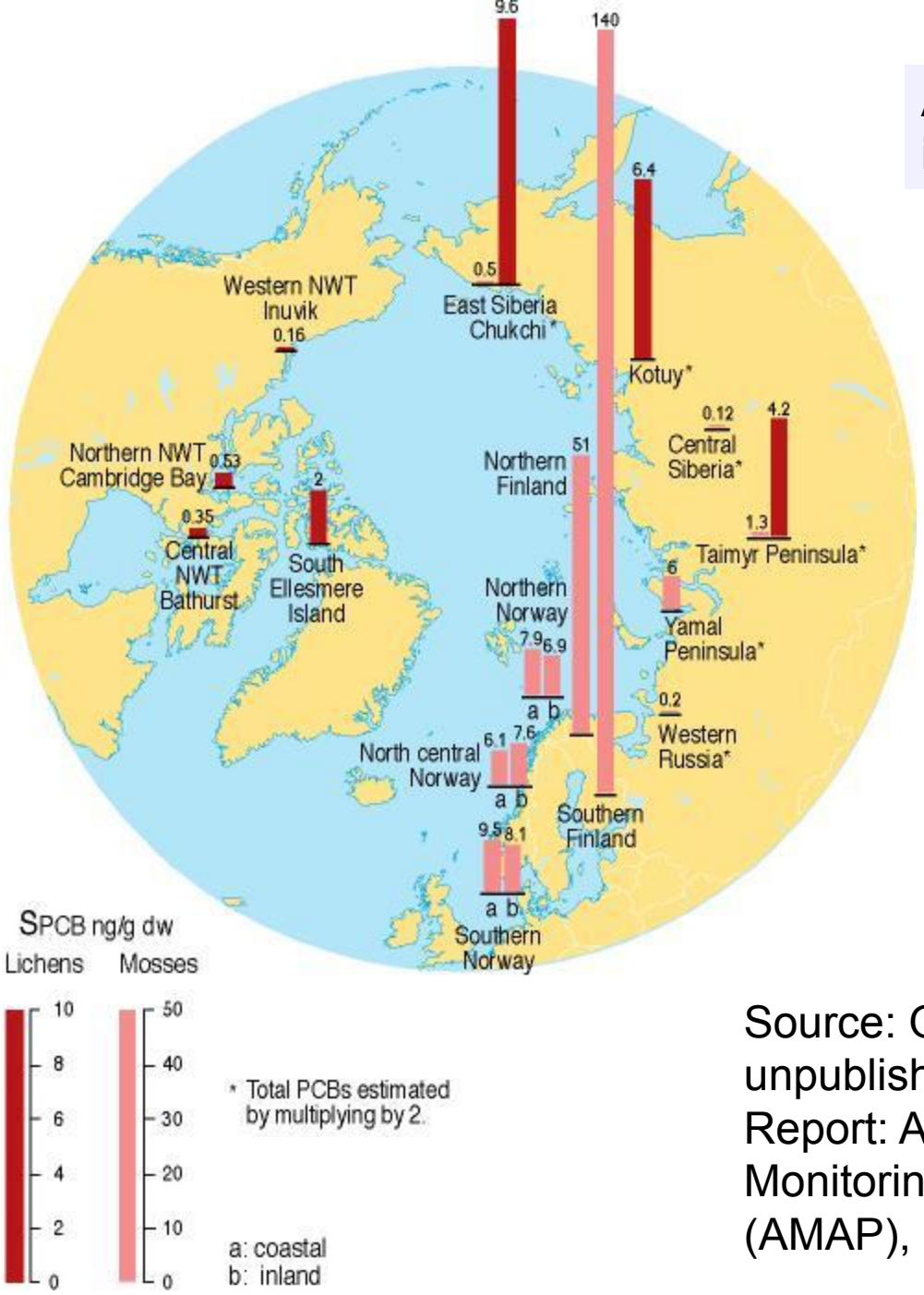
Source region for POPs in Arctic air based on 5-day back trajectories for elevated air concentration in various places in the Arctic area

Note: POPs observed here are HCH, Chlordane, Toxaphene and PCBs

Source: Result of questionnaires, Russian Association of Peoples of the North (RAIPON)

