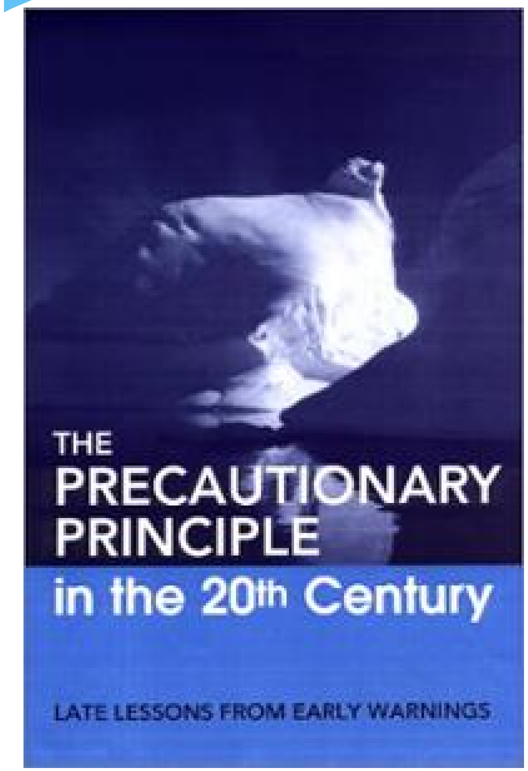
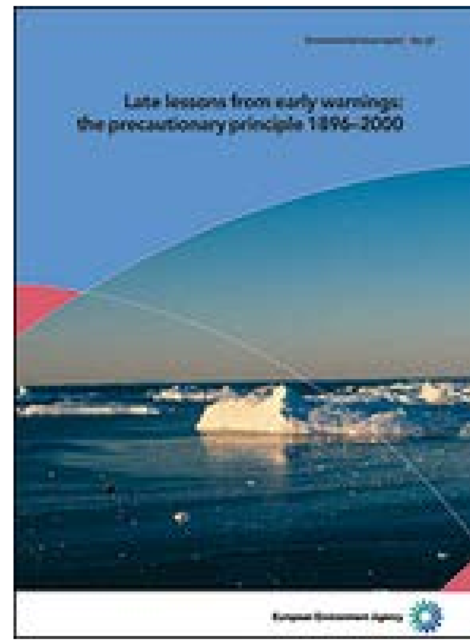
Chemical transport and fate in the environment

Simply Complicated

Silent Spring –Rachel Carson 1962

Late lessons from early warnings: the precautionary principle

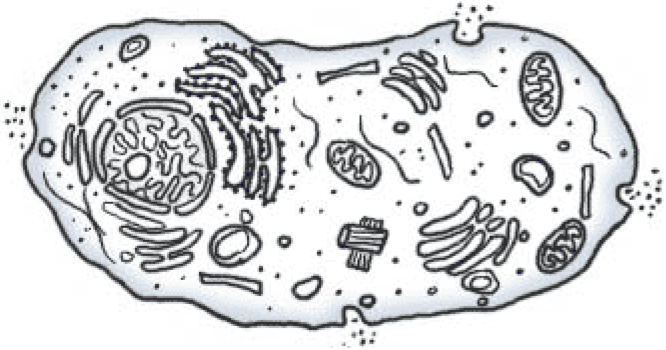




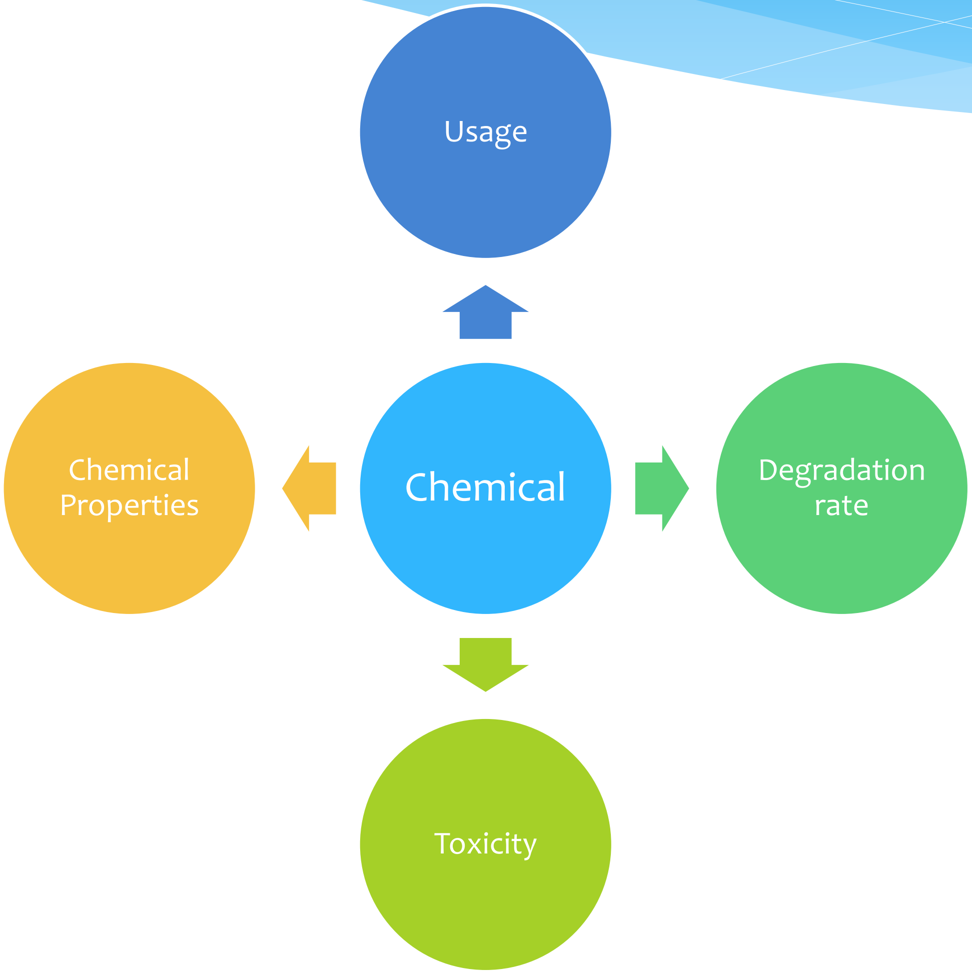
Aim

Go from the globe to you and beyond

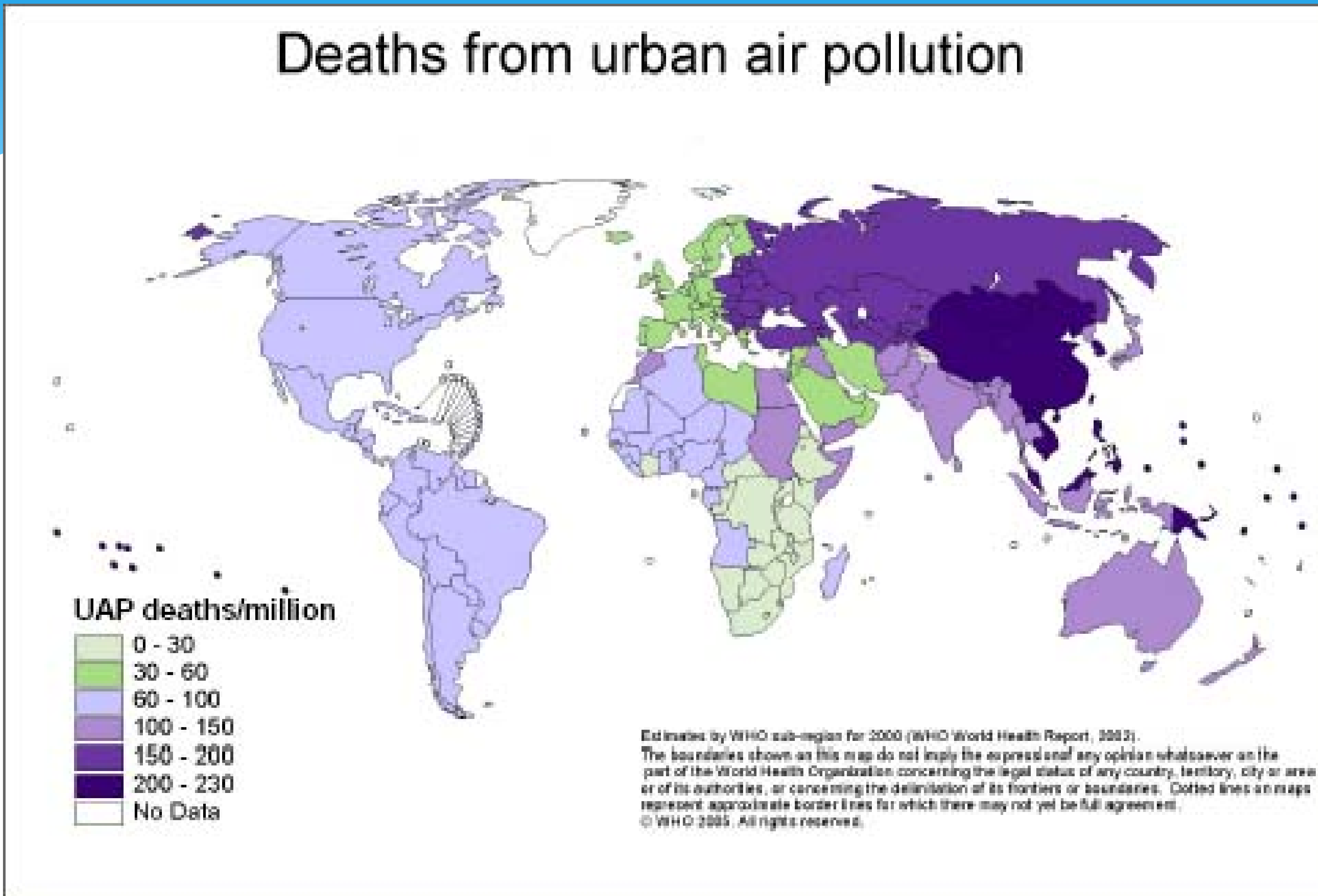
* What
* Where
* How
* When
* Why



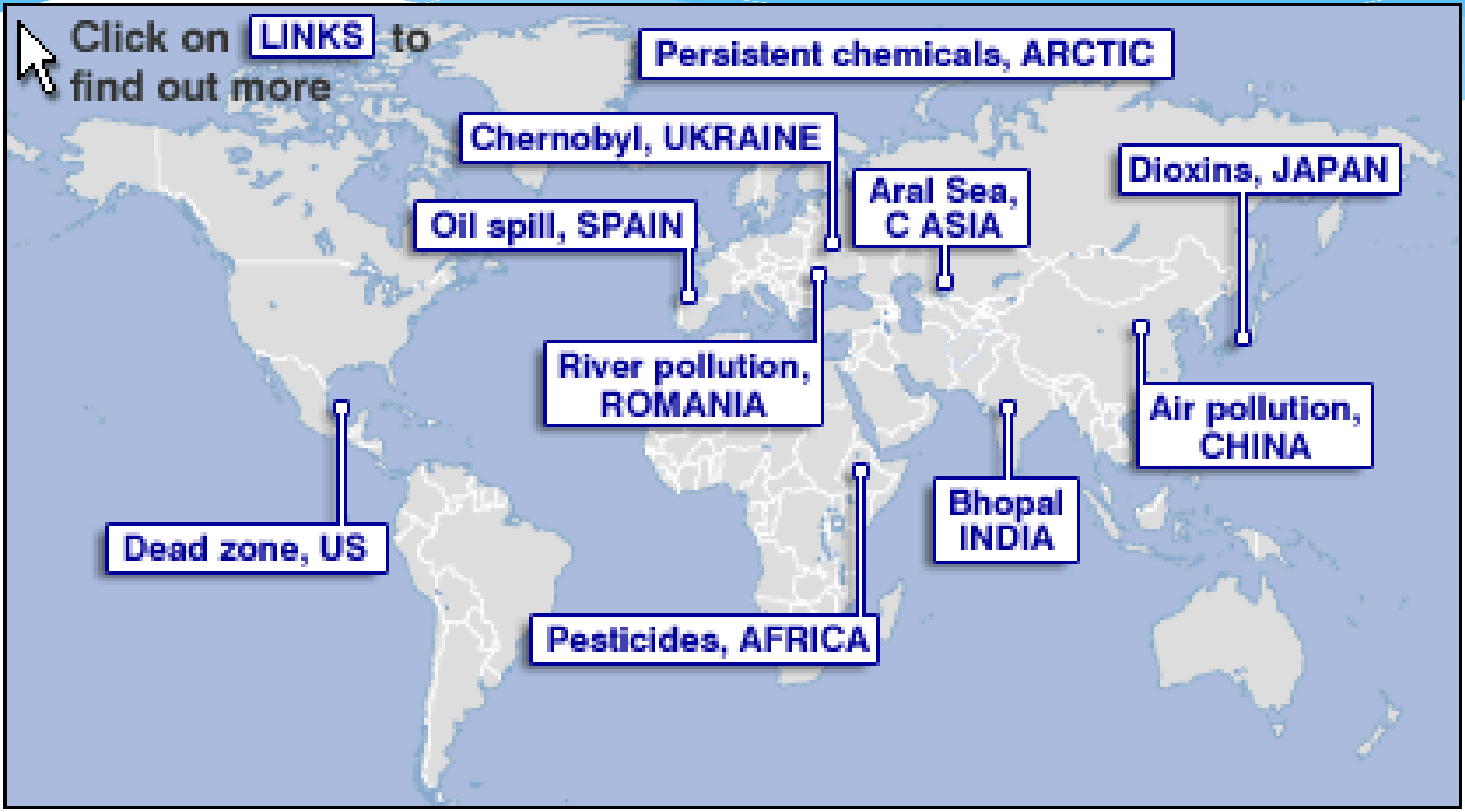
A chemical



Usage
Chemical Properties
Chemical
Degradation rate
Toxicity


Deaths from urban air pollution
UAP deaths/million
0 - 30
30 - 60
60 - 100
100 - 150
150 - 200
200 - 230
No Data
Estimates by WHO sub-region for 2000 (WHO World Health Report, 2002).