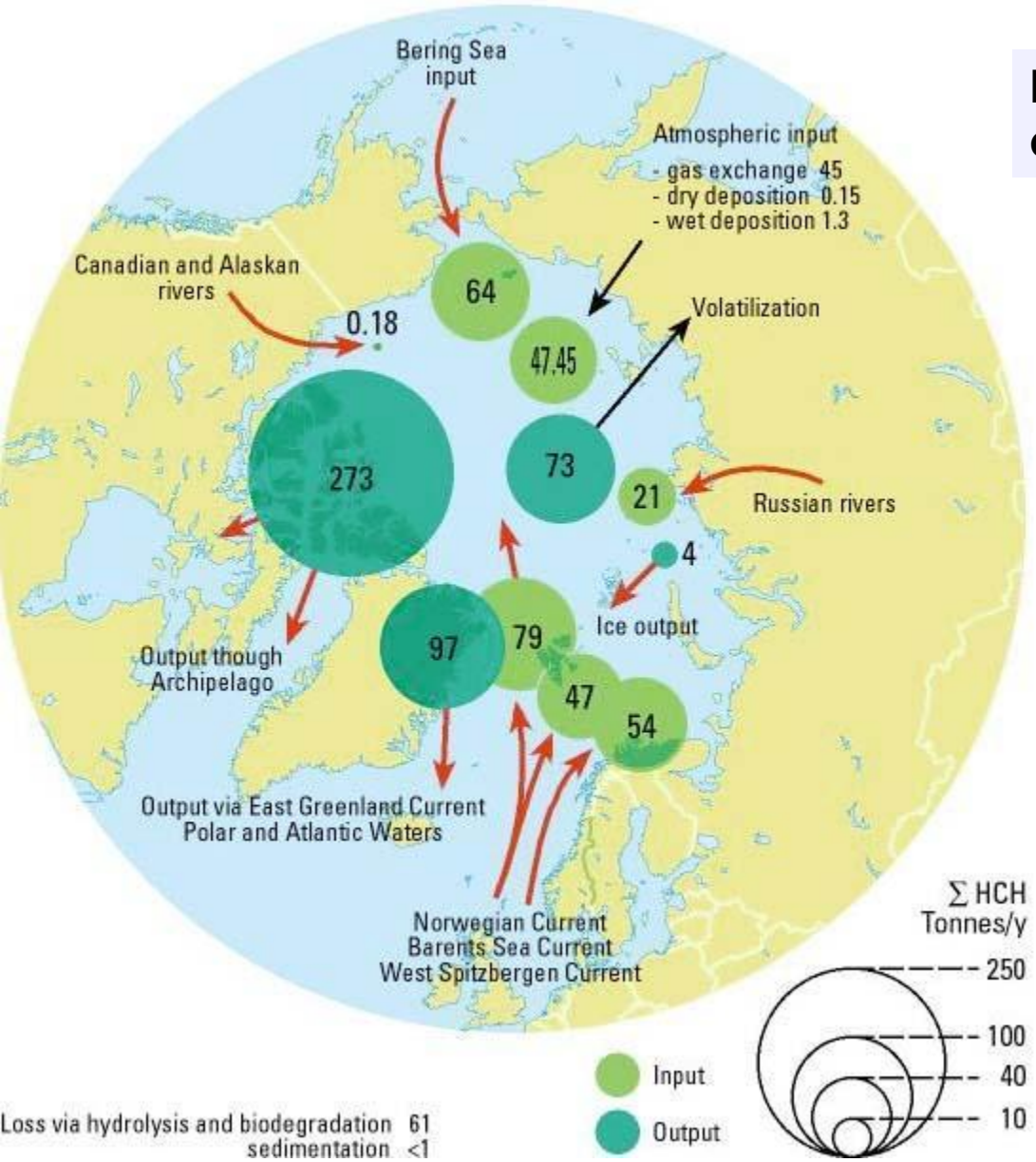
Source: Oehme et al. 1996, Barrie et al. unpublished data, in AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, 1998.

Average concentration of PCBs in the Arctic lichen and mosses

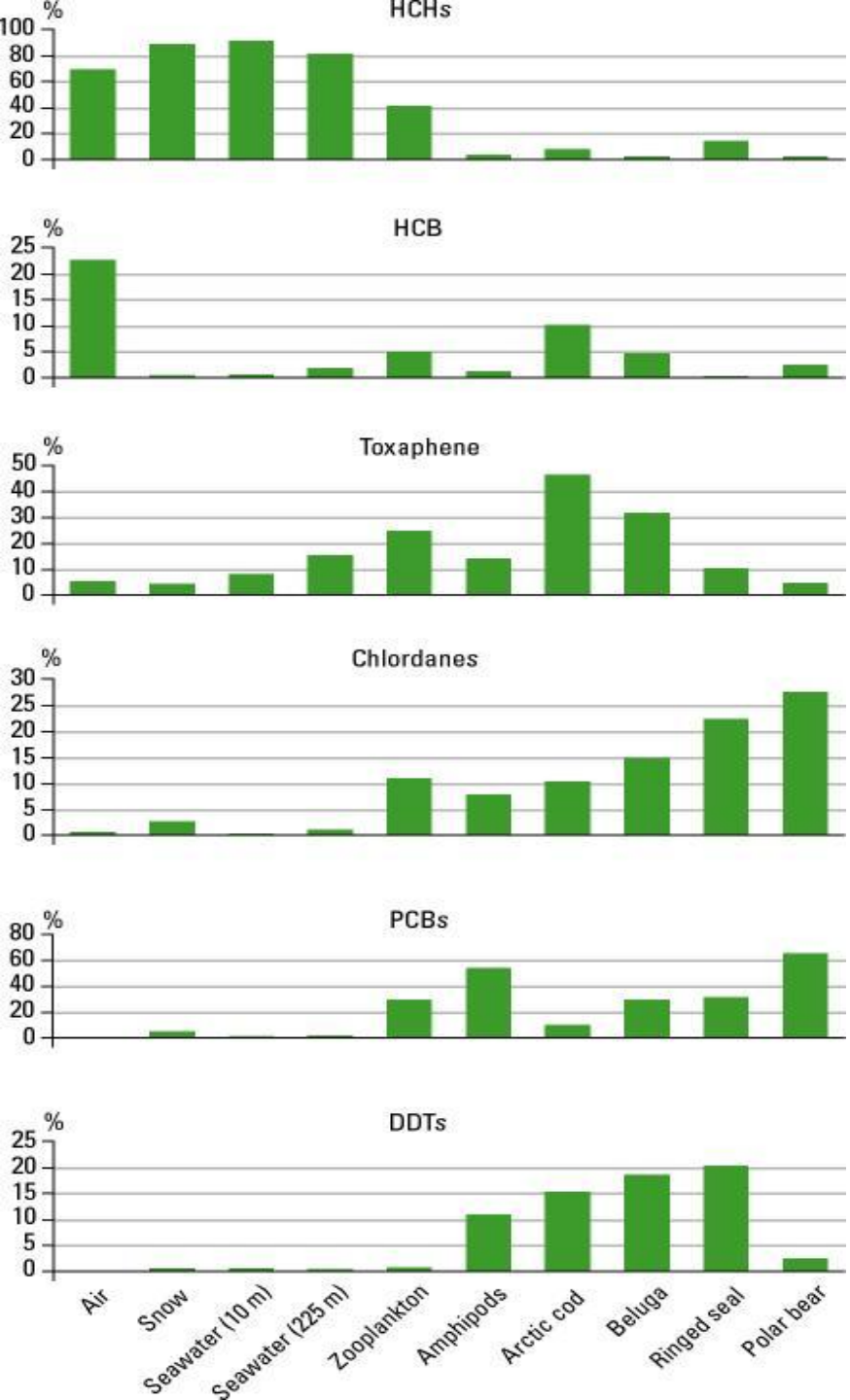


Source: Oehme et al. 1996, Barrie et al. unpublished data, in AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, 1998.

HCH budget for the Arctic ocean, in tonnes per year



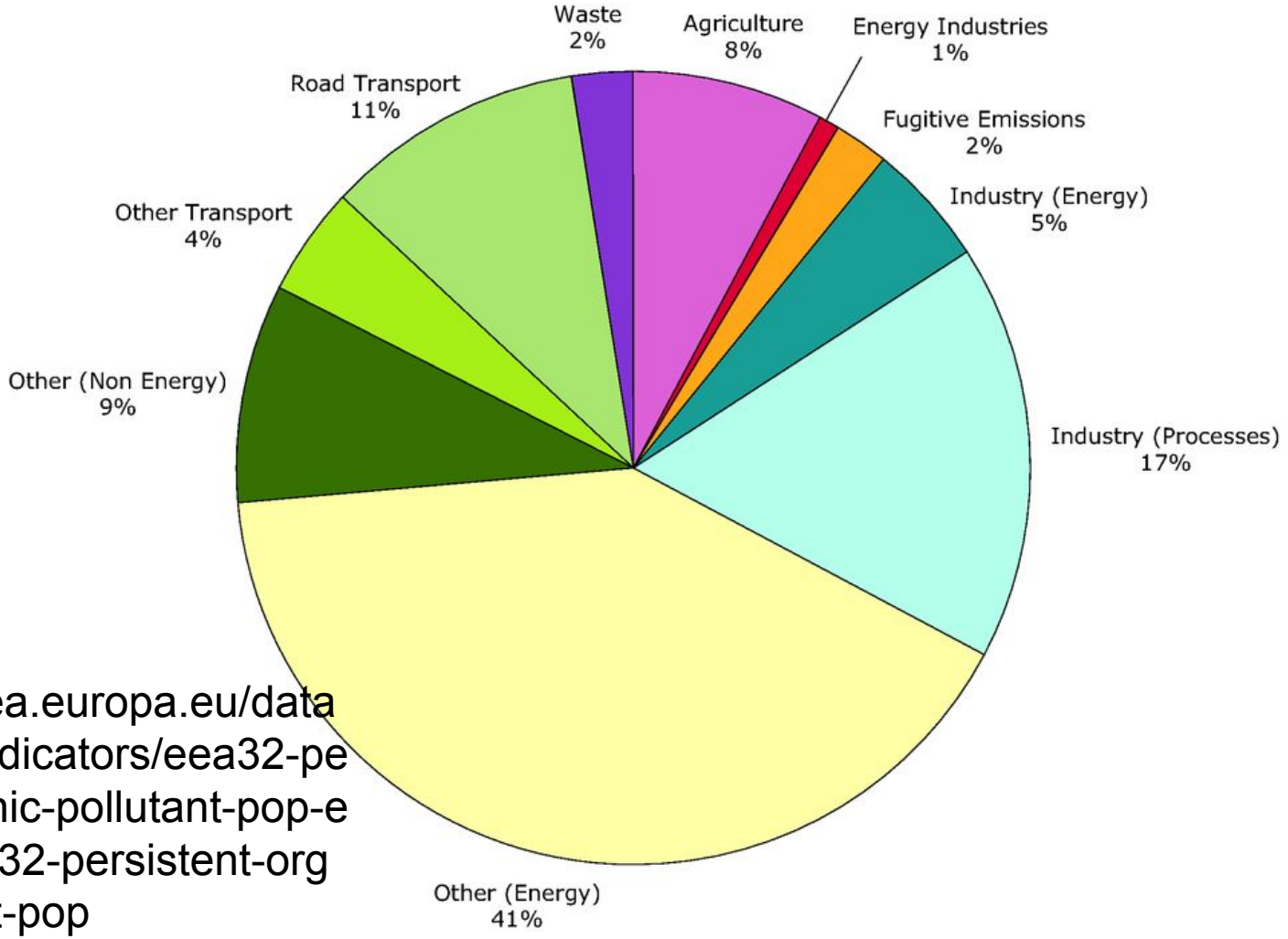
Source: AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, 1998.



Distribution of organochlorine contaminants (OCs) in the Arctic

Sources : Norstrom and Muir 1994., in AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, 1998.