Example of issues



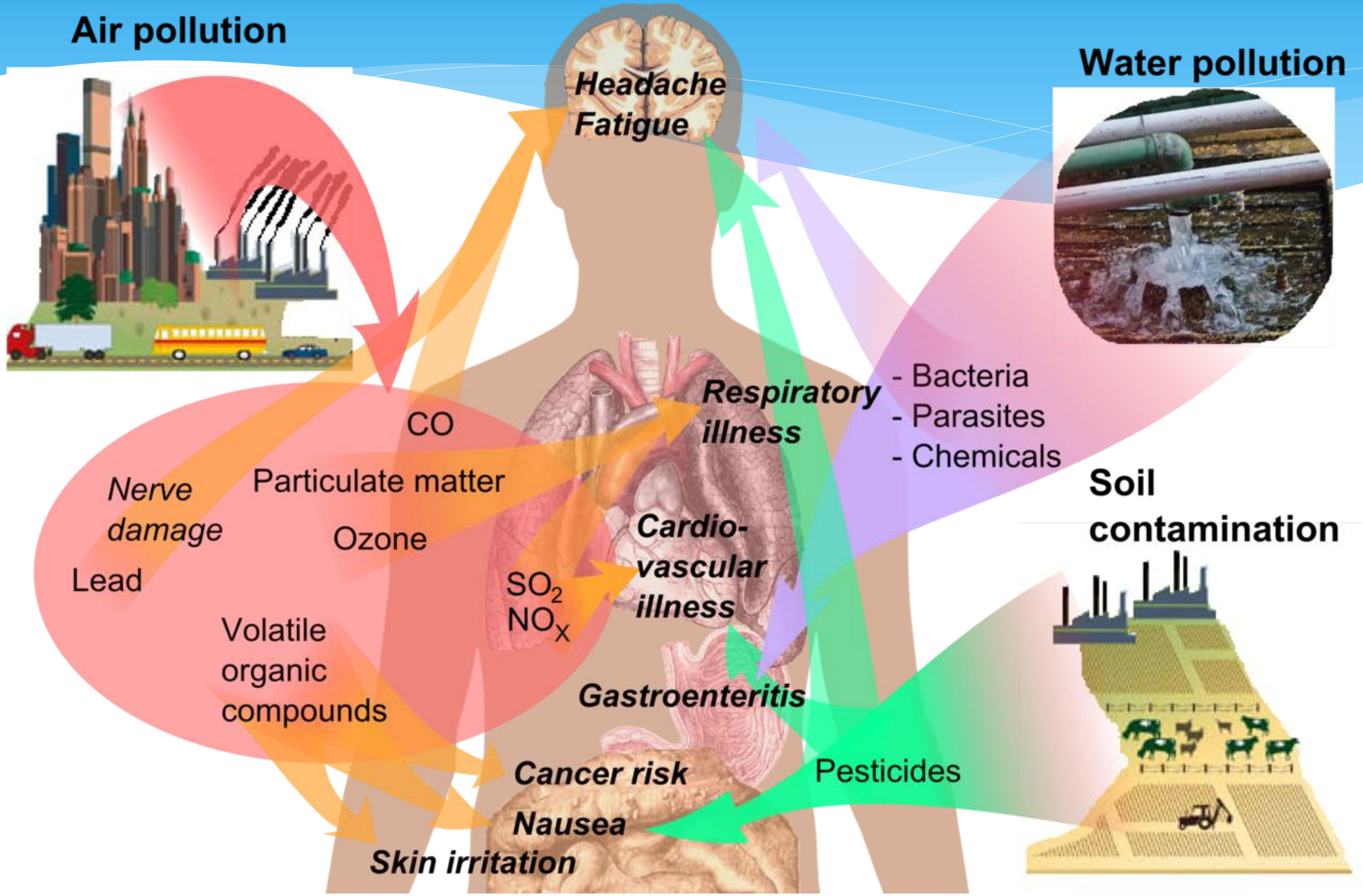
BBC News


.com
MORE THAN 80 HOSPITALIZED AFTER CHEMICAL INCIDENT
41 Action NEWS


DU PONT
KILLED AFTER CHEMICAL LEAK
53° 10:02
KHOU
OTHERS KILLED
DEADLY ACCIDENT
BOY FOUND SAFE

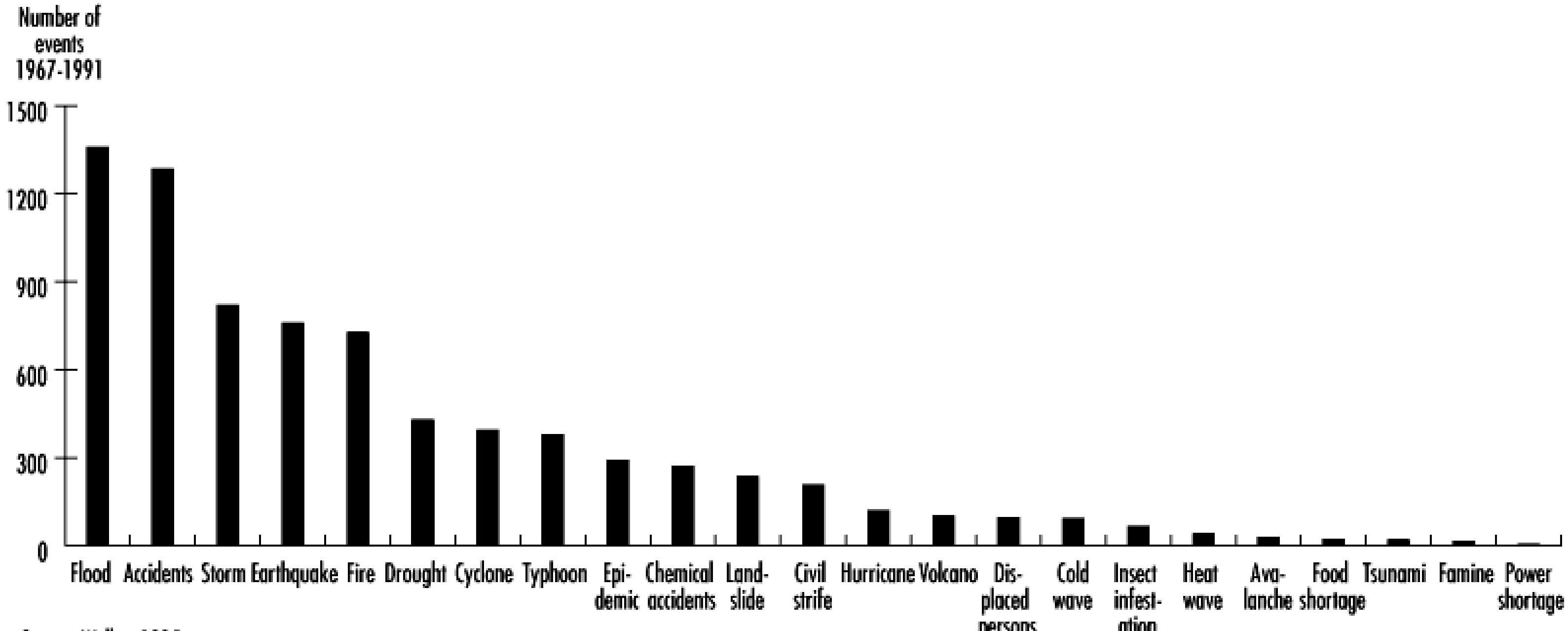

FLINT WATER PLANT

Heath Effects



Häggström, Mikael. "Medical gallery of Mikael Häggström 2014".

Disasters



Source: Walker 1995.

Chemical Disasters

Major Fire	Consequences		Place and date
Chemical involved	Death	Injuries	
Methane	136	77	Cleveland, Ohio, United States, 1944
Liquefied petroleum gas	18	90	Ferzyn, France, 1966
Liquefied natural gas	40	-	Staten Island, New York, United States, 1973
Methane	52	-	Santa Cruz, Mexico, 1978
Liquefied petroleum gas	650	2,500	Mexico City, Mexico, 1985

Explosion	Consequences		Place and date
Chemical involved	Death	Injuries	
Dimethyl ether	245	3,800	Ludwigshafen, Federal Republic of Germany, 1948
Kerosene	32	16	Bitburg, Federal Republic of Germany, 1948
Isobutane	7	13	Lake Charles, Louisiana, United States, 1967
Oil slops	2	85	Pernis, Netherlands, 1968
Propylene	-	230	East Saint Louis, Illinois, United States, 1972
Propane	7	152	Decatur, Illinois, United States, 1974
Cyclohexane	28	89	Flixborough, United Kingdom, 1974
Propylene	14	107	Beek, Netherlands, 1975

Toxic Release	Consequences		Place and date
Chemical involved	Death	Injuries	
Phosgene	10	-	Poza Rica, Mexico, 1950
Chlorine	7	-	Wilsum, Federal Republic of Germany, 1952
Dioxin/TCDD	-	193	Seveso, Italy, 1976
Ammonia	30	25	Cartagena, Colombia, 1977
Sulphur dioxide	-	100	Baltimore, Maryland, United States, 1978
Hydrogen sulphide	8	29	Chicago, Illinois, United States, 1978
Methyl isocyanate	2,500	200,000	Bhopal, India, 1984

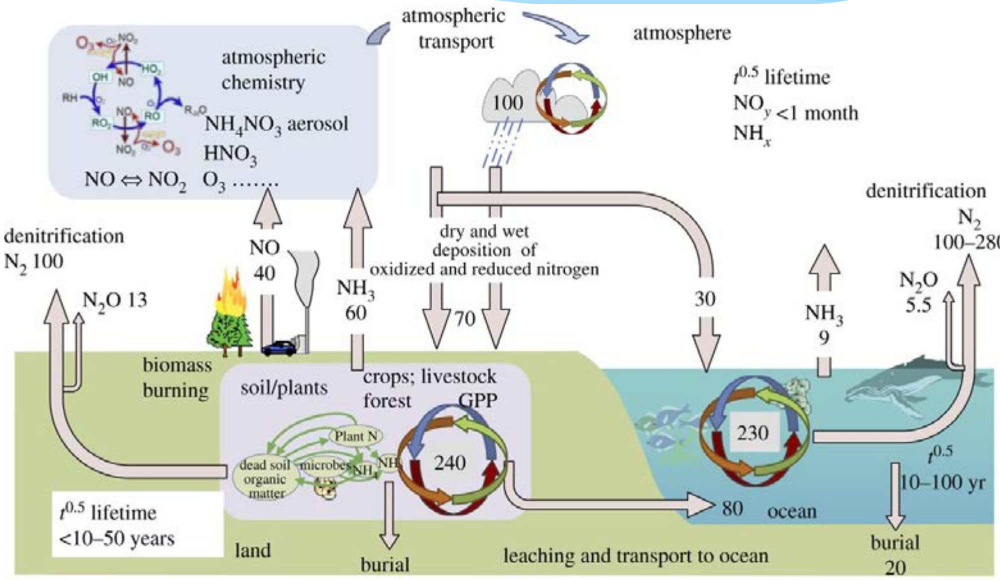
DISASTERS AND MAJOR ACCIDENTS, Pier Alberto Bertazzi

What makes a POP

* Bioaccumulation
* Long range transport
* Toxicity

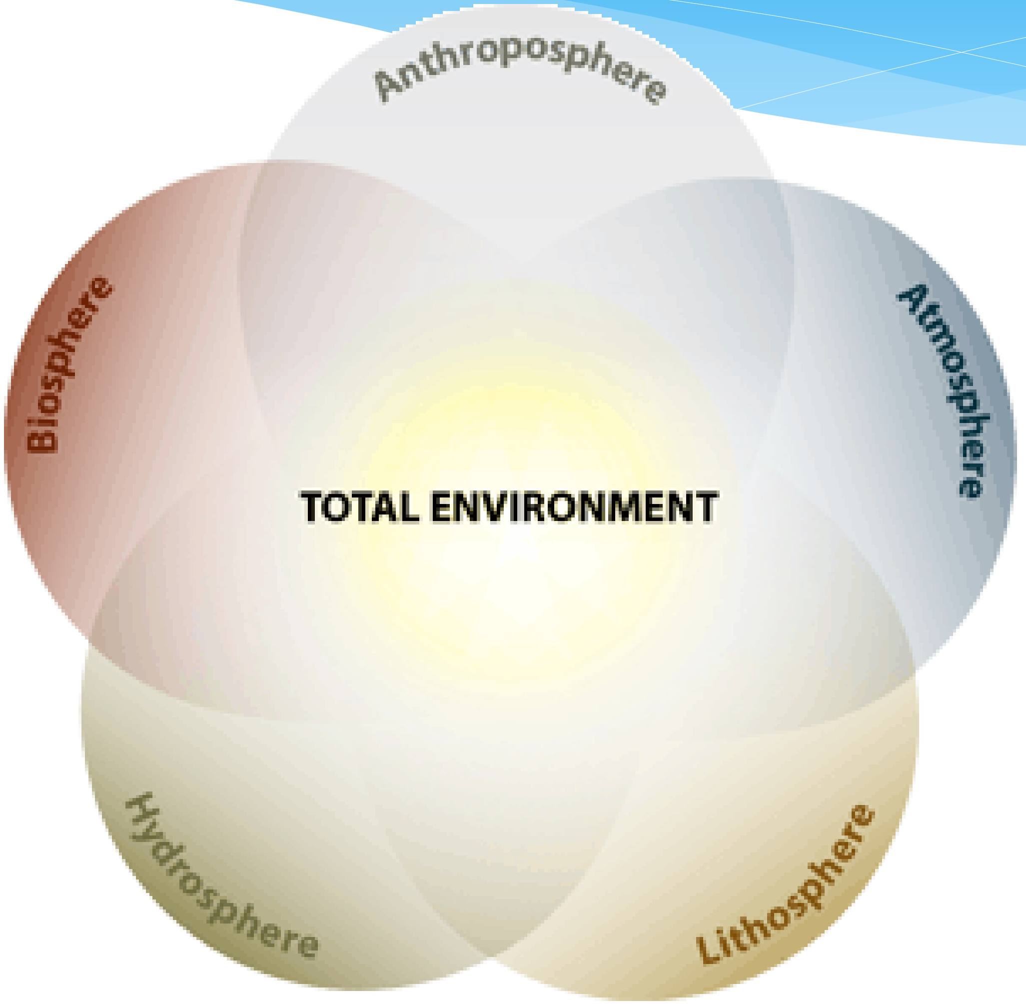
Transport and Fate

* Diffusion
* Dispersion and mixing
* Rivers and Streams
* Lakes and Reservoirs
* Wetlands
* Estuaries
* Local Air Pollution
* Regional and Continental Contamination
* Global Atmospheric Contamination

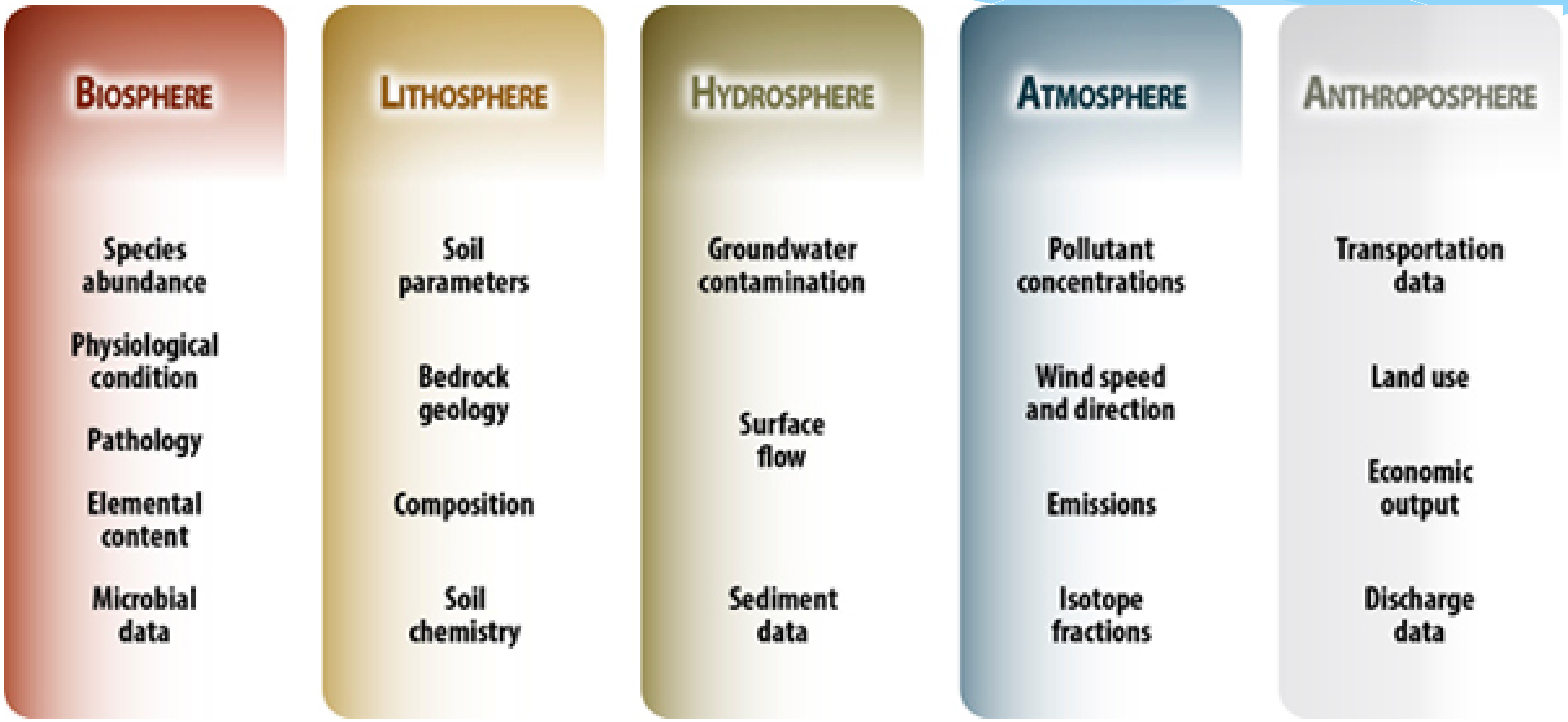


What is the Environment?

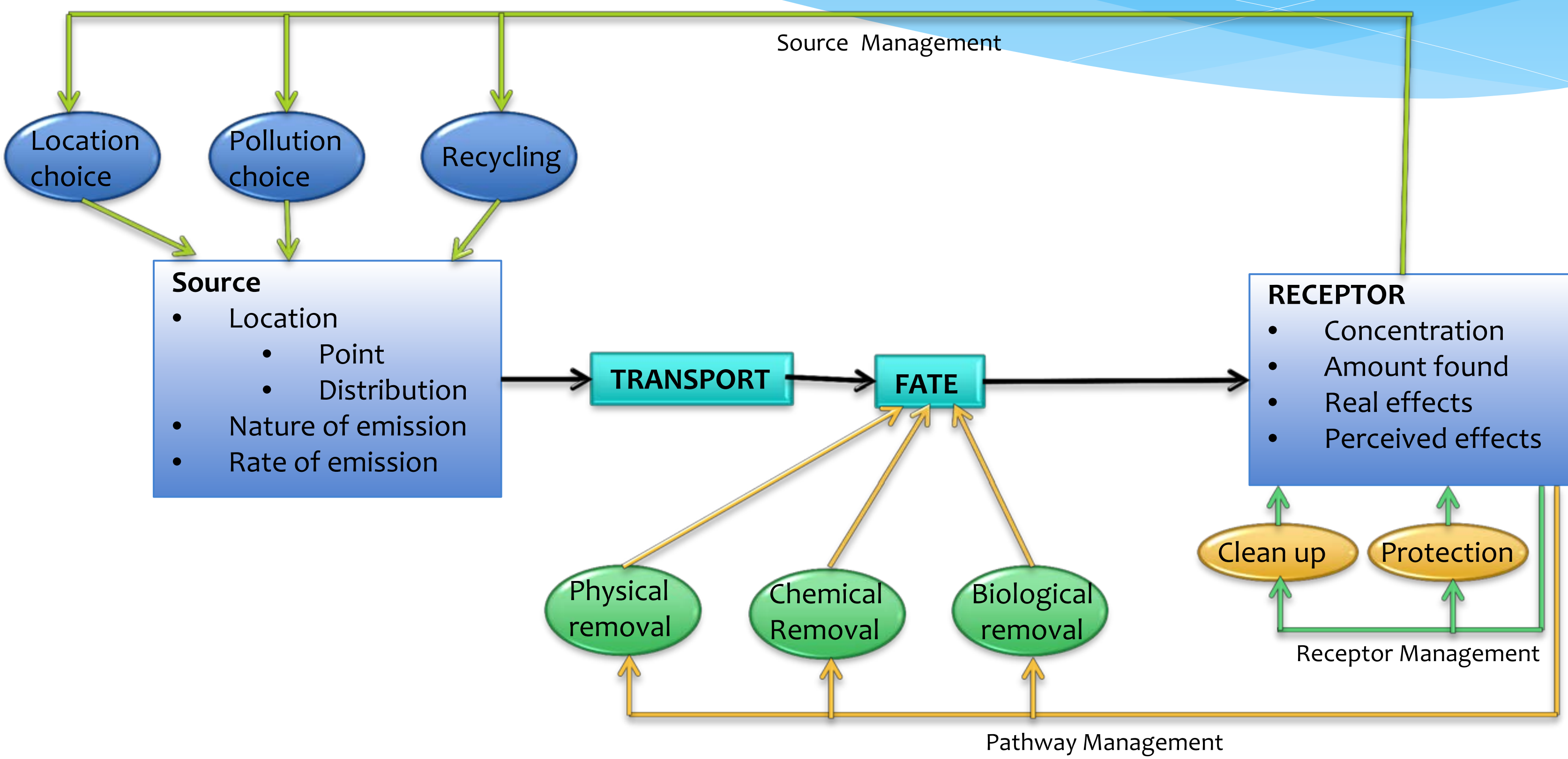
- Natural environment is all living and non-living things
- The physical and biological parameters with chemical interactions that affect and organism or group of organisms
- The physical system that interacts with exchange of mass, energy or other properties