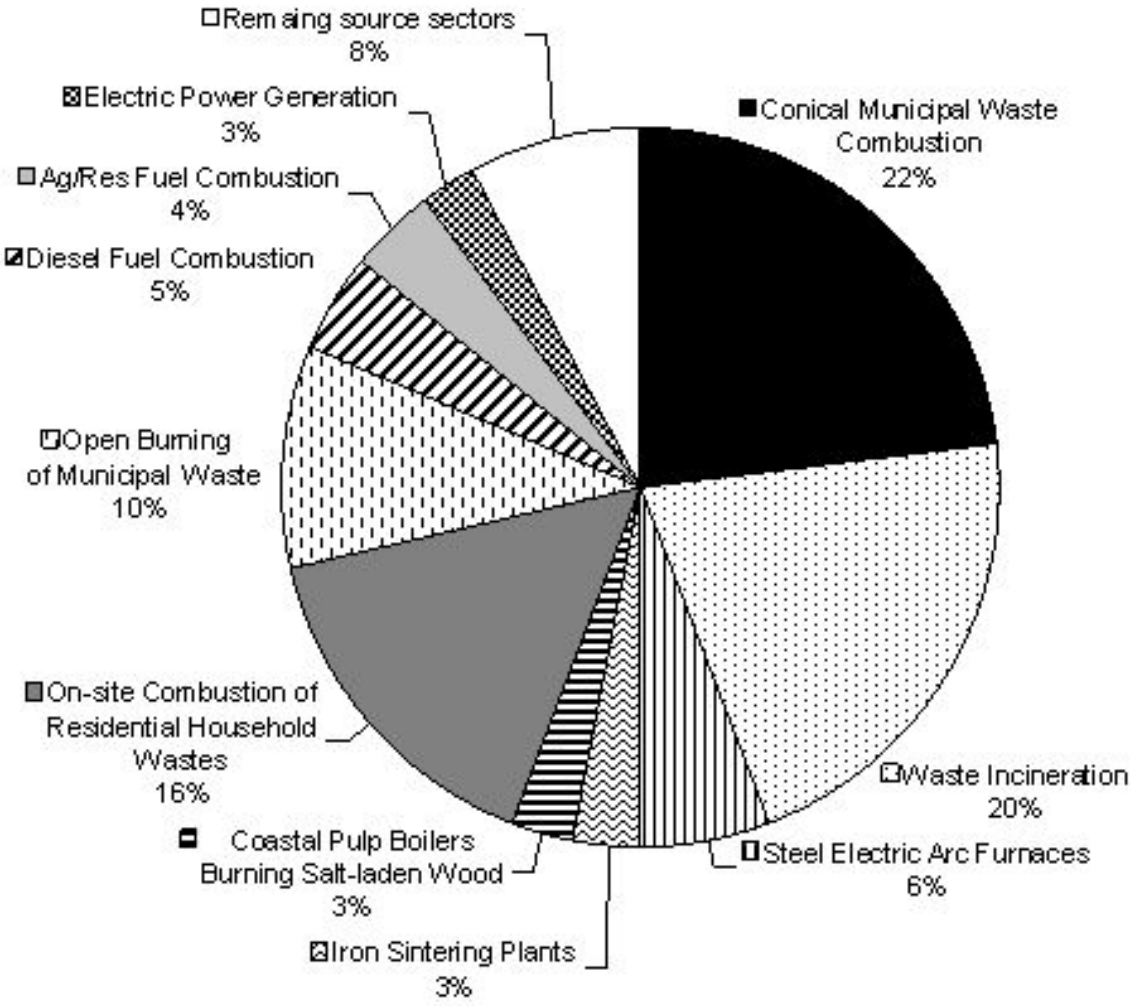
Sector share of PAH emissions (EEA member countries)



http://www.eea.europa.eu/data-and-maps/indicators/eea32-persistent-organic-pollutant-pop-emissions/eea32-persistent-organic-pollutant-pop

Estimated Percent Contribution of Sector Dioxins and Furans

Releases to the Atmosphere (1999)



https://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=CAE9F571=1&wsdoc=A027B74F-FAC4-DC47-CDC0-B41DDEAE61AD

Exchange of POPs between the environmental compartments

- In the air POPs can associate with particles.
- Contaminated water can run through soil into a fresh water compartment and from there through rivers into the ocean.
- Finally, POPs are uptaken by animals.

Reactions with other environmental constituents

- In air there are mainly two types of reactions: photolysis and oxidation.

Photolysis happens when chemical reactions or rupture of chemical bonds are sparked by the energy in sun light.

The main **oxidation** of POPs are reactions with OH·, but there can also be reaction with other radicals, such as the nitrate (NO_3^-) radical and ozone (O_3).

- In water POPs are subject to hydrolysis, a process in which the compounds reacts with water, hydrogen ion or hydroxyl ion.
- Finally, POPs undergo biodegradation, which occur in both water and soil. This term covers a wide range of processes in microbial organisms.

Environmental fate of POPs

- According to the global fractionation hypothesis' differences in volatility arising from different physical-chemical properties (especially the vapour pressure) leads to different atmospheric transport distances, and thereby a fractionation of the compounds