Anthroposphere
Biosphere
Atmosphere
TOTAL ENVIRONMENT
Hydrosphere
Lithosphere

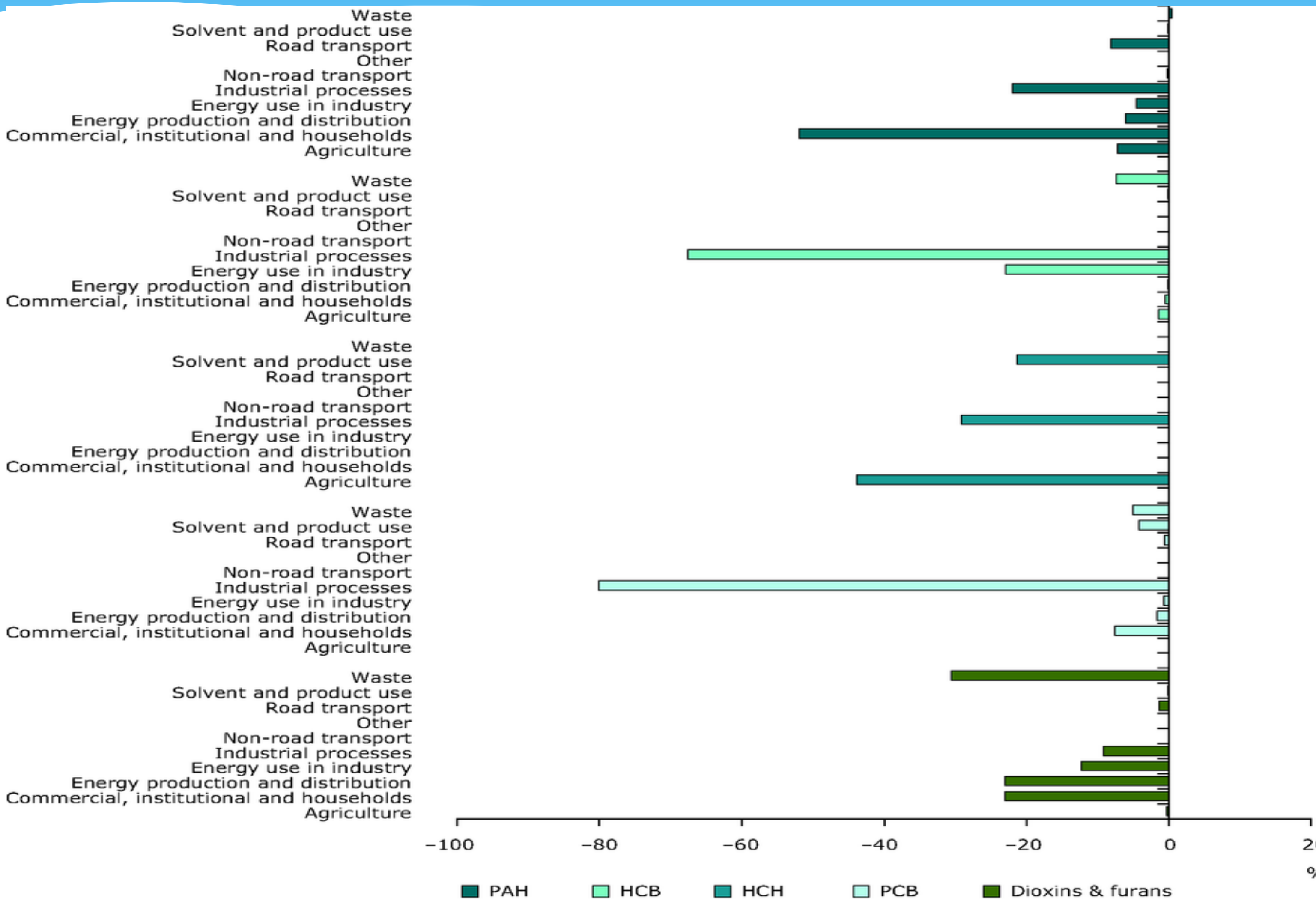
What may we need to know



Source Pathways



Source



Waste
Solvent and product use
Road transport
Other
Non-road transport
Industrial processes
Energy use in industry
Energy production and distribution
Commercial, institutional and households
Agriculture
Waste
Solvent and product use
Road transport
Other
Non-road transport
Industrial processes
Energy use in industry
Energy production and distribution
Commercial, institutional and households
Agriculture
Waste
Solvent and product use
Road transport
Other
Non-road transport
Industrial processes
Energy use in industry
Energy production and distribution
Commercial, institutional and households
Agriculture
Waste
Solvent and product use
Road transport
Other
Non-road transport
Industrial processes
Energy use in industry
Energy production and distribution
Commercial, institutional and households
Agriculture
Waste
Solvent and product use
Road transport
Other
Non-road transport
Industrial processes
Energy use in industry
Energy production and distribution
Commercial, institutional and households
Agriculture
−100
−80
−60
−40
−20
0
20
%
PAH
HCB
HCH
PCB
Dioxins & furans

Individual

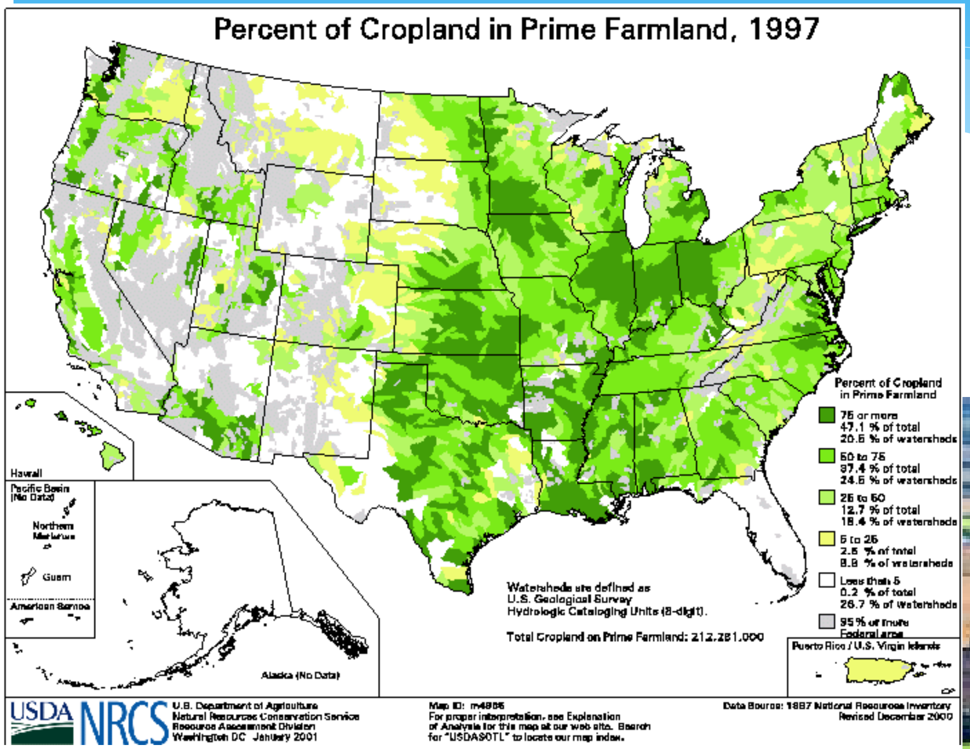
Point sources

Industrial

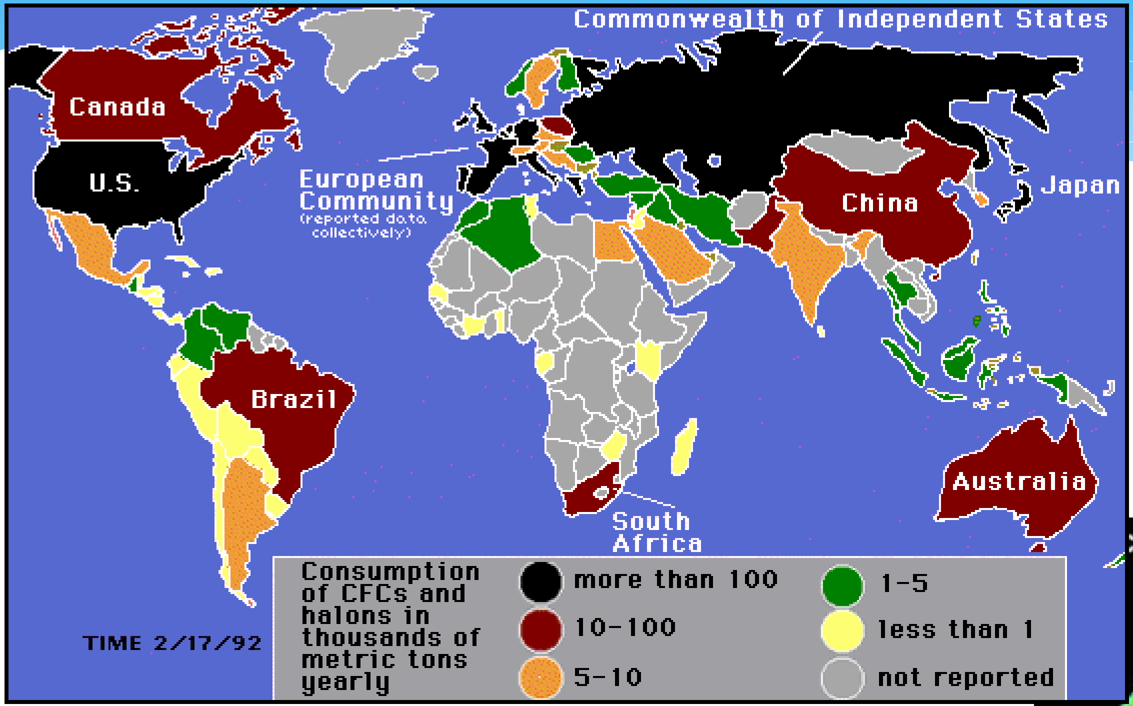
Diffuse Sources

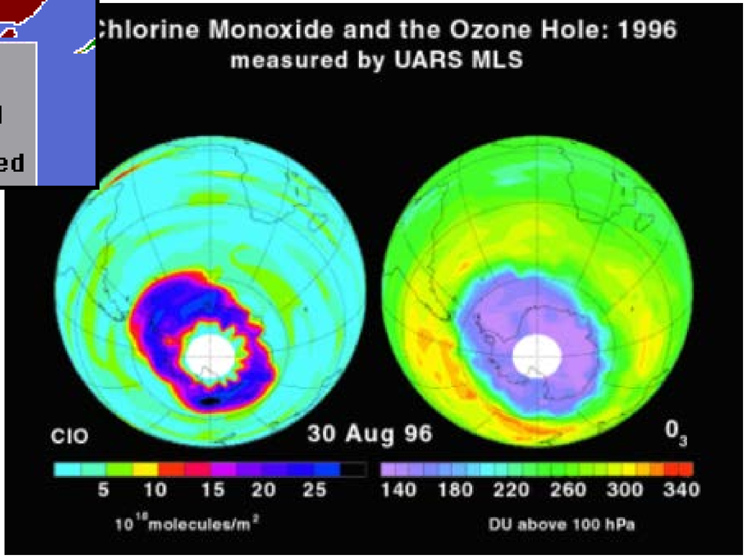
Mexico City

Regional Sources



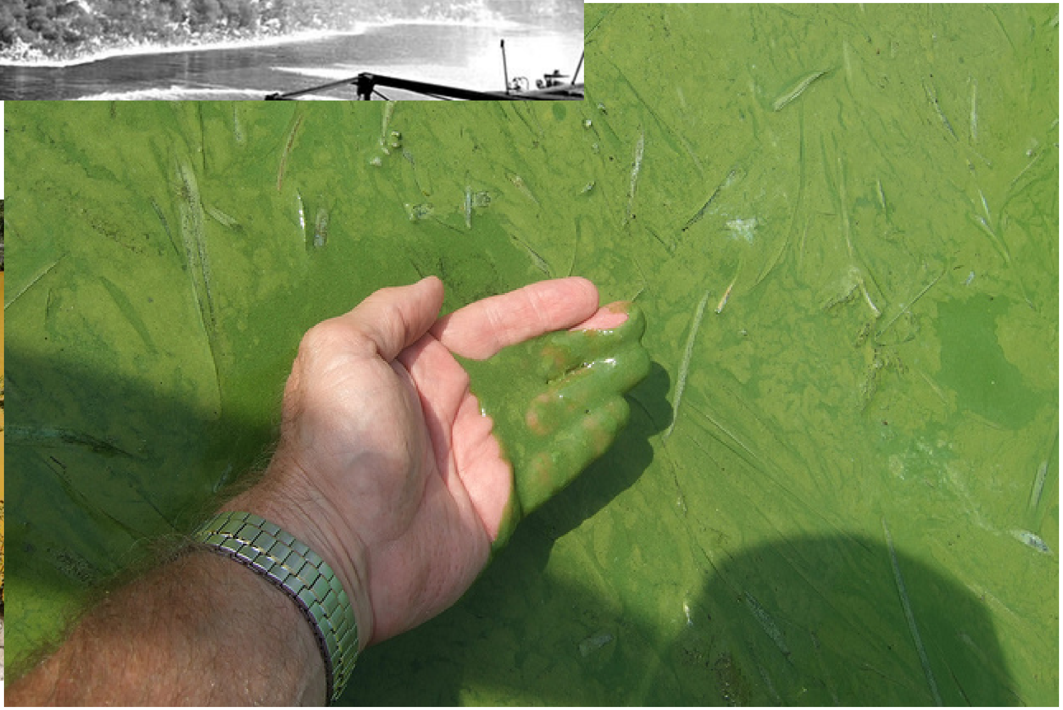
Global





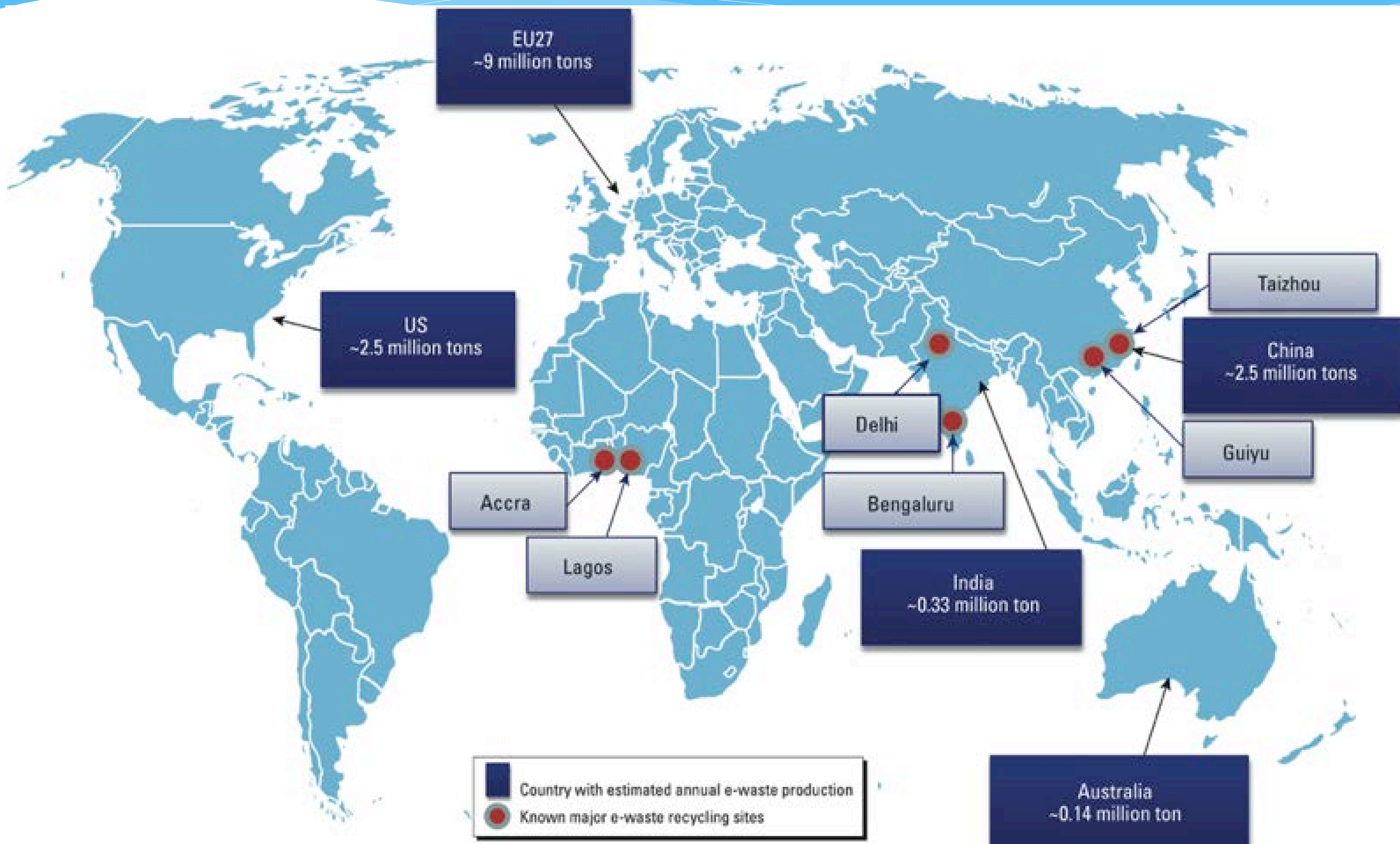
* E.g. CFC

Lakes and Rivers



Ewaste

E waste production



Environmental impacts

- Studies conducted in China discovered heavy contamination in e-waste recycling regions
  - Soil, air, water, and sediments all contained high levels of contamination
    - Trace metals (Lead, Zinc, Nickel, Copper, Mercury, and Cadmium)
    - Polychlorinated Biphenyls
    - Polycyclic Aromatic Hydrocarbons
    - Dioxins