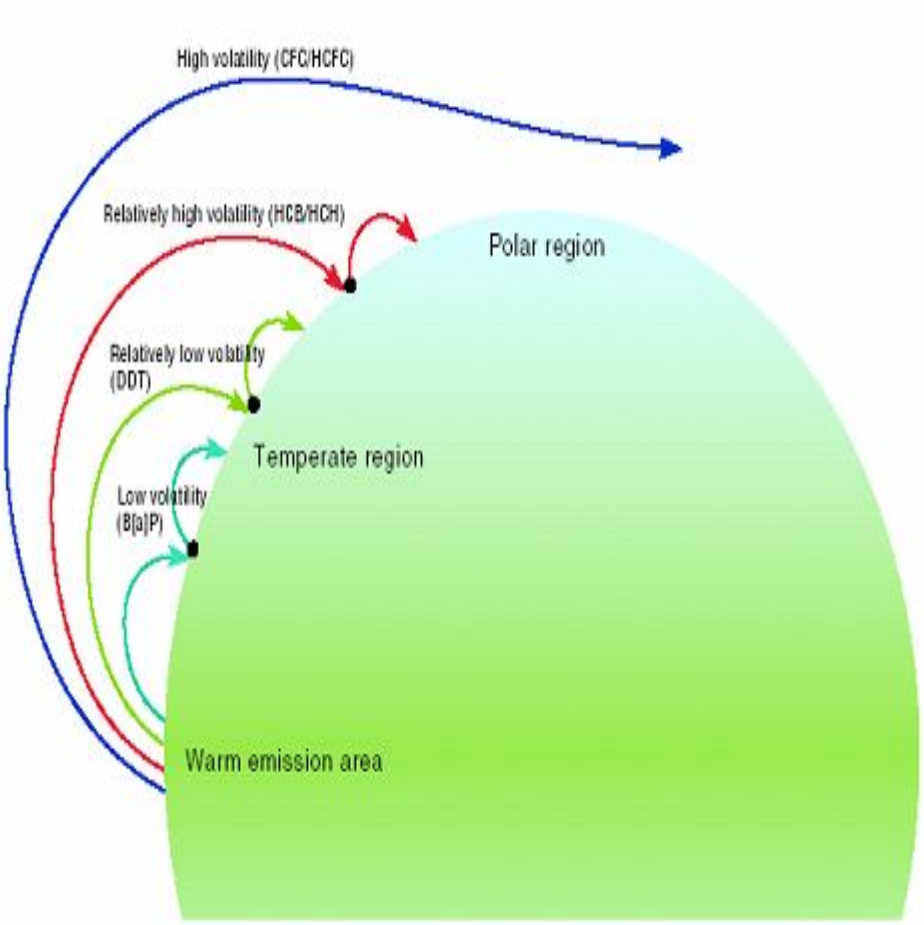


Figure: An illustration of `the global fractionation' hypothesis. Differences in volatility leads to a global fractionation of POPs. From AMAP [2004].

Environmental fate of POPs

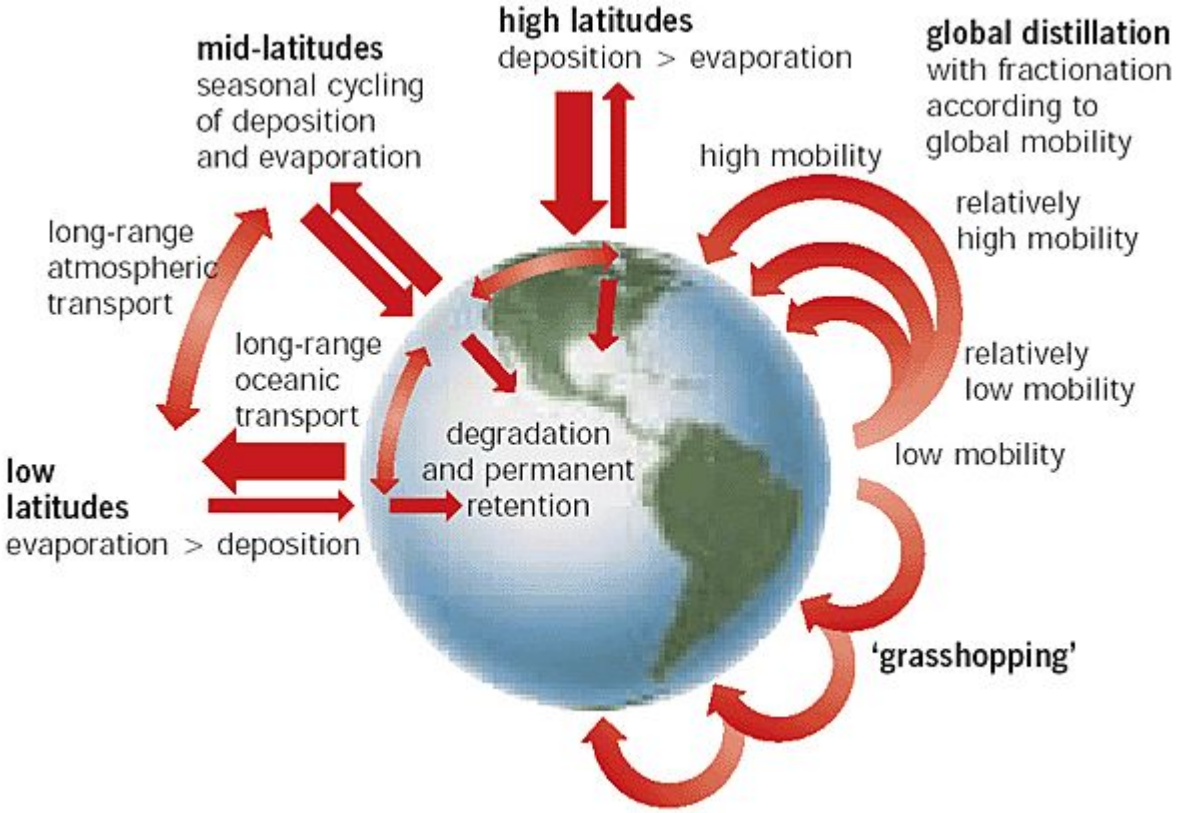
- POPs are deposited to the surface through either wet or dry deposition.

On the ground, POPs may be sorbed onto the surface of vegetation or soil or be dissolved in water.

If the temperature rises, the surface-sorbed or dissolved POPs may re-volatilise into the atmosphere due to their temperature dependent physical-chemical properties, and here they can undergo further atmospheric transport.

This effect is termed the `grasshopper effect'.