Environmental prediction

* Physical and chemical properties
* Routes of transfer
  * To the environment
  * Through the environment
* Distribution

Predicting is Complex

$$\ln\left(\frac{P_1}{P_2}\right) = \left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

PV = nRT

$$R = \frac{PV}{nT}$$

8.3144598(48) J mol^{-1} K^{-1}

p[nΔx,(m + 1)Δt] = 1 /2 p(nΔx, mΔt) + 1/ 4 p[(n − 1)Δx, mΔt] + 1 /4 p[(n + 1)Δx, mΔt]

$$R = \frac{Work}{Amount\ x\ Temperature}$$

$$PV = NRT = mRspecificT$$

$$K_{aw} = {}^{H}/_{RT}$$

c = S/KV + (c_o – S/KV) e $^{-Kt}$

$$R = \frac{\frac{Force}{(length)^2} x\ (length)^2}{Amount\ x\ Temperature}$$

$$H = \left(\frac{Cg}{RT}\right)/Cw$$

Chemical Factors

- molecular mass
- vapour pressure (P_L)
- aqueous solubility (S_L)
- Henry's Law constant (H)
- Partitioning Co-efficient
  - octanol/water (Log K_{OW})
  - octanol/air (Log K_{OA})
  - air/water (Log K_{AW})
  - humic acid/water (Log $K_{HA/W}$)
  - particle-gas (K_p)

Wania and Dugani., 2003; Wania and Makay, 1995; Macdonald et al., 2005

Units of Concentration

Mass per volume

Air –m^3

Water –L^{-1}

Soil –g^{-1}

Other Terms

PPM, PPT, PPB

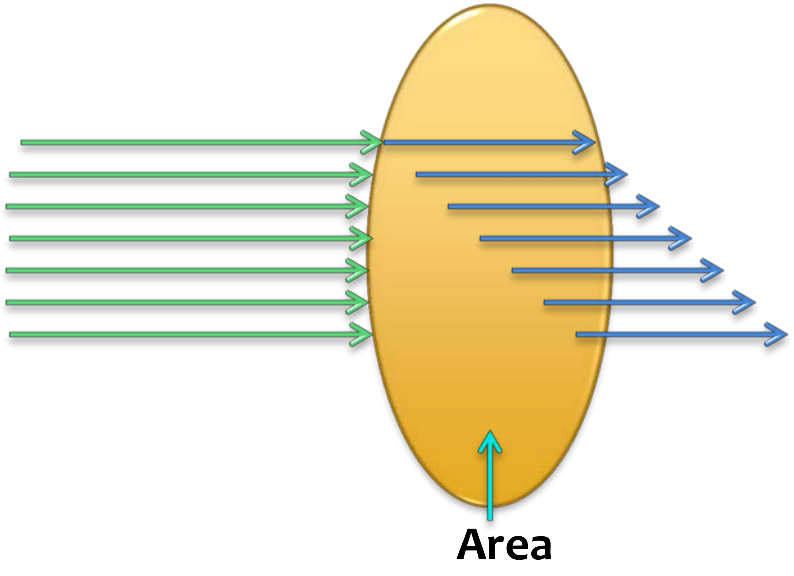
Mole (6.02 x 10^{23} atoms)

Wet weight/Dry weight

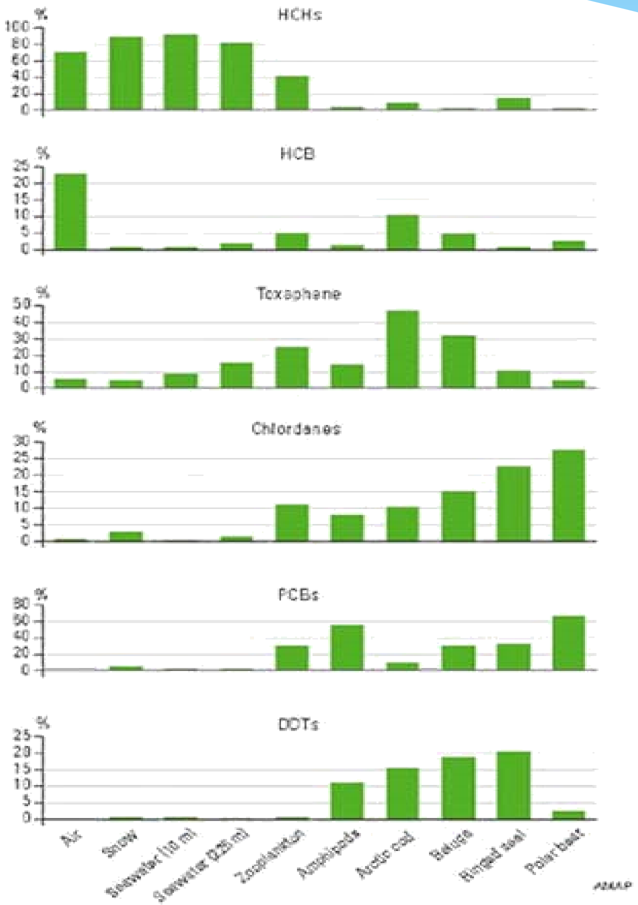
Normalized

Terms

* Concentration –unit per volume
* Flux Quantity that passes though in a fixed period

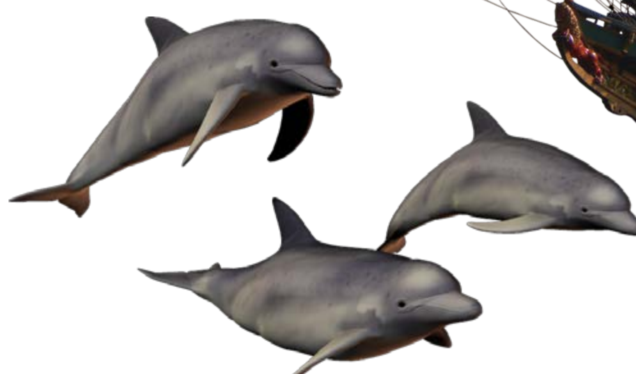


What is the Matrix



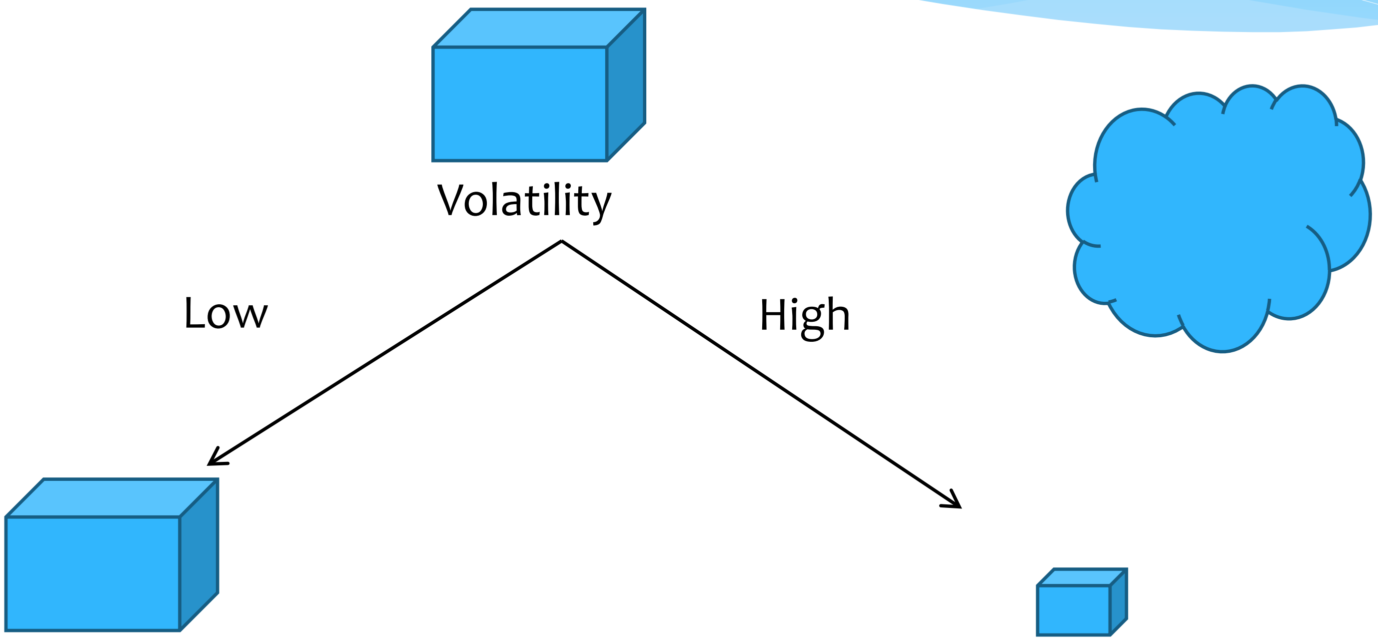
Transport Routes

- Atmospheric Transport
- Water Transport
- Biovectors



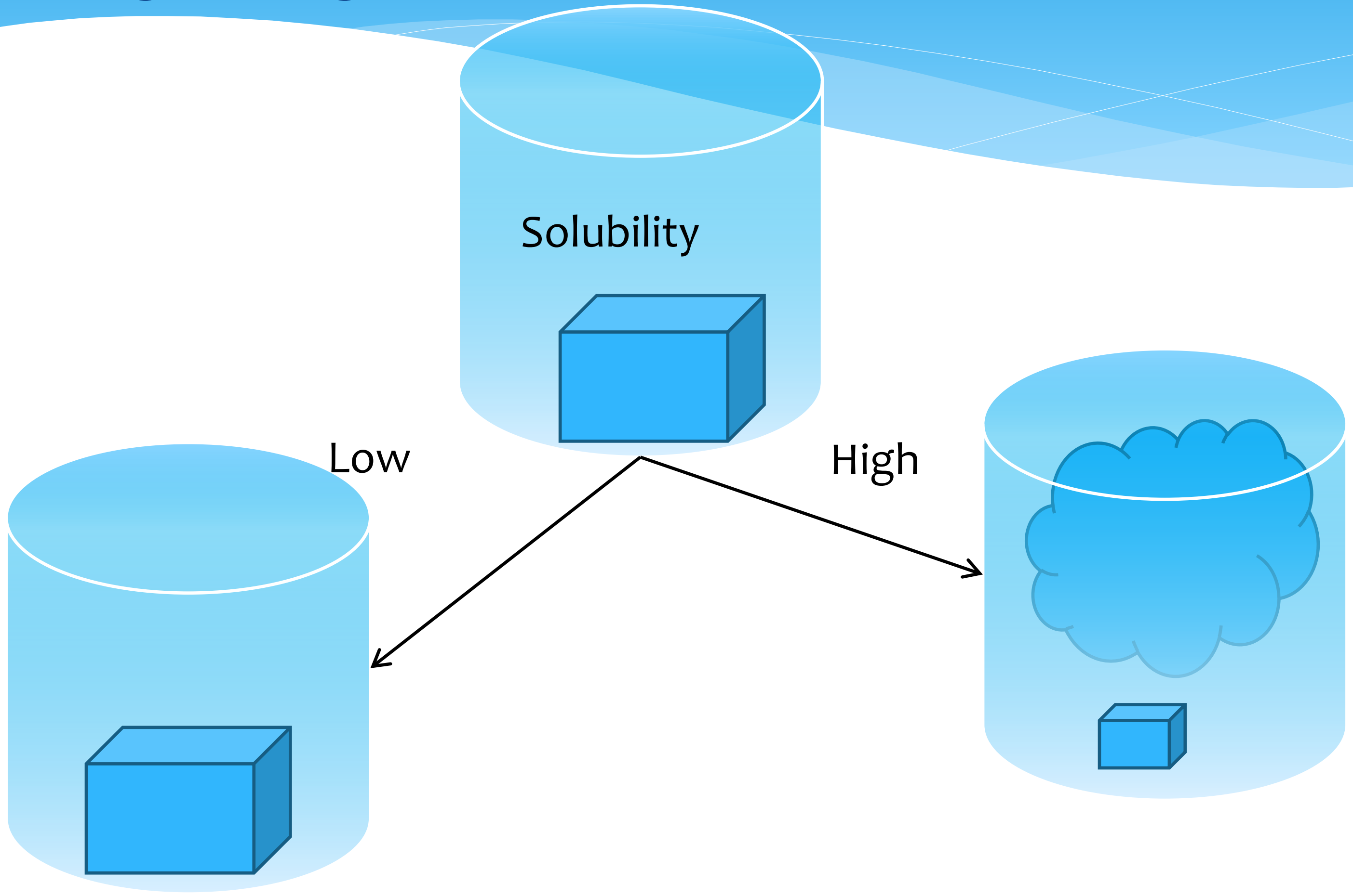
Mass Balance

- What goes in goes where

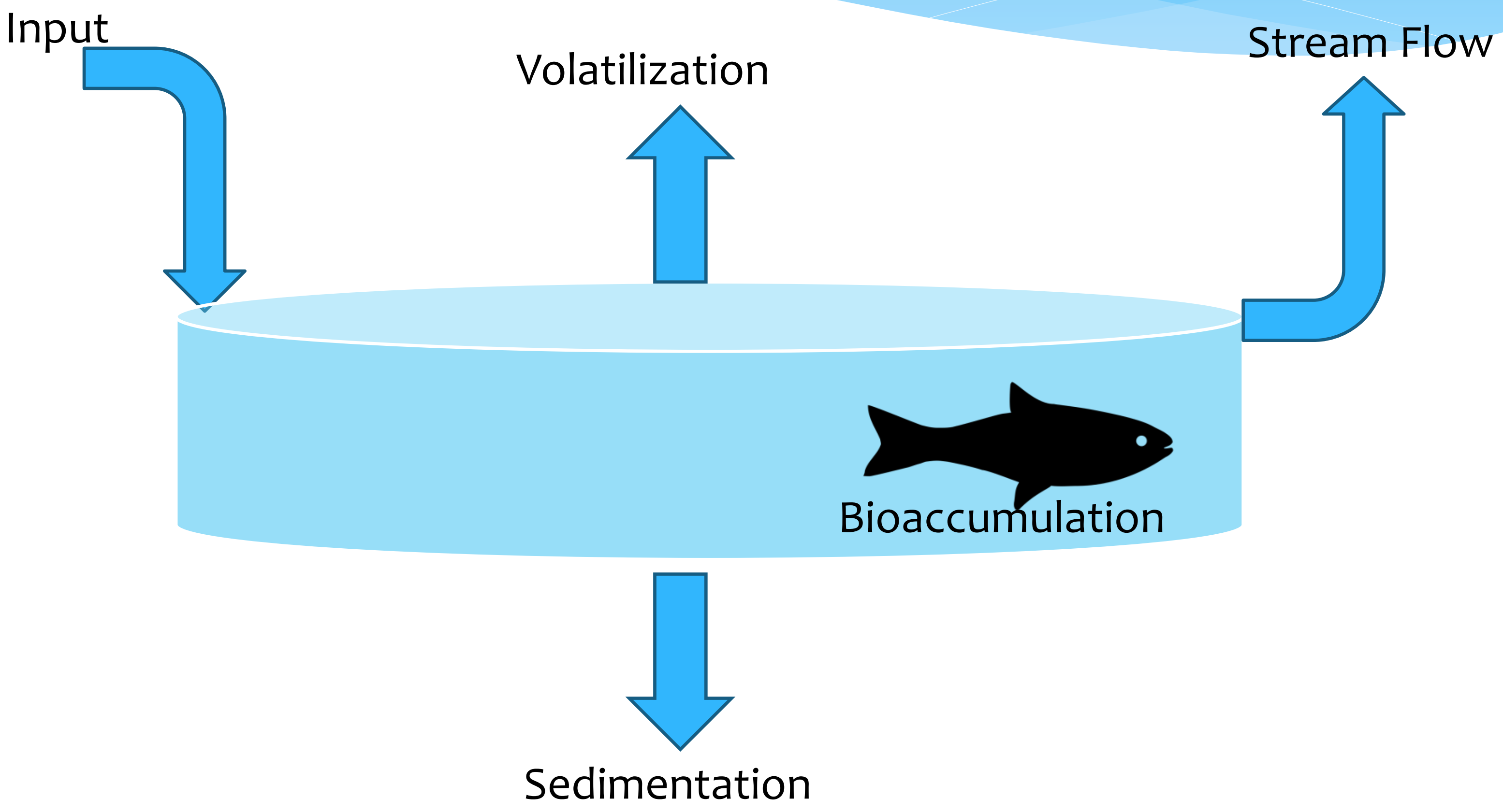


Mass Balance

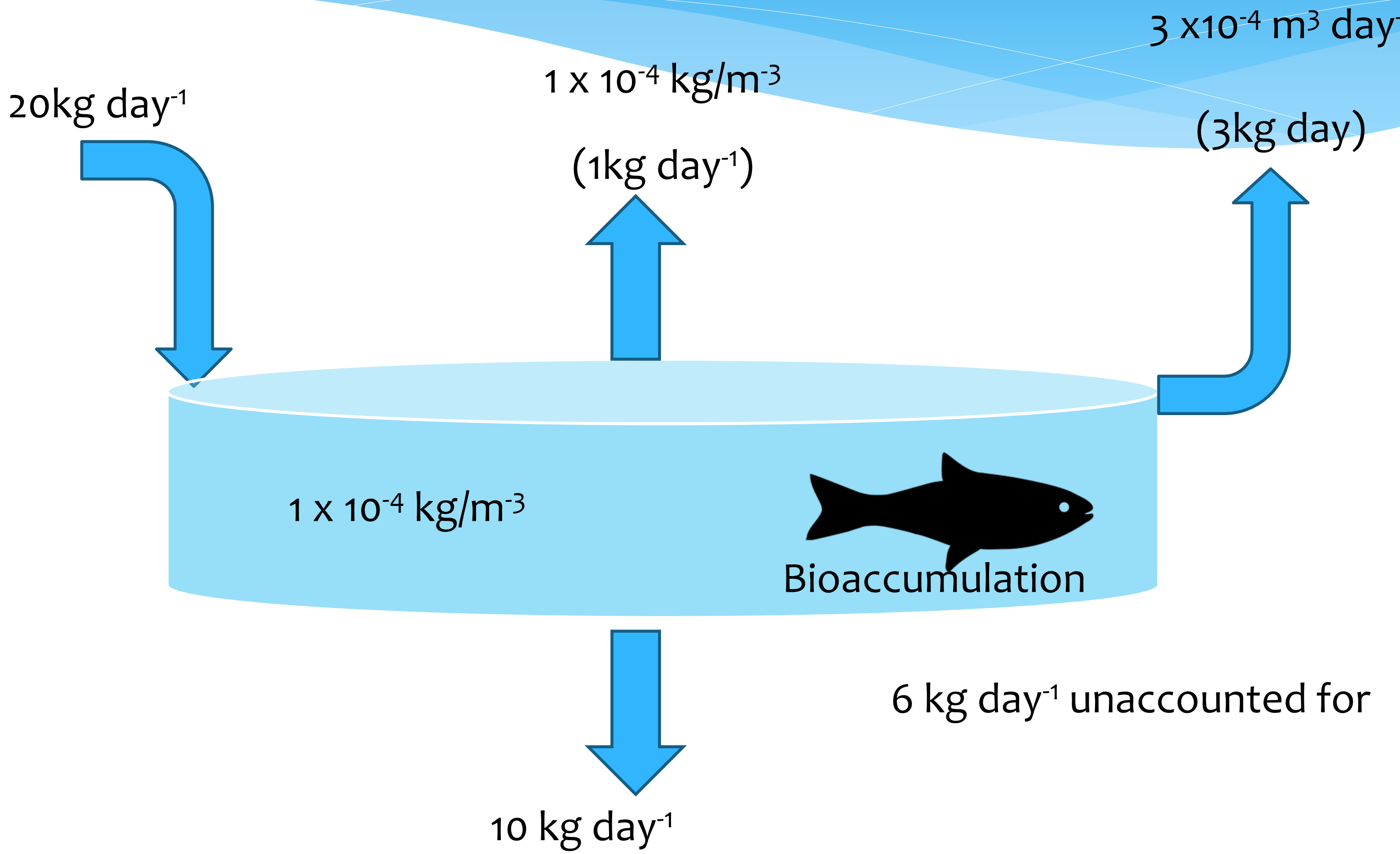
* What goes in goes where



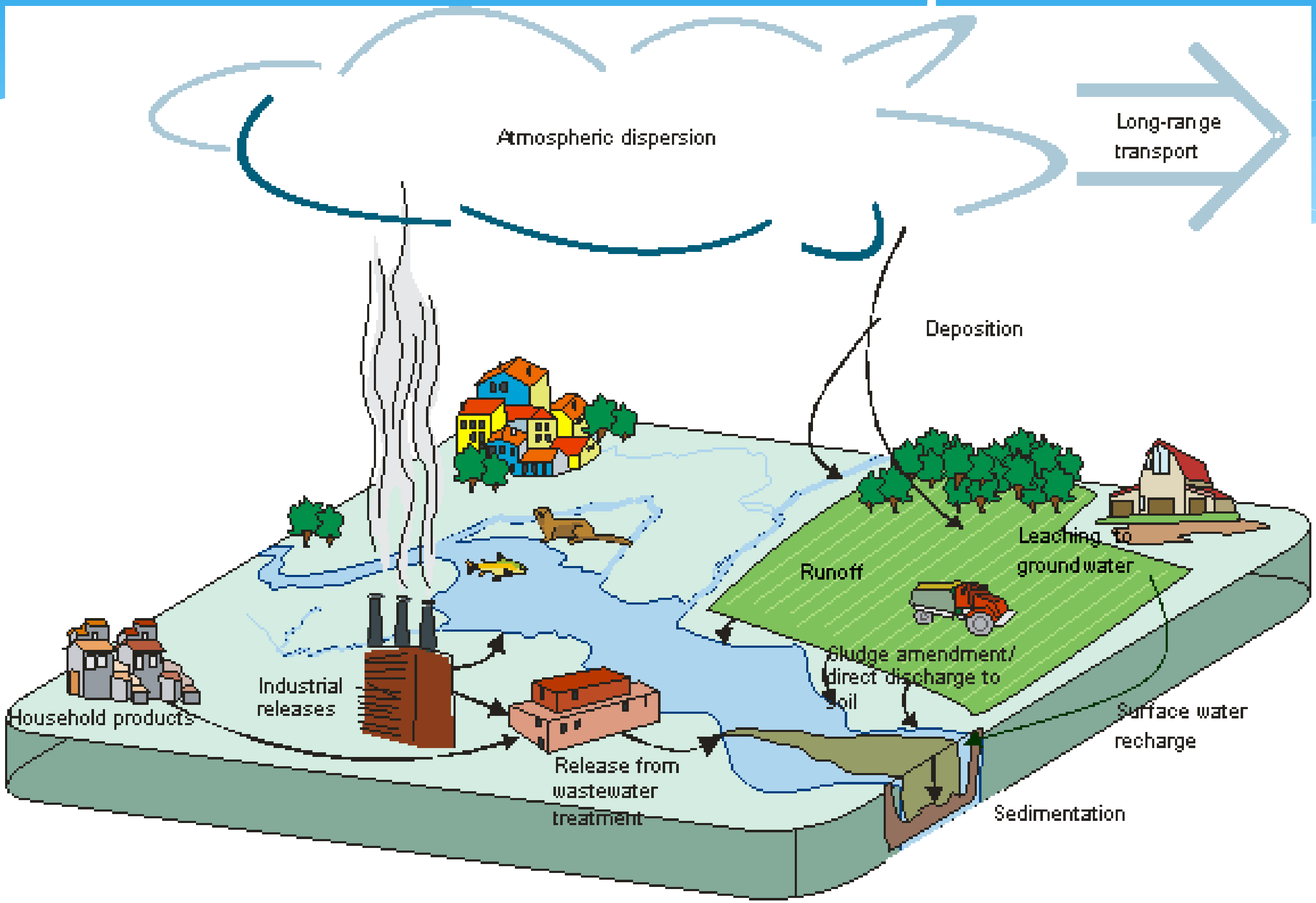
So for an Lake system



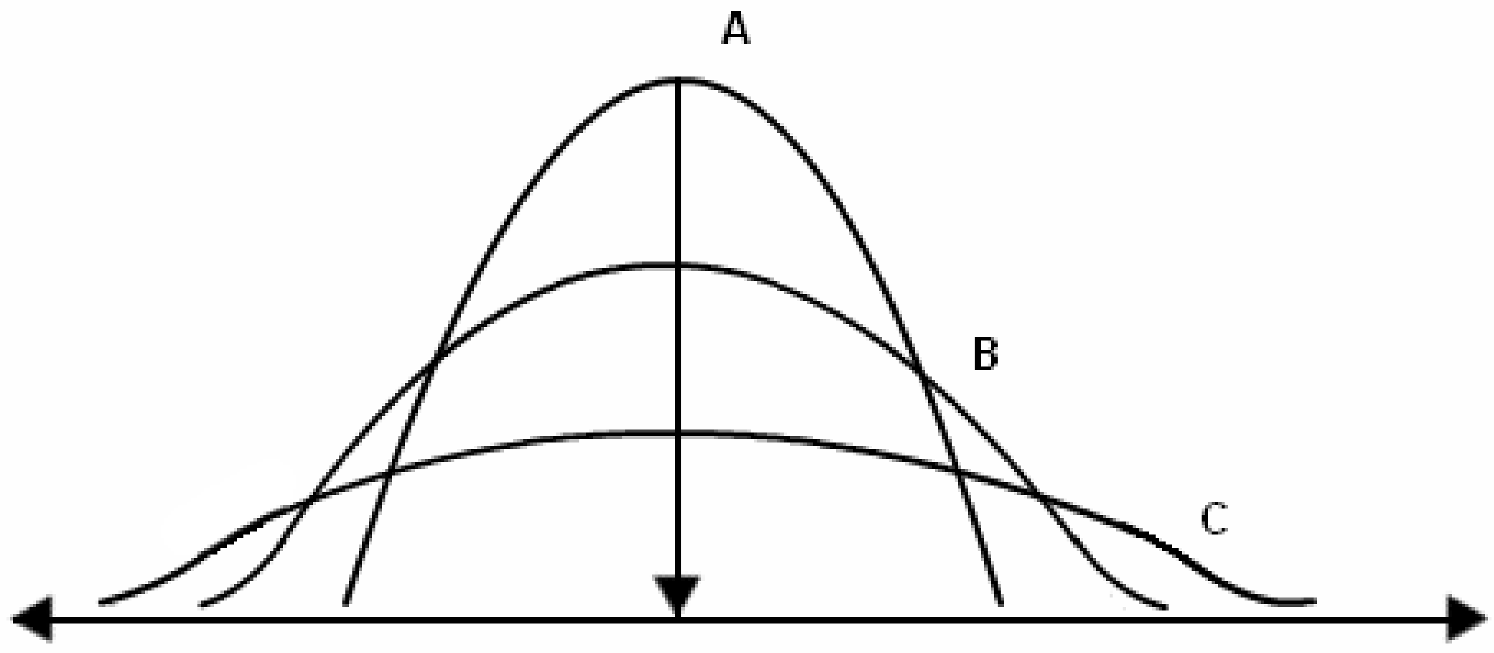
So for an Lake system



It's a bit more complicated

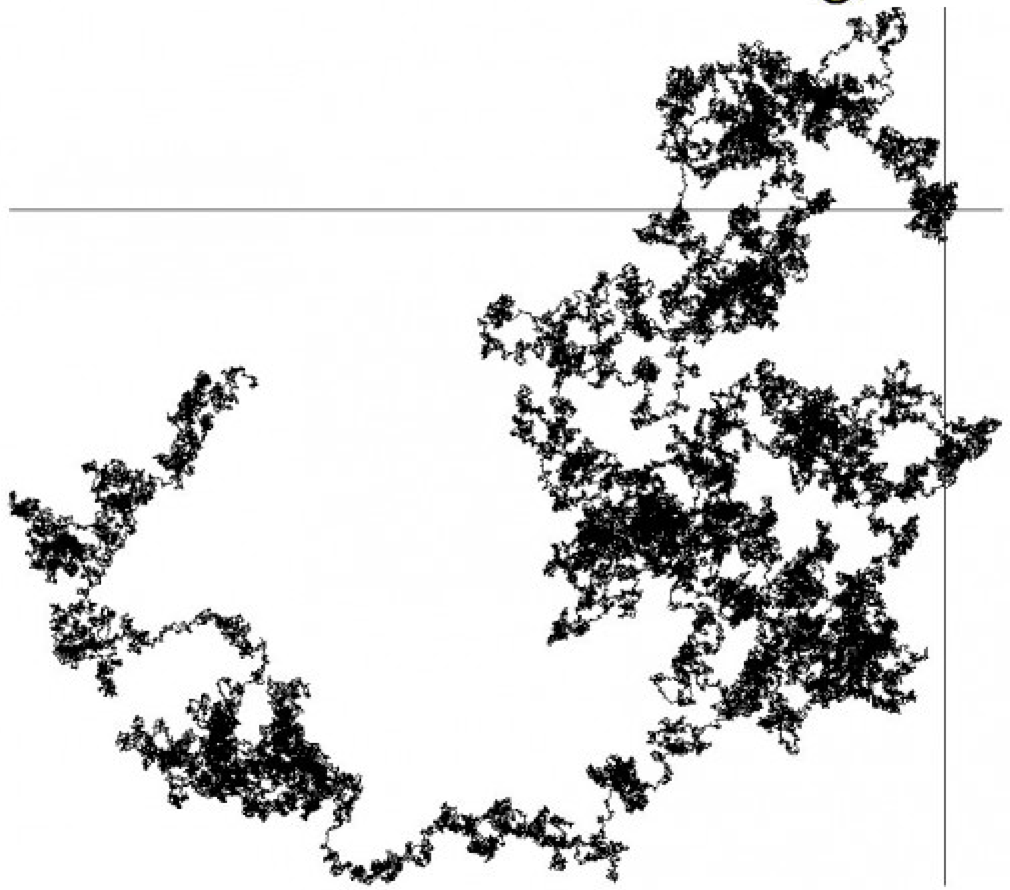


Dispersion



The Drunkards Walk

* There is randomness to movement
* For every step there is a series of choices



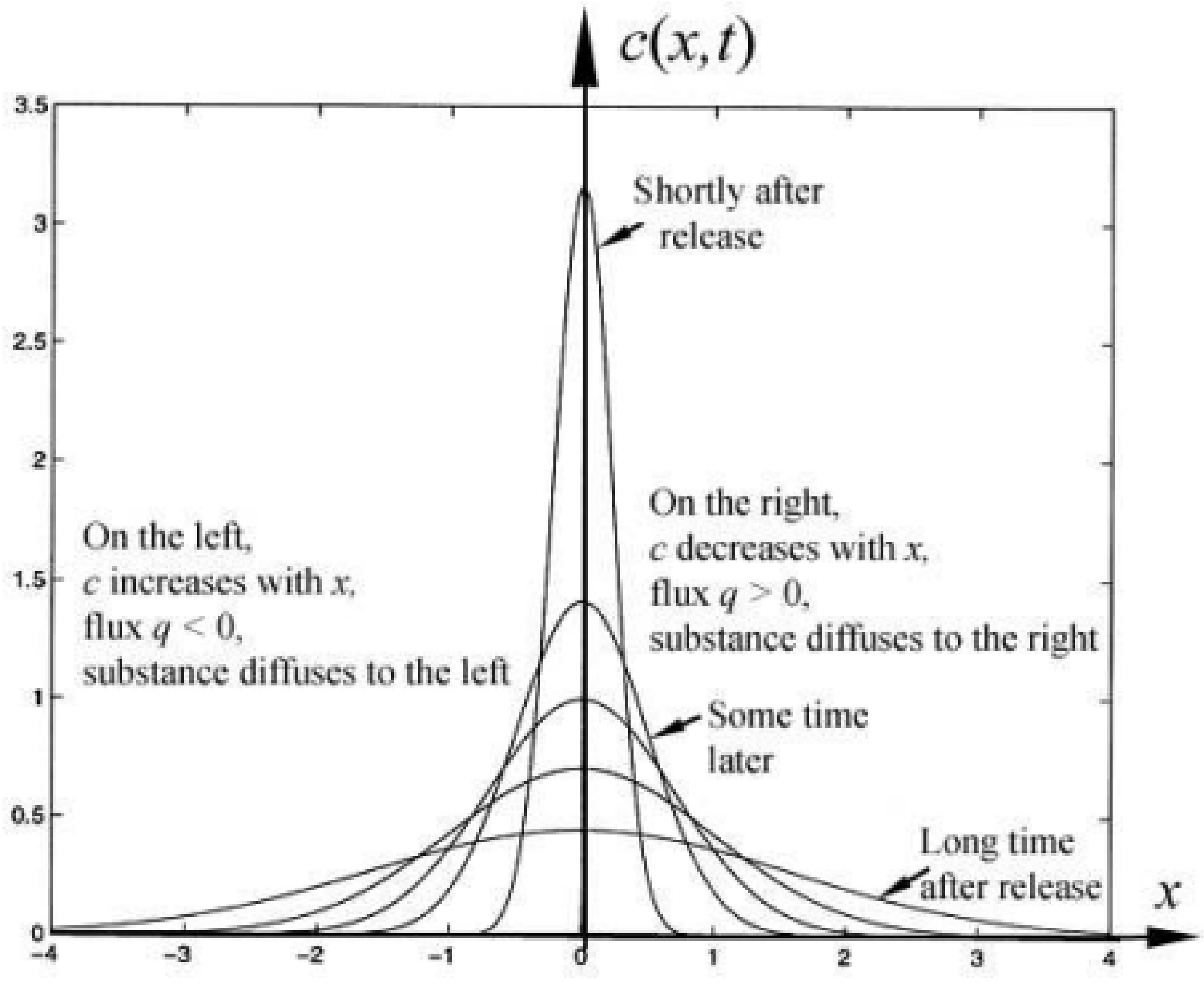
Random Walk Model

$$p(n\Delta x, m\Delta t)$$

- m are intervals
- t is time
- n probability it stays there and remains

Einstein, A., Investigations on the Theory of Brownian Movement, Dover Publications, 1956, 122 pages

Diffusion



c(x,t)
Shortly after release
On the left, c increases with x, flux q < 0, substance diffuses to the left
On the right, c decreases with x, flux q > 0, substance diffuses to the right
Some time later
Long time after release
x
3.5
3
2.5
2
1.5
1
0.5
0
−4
−3
−2
−1
0
1
2
3
4