`grasshopper effect'

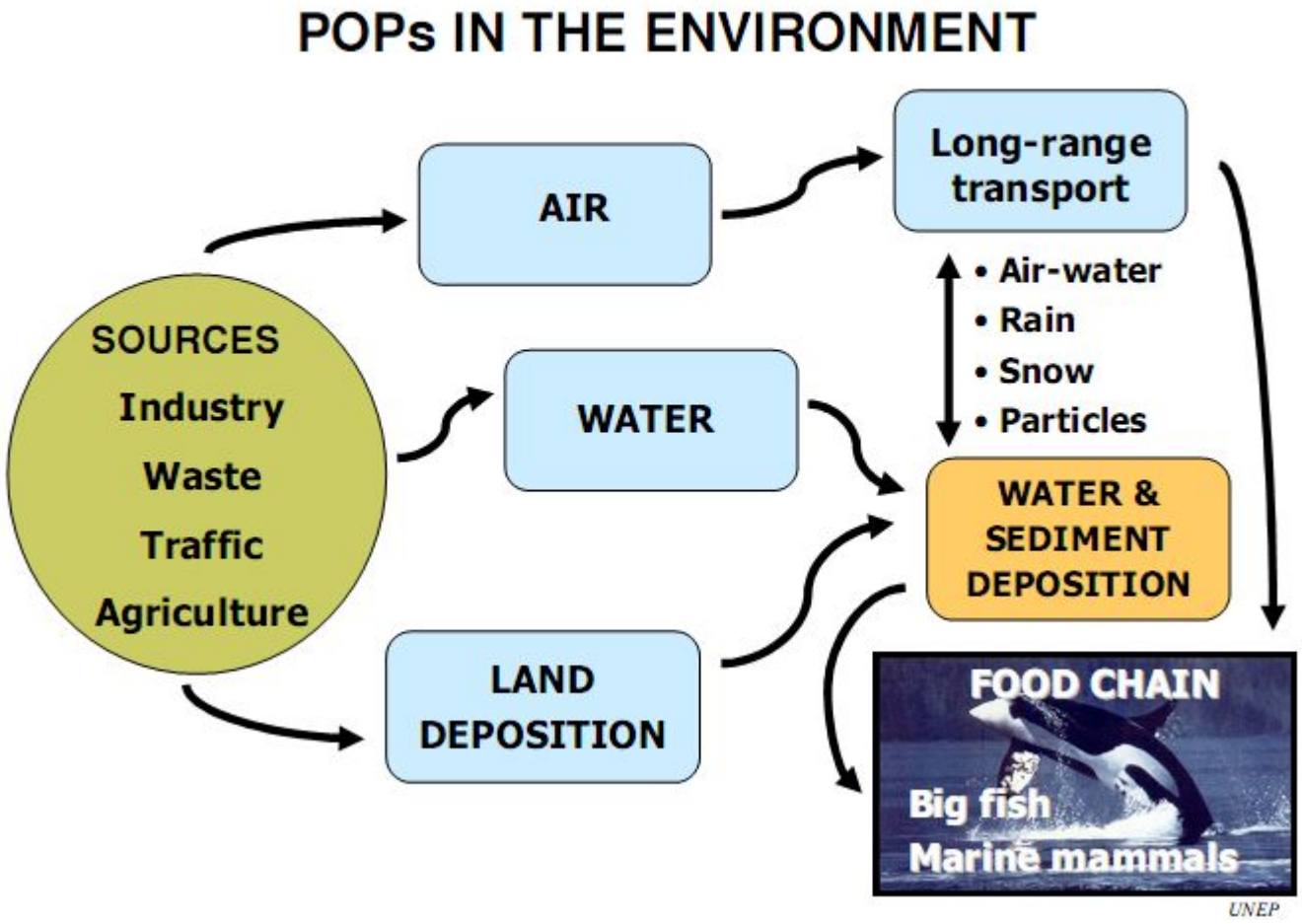


Environmental fate of POPs

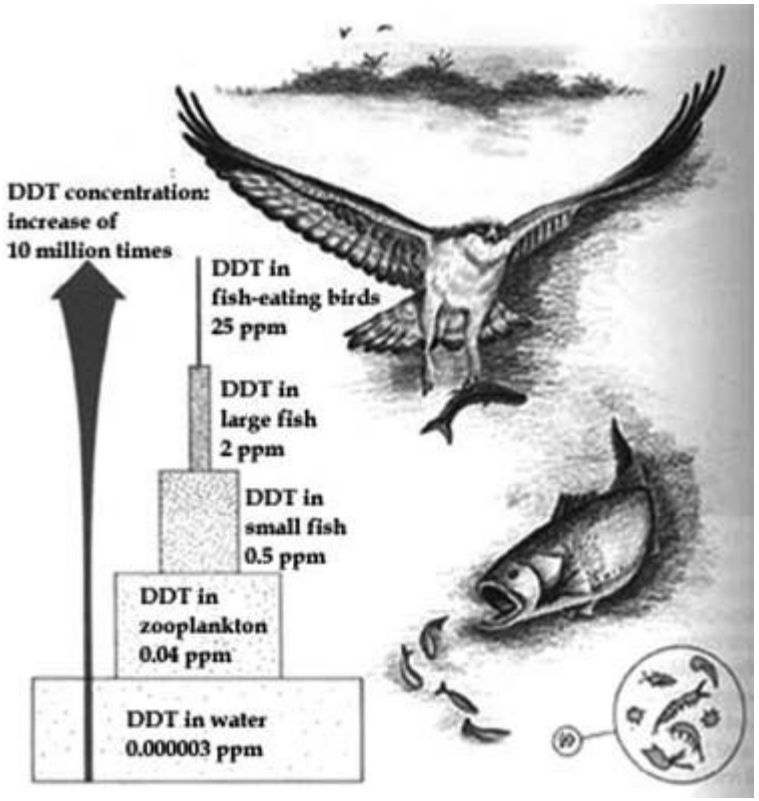
The temperature dependence of the volatility has another effect. When POPs reach cold environments such as the Arctic the low temperatures make it diffcult for them to escape the region and they are thus `trapped'. This phenomenon has been named `cold condensation'.