Simple Example

25% 25%

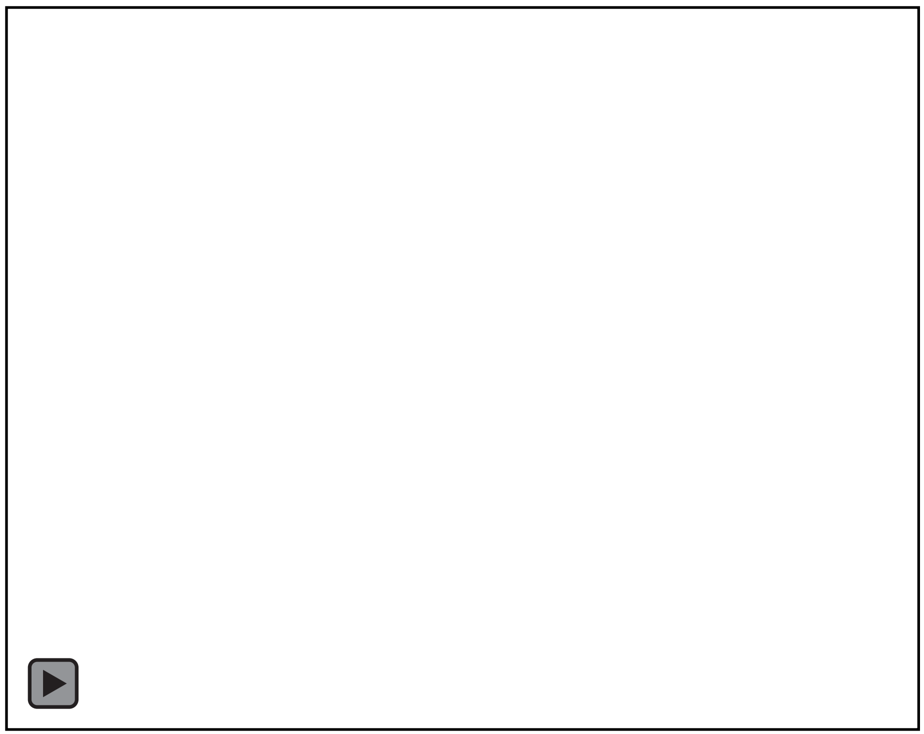
50%

$$p[n\Delta x,(m+1)\Delta t] = 1/2\, p(n\Delta x, m\Delta t) + 1/4\, p[(n-1)\Delta x, m\Delta t] + 1/4\, p[(n+1)\Delta x, m\Delta t]$$

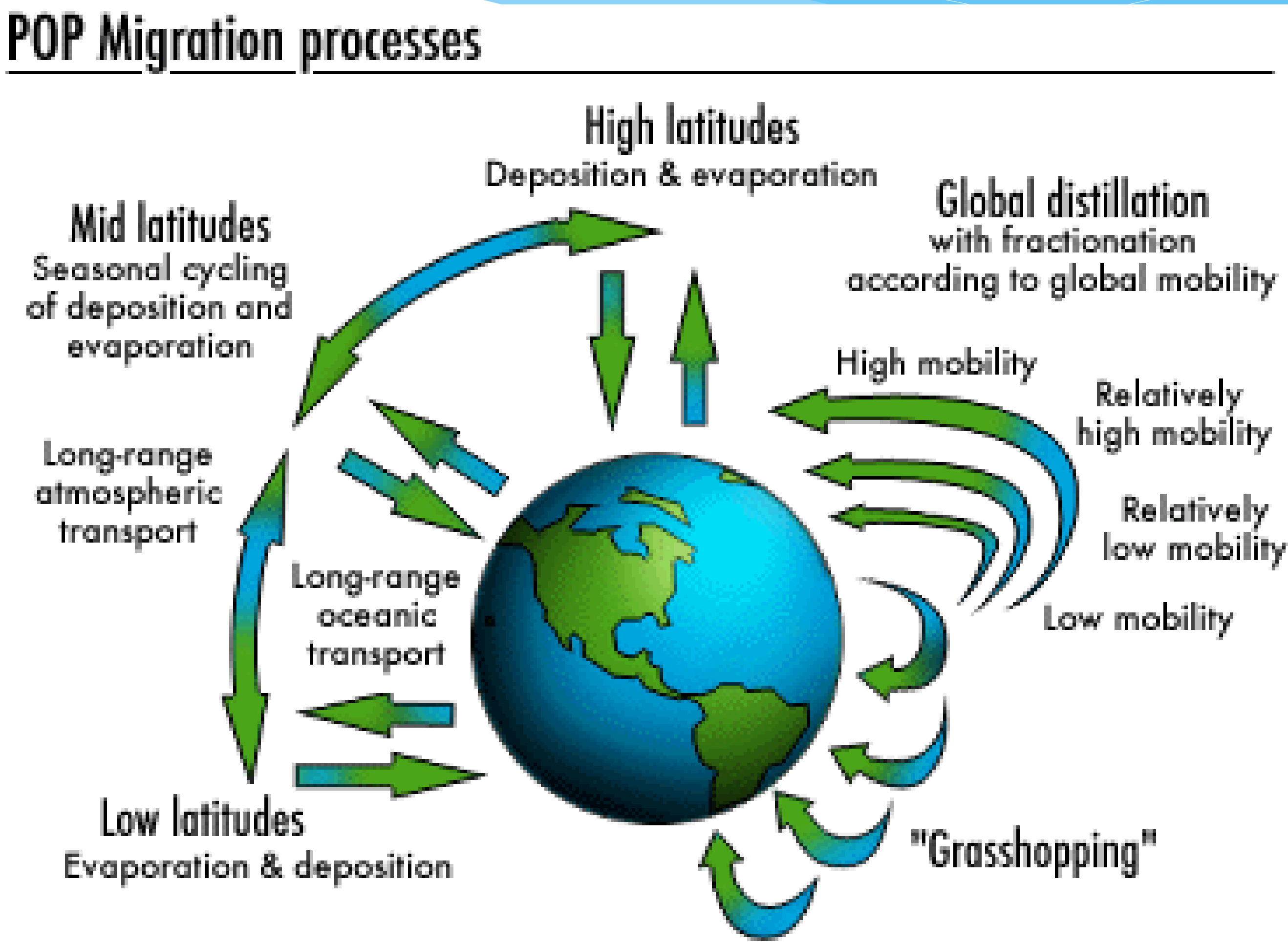
Box of Kittens

n =	−5	−4	−3	−2	−1	0	+1	+2	+3	+4	+5
m=0						1.000					
m=1					0.250	0.500	0.250				
m=2				0.063	0.250	0.375	0.250	0.063			
m=3			0.016	0.094	0.234	0.313	0.234	0.094	0.016		
m=4		0.004	0.031	0.109	0.219	0.273	0.219	0.109	0.031	0.004	
m=5	0.0010	0.010	0.044	0.117	0.205	0.246	0.205	0.117	0.044	0.010	0.0010
m=6	0.0029	0.016	0.054	0.121	0.193	0.226	0.193	0.121	0.054	0.016	0.0029

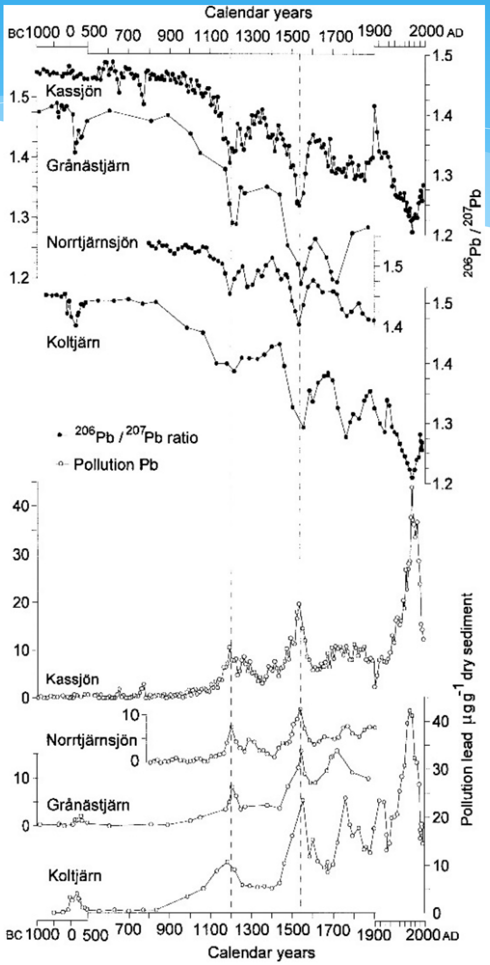
Environmental Air Transport



Atmospheric Transport



Air Contamination is not new



Published in: Maja-Lena Brännvall; Richard Bindler; Ingemar Renberg; Published in: Ove Emteryd; Published in: Jerzy Bartnicki; Published in: Kjell Billström; *Environ. Sci. Technol.* **1999,** 33, 4391-4395.
DOI: 10.1021/es990279n

National Air Quality Standards

Pollutant	Exposure duration	Standard	Cause for concern
CO Carbon Monoxide	1 hour 8 hours	35 ppm 9 ppm	Headaches, asphyxiation Decreased exercise tolerance angina pectoris
NO_2 Nitrogen Dioxide	1 year	0,53 ppm	Aggravation of respiratory disease
SO_2 Sulphur Dioxide	3 hours 1 day 1 year	0,50 ppm 0,14 ppm 0,03 ppm	Shortness of breath wheezing odor acid precipitation damage to vegetables
O_3 Ozone	1 hour 8 hours	0,12 ppm 0.08 ppm	Eye irritation interference with breathing damage to materials and plants
Pb Lead	3 months	1.5 ug/m^3	Blood poisoning infant development
PM2.5	24 hours 1 year	60 ug/m^3 15 ug/m^3	Lung disease
PM10	24 hours 1 year	150 ug/m^3 50 ug/m^3	Visibility respiratory disease

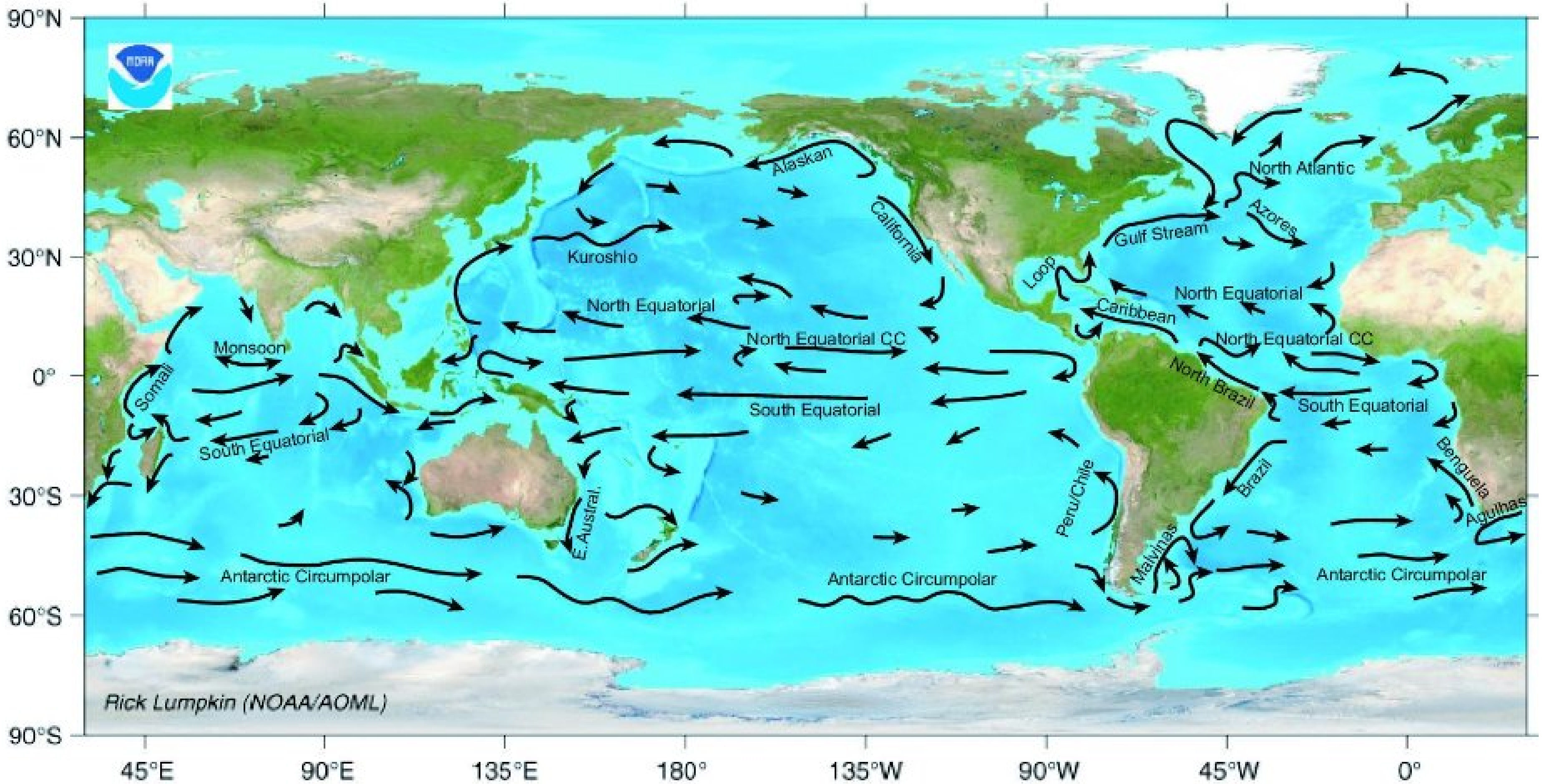
The six chemicals designated as criteria pollutants by the US Environmental Protection Agency and the corresponding National Ambient Air Quality Standards.