This is due to the relatively small size of the Arctic as a whole and especially of the environmental organic phases with capacity of retaining POPs. Measurements have shown that mountain regions also can act as cold traps of POPs.

POPs


POPs IN THE ENVIRONMENT
SOURCES
Industry
Waste
Traffic
Agriculture
AIR
WATER
LAND
DEPOSITION
Long-range
transport
• Air-water
• Rain
• Snow
• Particles
WATER &
SEDIMENT
DEPOSITION
FOOD CHAIN
Big fish
Marine mammals
UNEP

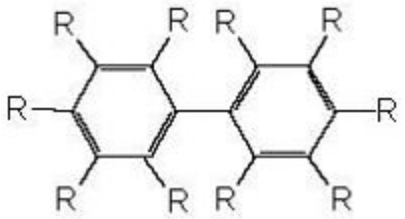
Biomagnification of DDT in the food web.



Credit: US Fish & Wildlife Service

EXAMPLES OF EFFECTS OF POPs ON WILDLIFE

- Reproductive impairment and malformations
- Immune system is sensitive
- Altered liver enzyme function
- Increased risk of tumours



UNEP

Mammals:	reproductive and immune effects in Baltic seals
Birds:	eggshell thinning, gonadal and embryo alterations
Reptiles:	decline in number of alligators
Fish:	reproductive alterations
Snails:	masculinization and population decrease (marine)

AN EXAMPLE: PCBs

- Effects in humans after high-level exposure:
  - Skin rash, eyelid swelling
  - Hyperpigmentation – CHLORACNE
  - Headaches, vomiting
- Effects of long-term exposures:
  - Hepato-, immuno-, reproductive and dermal toxicities
- Fetal exposures to PCBs:
  - Neural and developmental changes
  - Lower psychomotor scores
  - Short-term memory and spatial learning effects
  - Long-term effects on intellectual function

PCB: HUMAN HEALTH INCIDENTS

Toxic effects at *high* levels of exposure, accidental or occupational:

- Dermal
- Ocular
- Blood and liver enzyme alteration
- Respiratory
- Immune system
- Neurological system
- Reproductive
- Developmental

"Yusho" & "Yu-Cheng"

Adverse, persistent effects in newborns

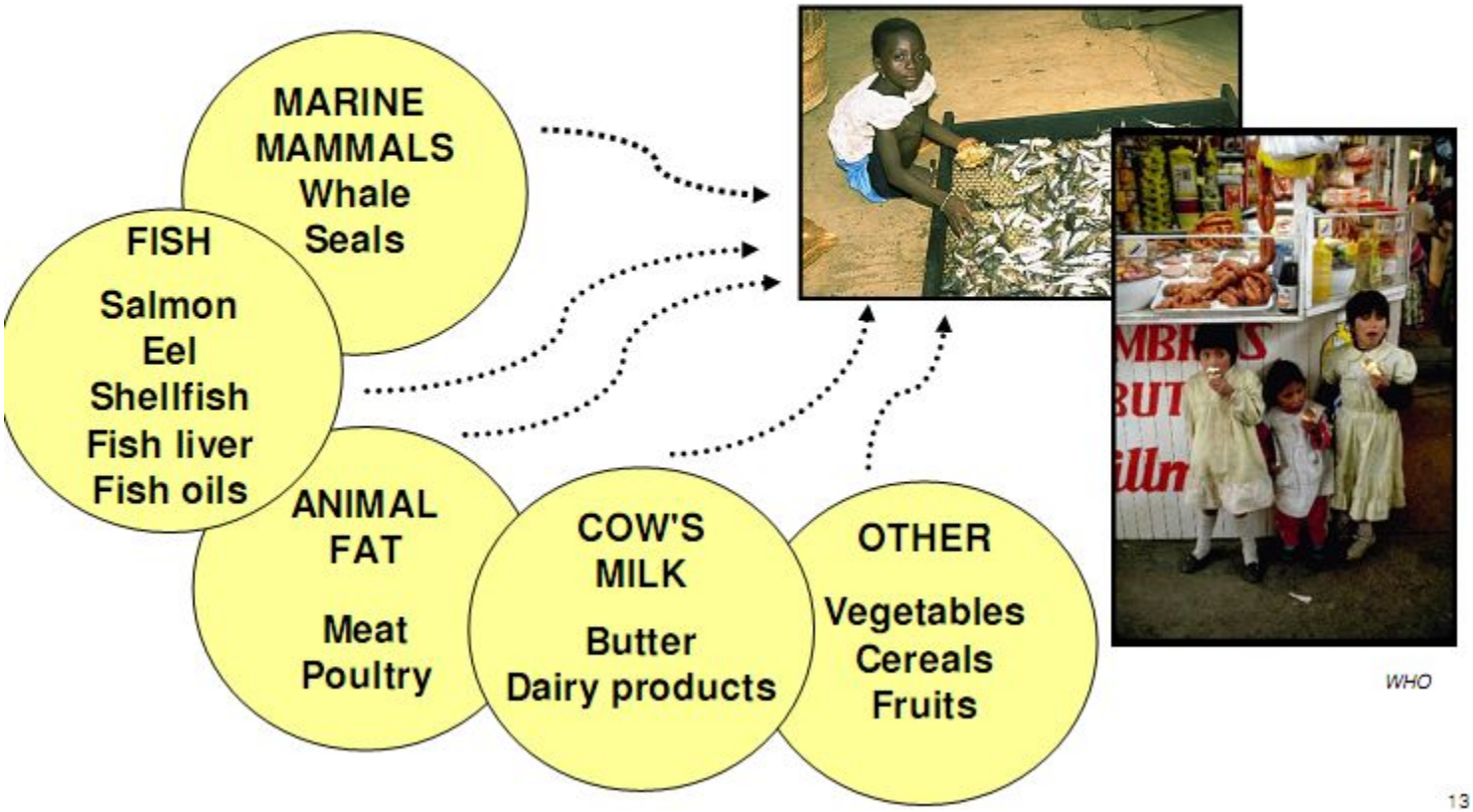
- Low birth weight
- Reduced growth
- Hyperpigmentation
- Gingival hyperplasia
- Eye oedema
- Dentition at birth
- Skull calcifications