Water Transport

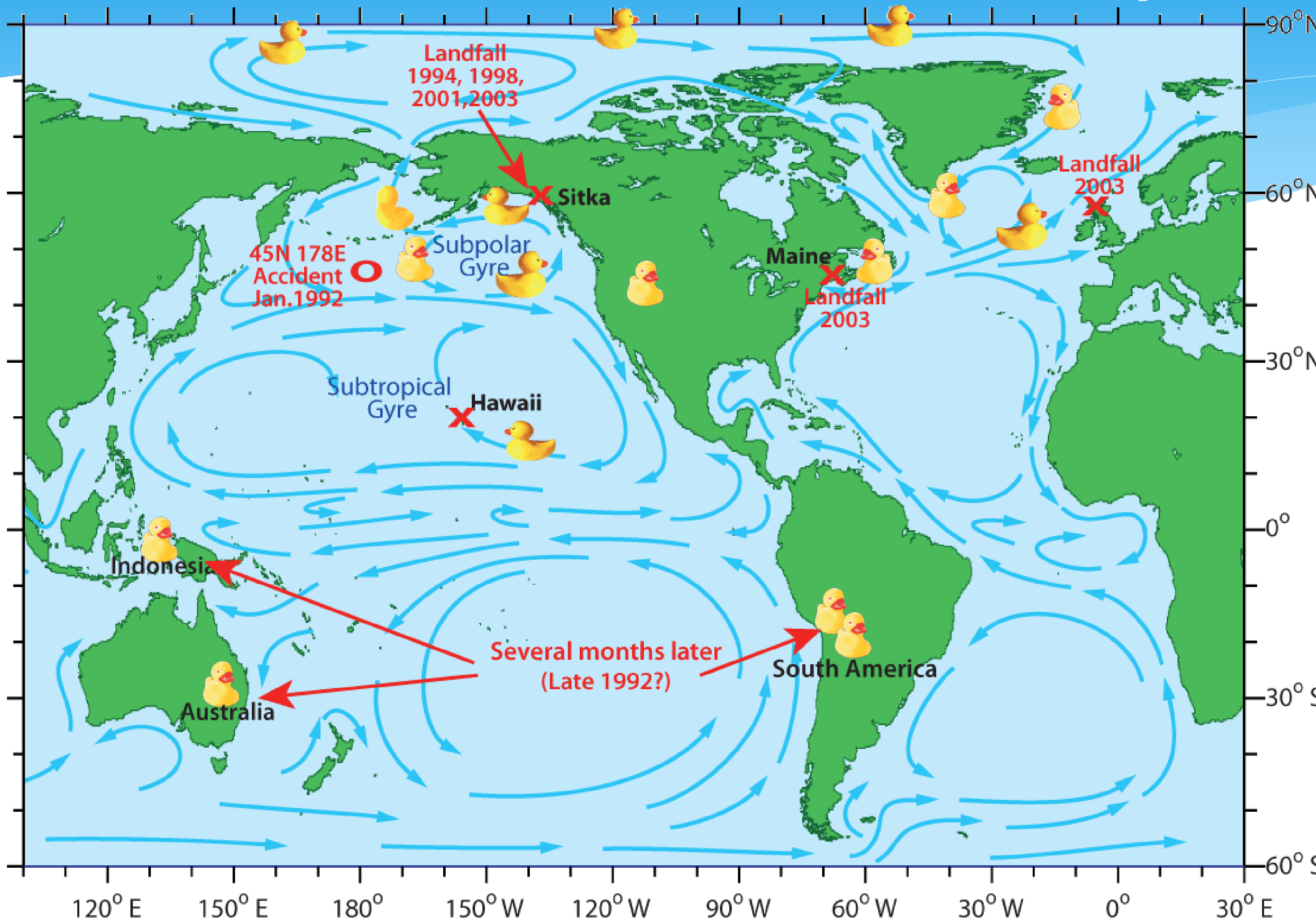
Water

- Liquid water
- Salinity
- pH
- Conductivity
- Temperature
- Snow
- Ice

Surface Circulation

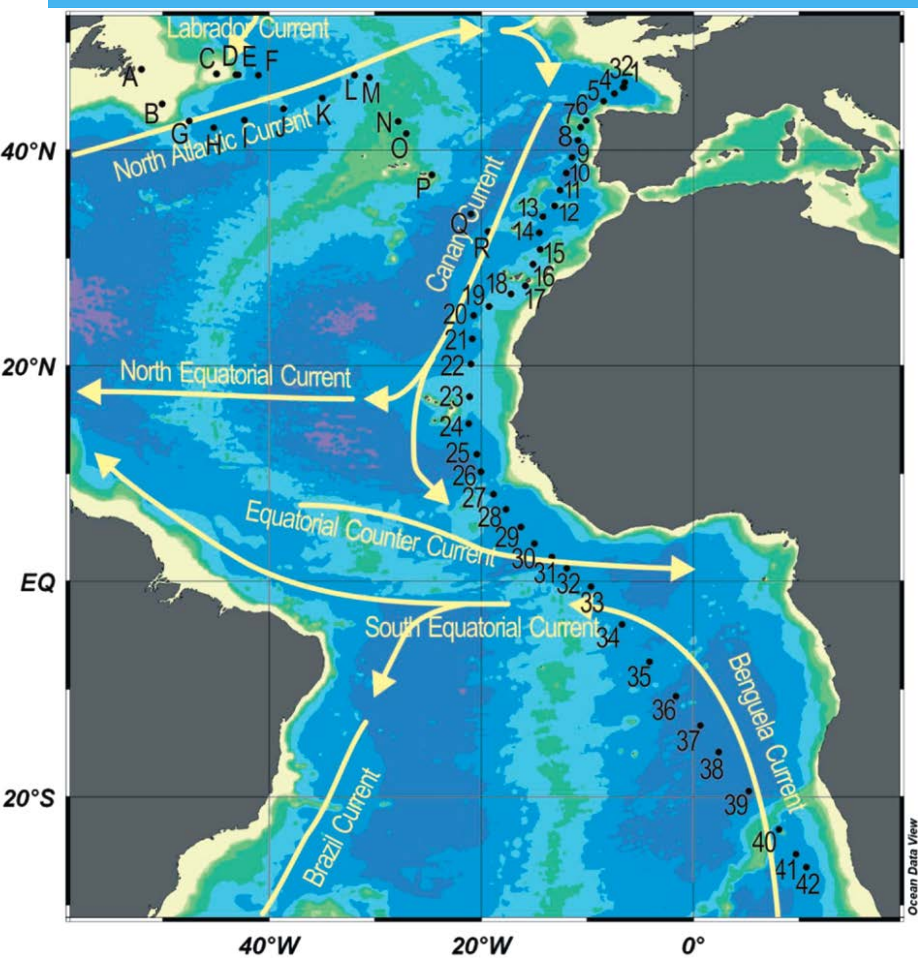


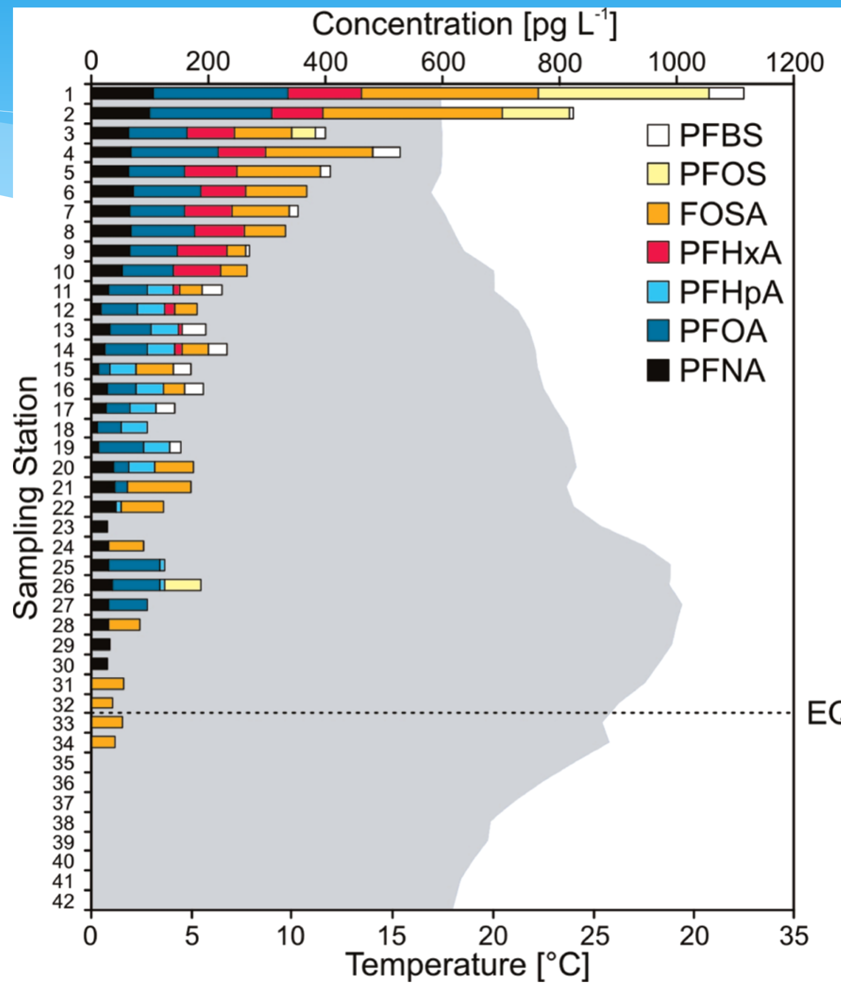
The Great Rubber Duck Escape



Macro Contaminants

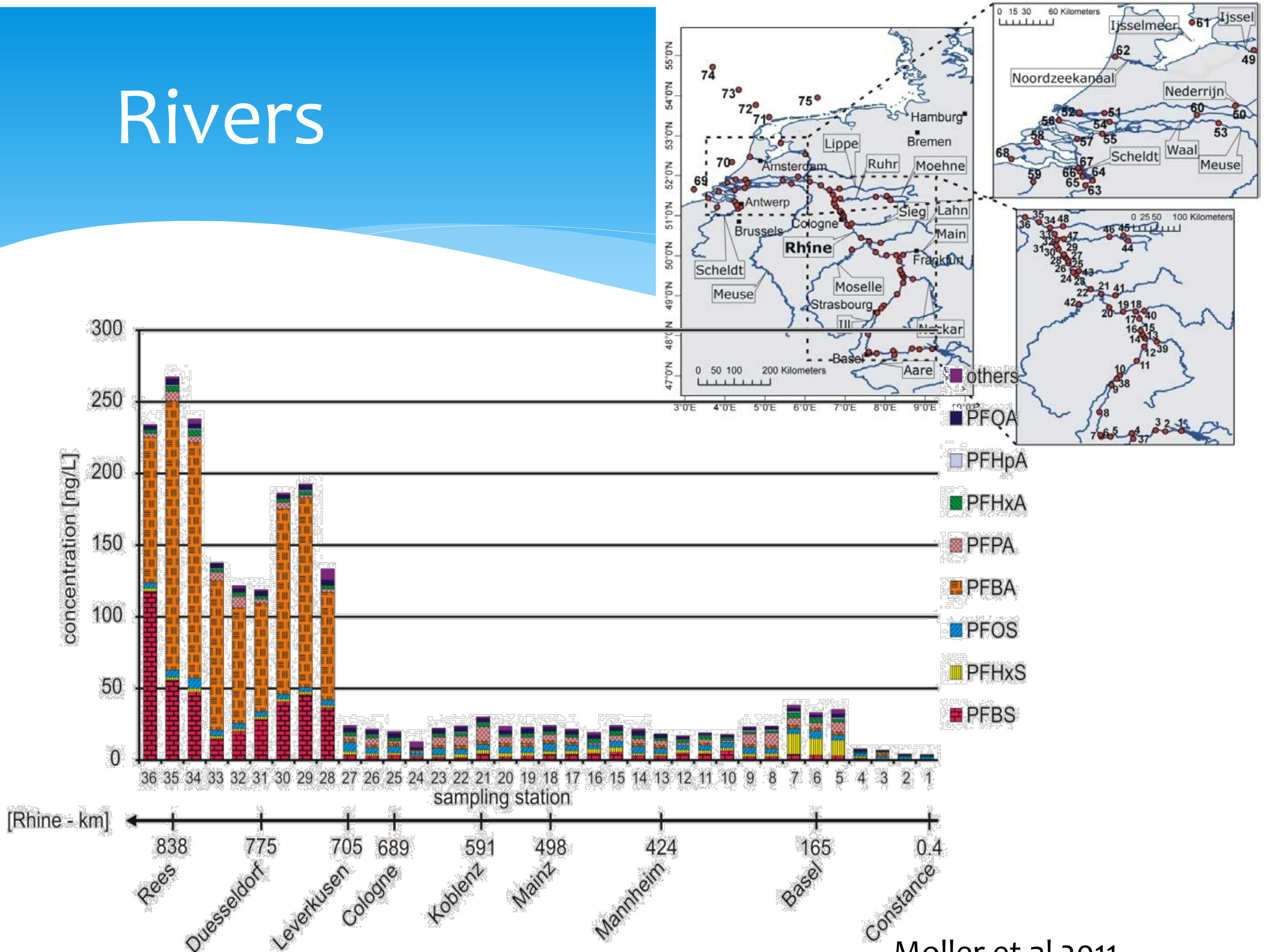
Ocean Water PFCs





Ahrens Et al

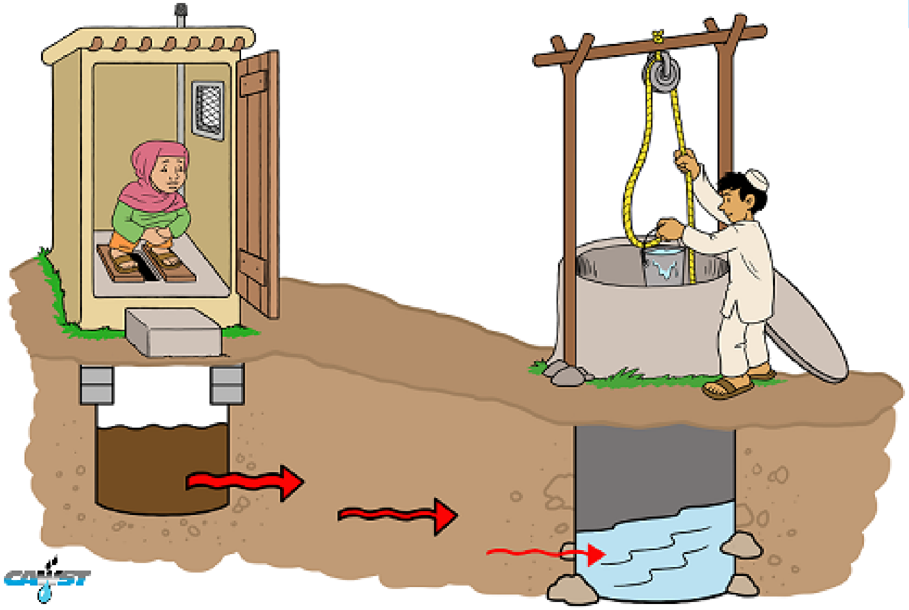
Rivers



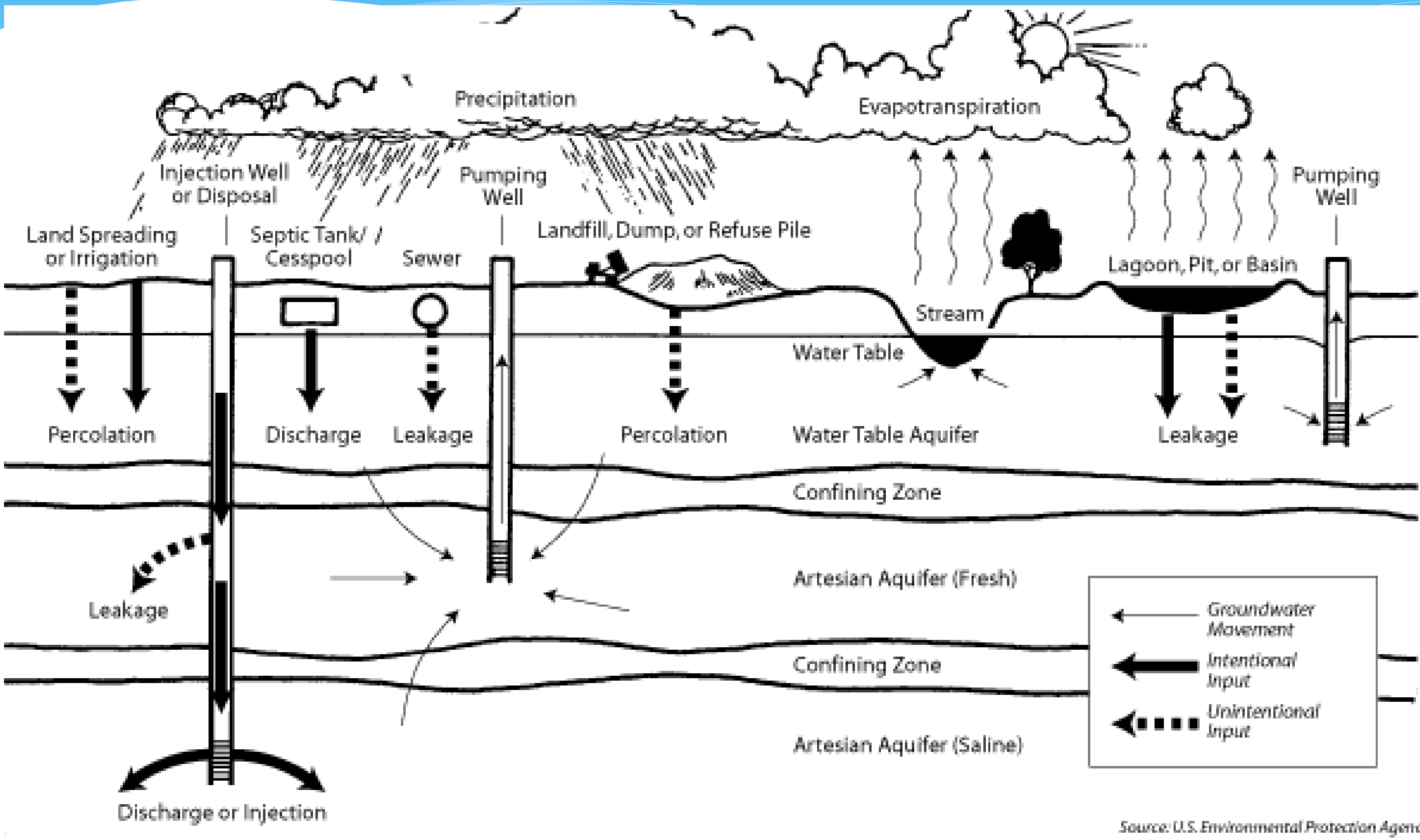
Moller et al 2011

Groundwater

* Metals –natural
* Agriculture
* Commerce
* Industry
* Residence
* Waste Management