Major Sources of Human Exposure

Source	How POPs enter body
Food	Deposited in waterways, taken up by invertebrates, accumulate in fish and animals eaten by people; pesticide residues in foods.
Soil	Transported by air currents and storm systems. Deposited through contact with solid surfaces or through precipitation then ingested or absorbed through skin.
	Persistent soil residues of banned pesticides such as DDT, dieldrin are ingested or absorbed through skin
Indoor environment	Building materials, furniture, textiles carpets and curtains, packing materials, electric and electronic appliances containing PBDEs.
Toys, other objects	Chemical released when object is mouthed
Air	Inhalation of fumes from burning of items containing PCBs, PBDEs. Heating of transformers, waste burning in the open.
Leaching from medical products	Phthalates are examples of chemicals (not considered POPs) that may leach from intravenous tubing attached to patients.

POPs

MAIN ROUTE OF EXPOSURE TO PCBs: DIETARY



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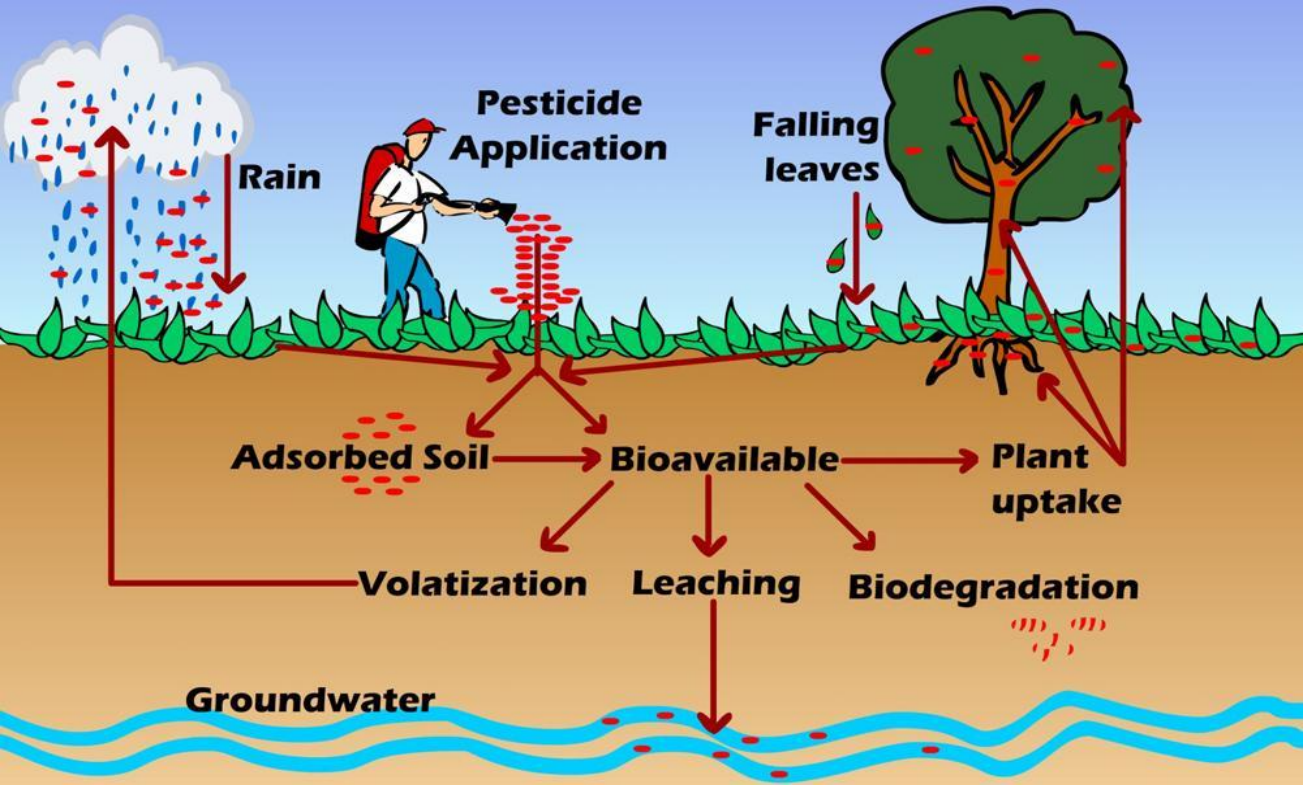
AN EXAMPLE: PCBs

- PCBs accumulate in human adipose tissue and breast milk
- In adipose tissue: <1 to 5 mg/kg, on fat basis
- Average concentration in human milk: 0.5 to 1.5 mg/kg fat
- PCB levels are higher in some areas or in relation to diet
- Concern: low-level exposures and neurodevelopment


Pesticide
Application
Rain
Falling
leaves
Adsorbed Soil
Bioavailable
Plant
uptake
Volatization
Leaching
Biodegradation
Groundwater