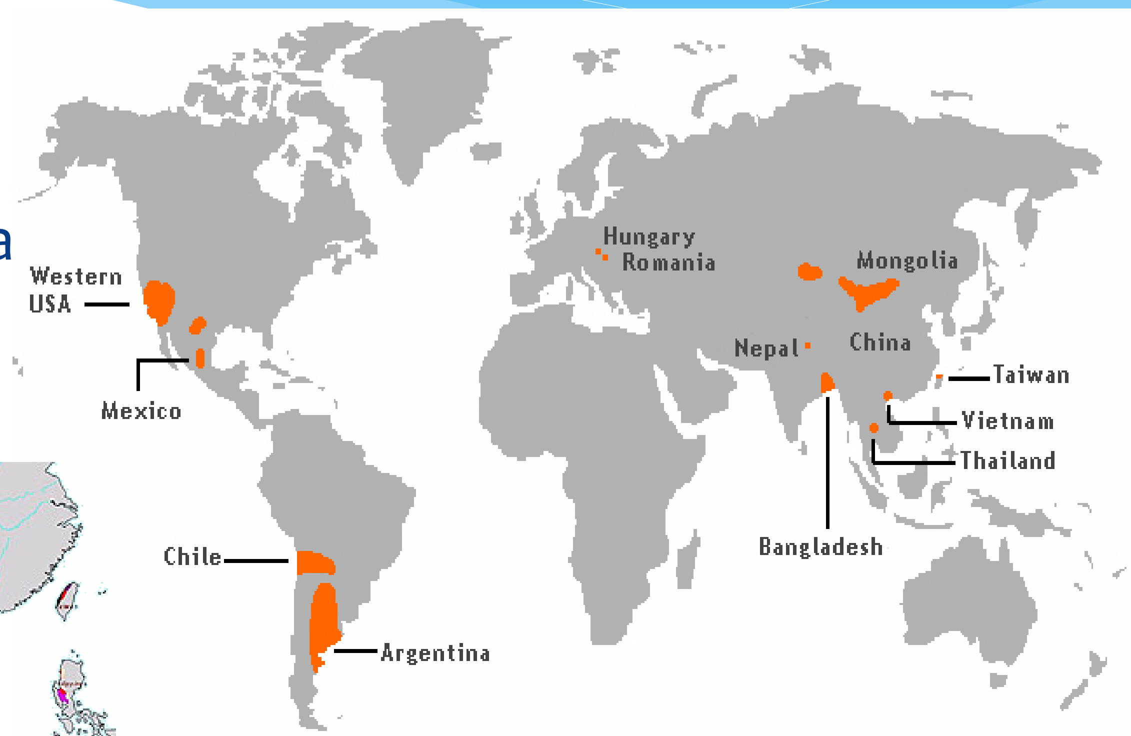


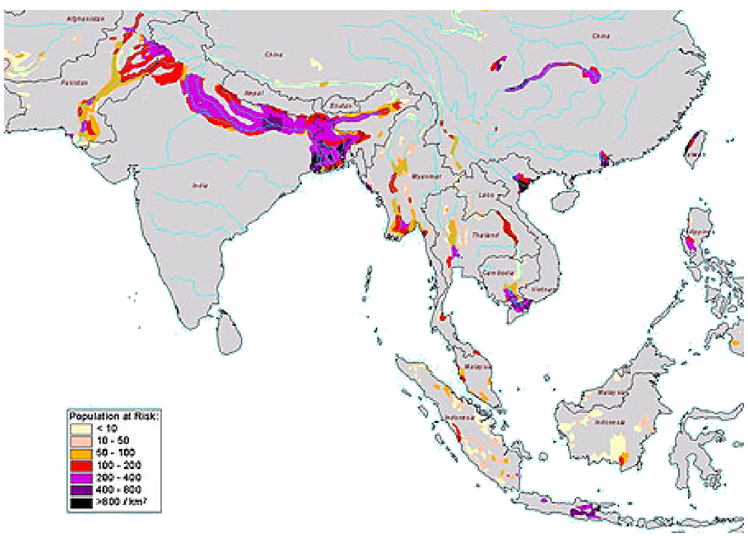
Contamination of Groundwater



Arsenic groundwater

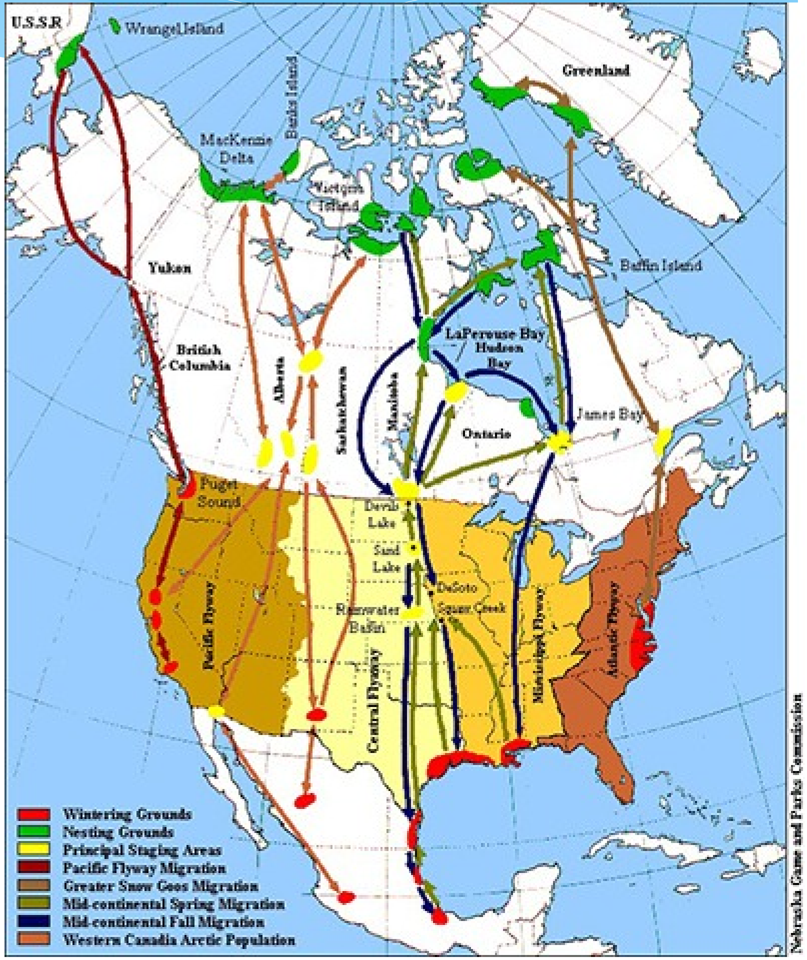
* 100 million people a
  risk





Biovectors

- Any organism that travels can transport chemicals
  - Salmon
  - Reindeer
  - Whales



Amplification

Evenset et al., 2007, Choy et al., 2010 Blais et al., 2005; 2007

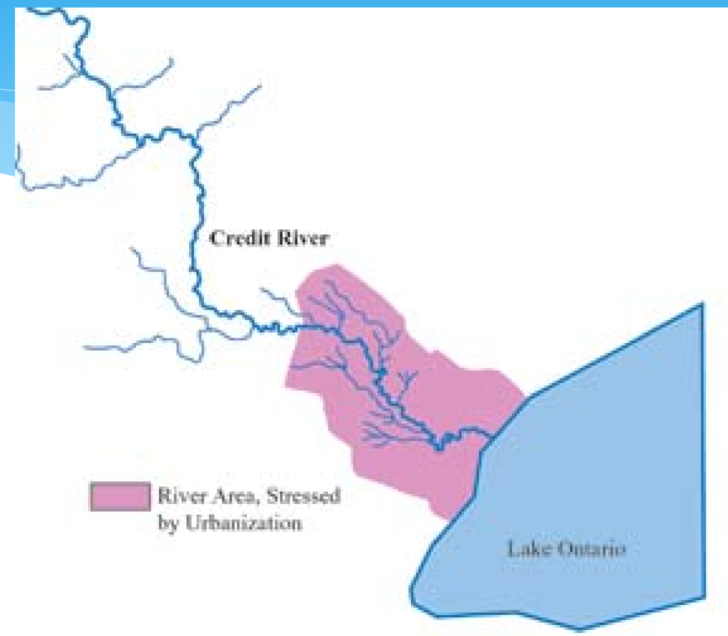
New Burdens

* LRT can transport many chemicals
* But biovectors can go against the flow.

(Blais et al., 2007; *Christensen et al.*, 2005).

Credit River

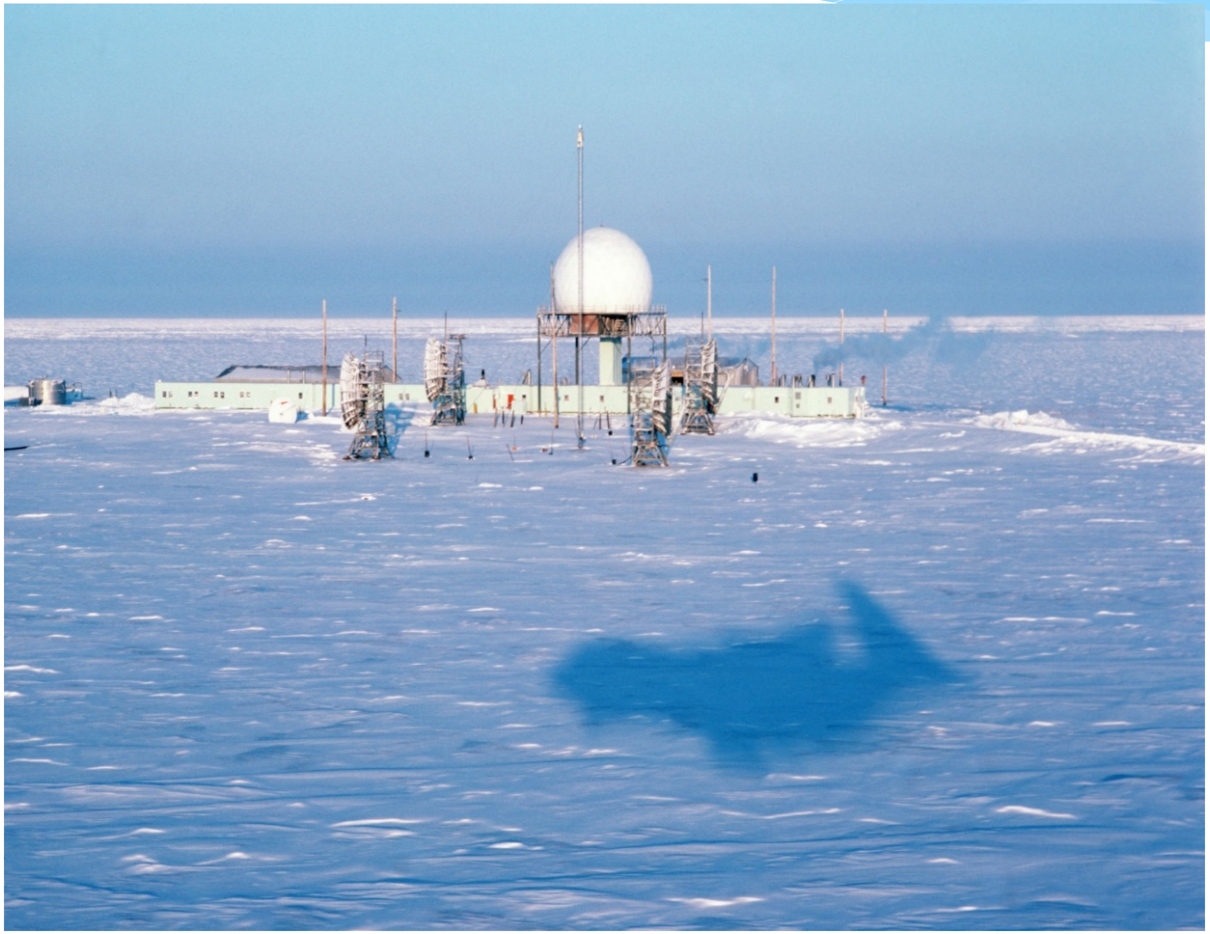
- Annually 20'000 Chinook salmon (*Oncorhynchus tshawytscha*) spawn and die in the Credit River,
- Passive water monitoring devices (SPMDs, (semi-permeable membranes devices)
- ~75g of ∑PCBs and 25g of DDT to the river over a few weeks



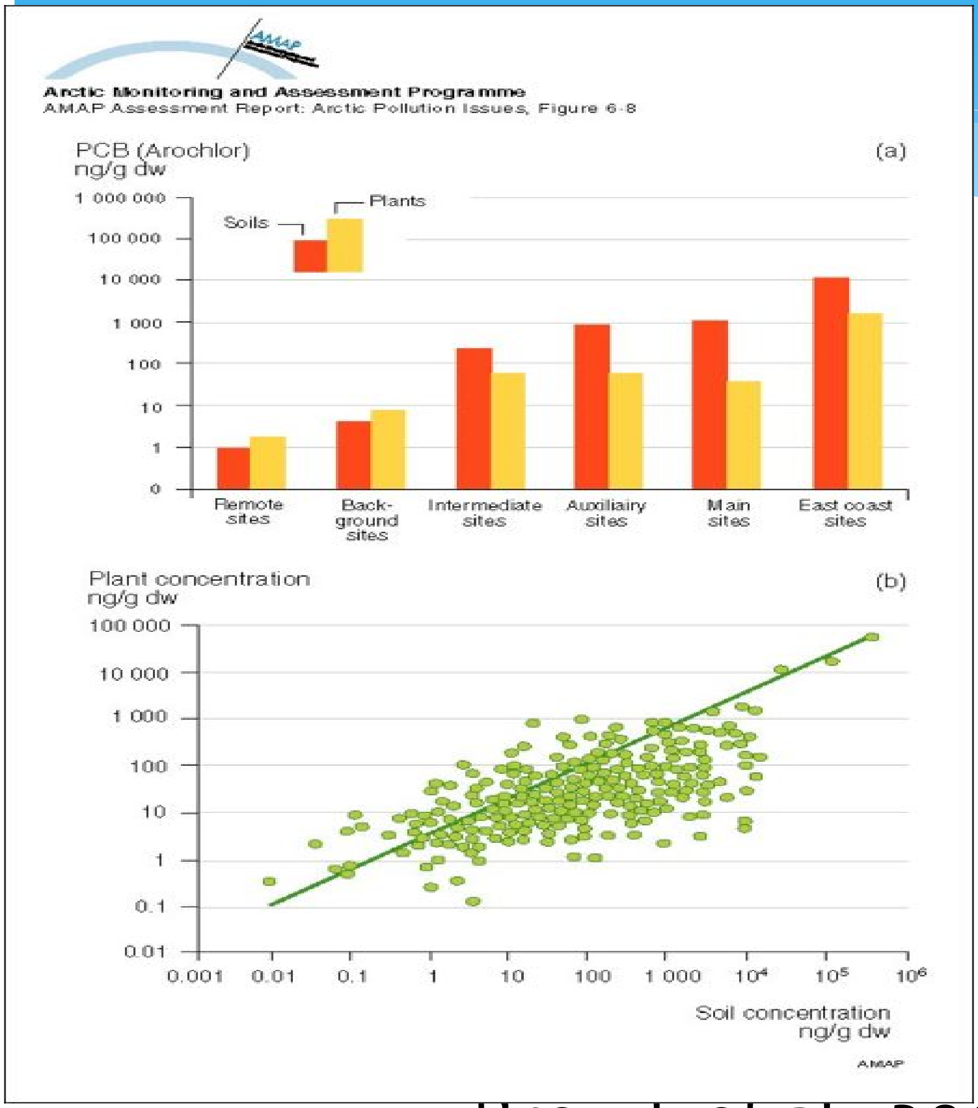
(O'Toole et al 2005).

Transport Halo

* DEW sites (distance early warning)



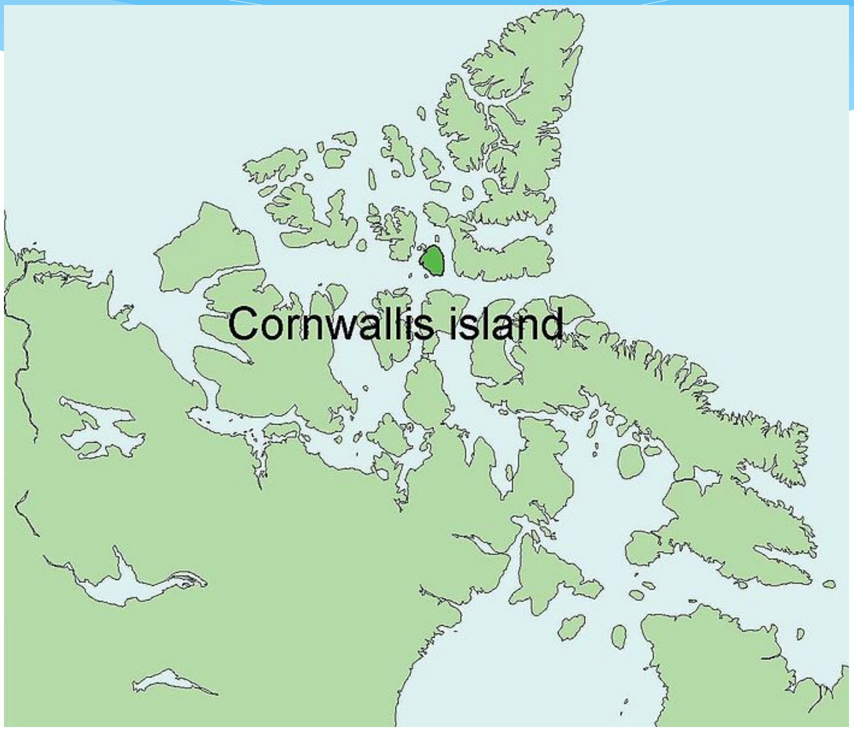
PCB Halo

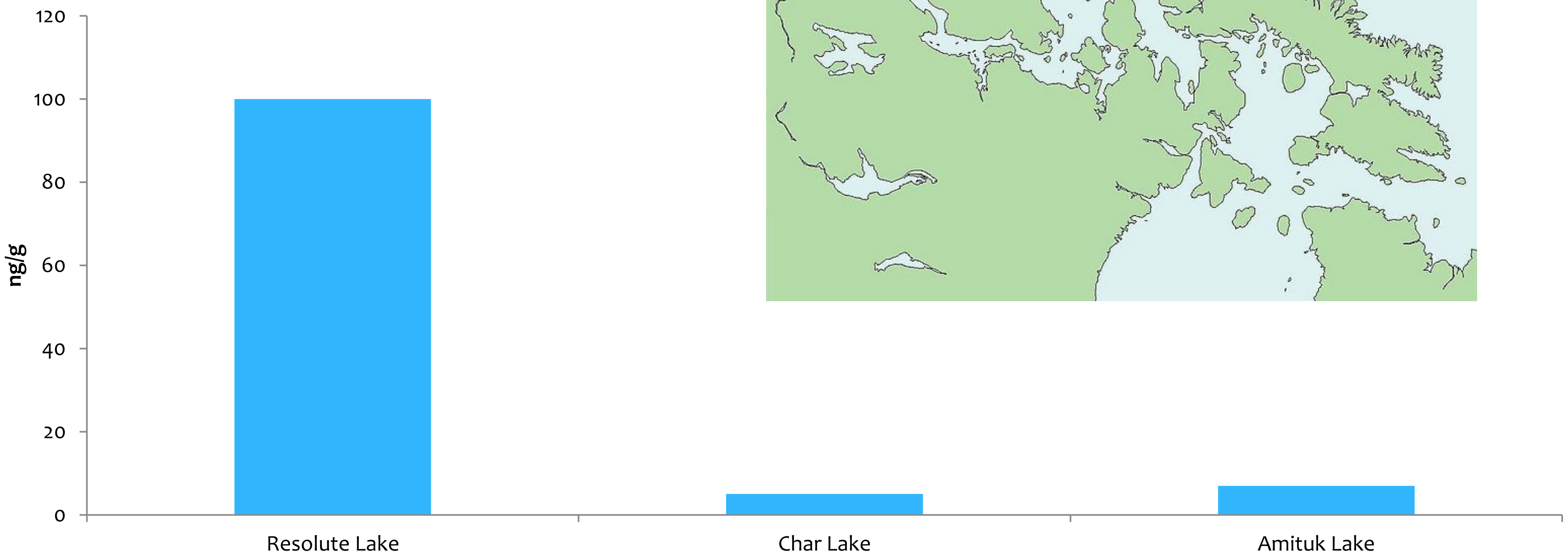


- ~119 kg of PCB waste dumped
- 42 sites

Breivik et al., 2004

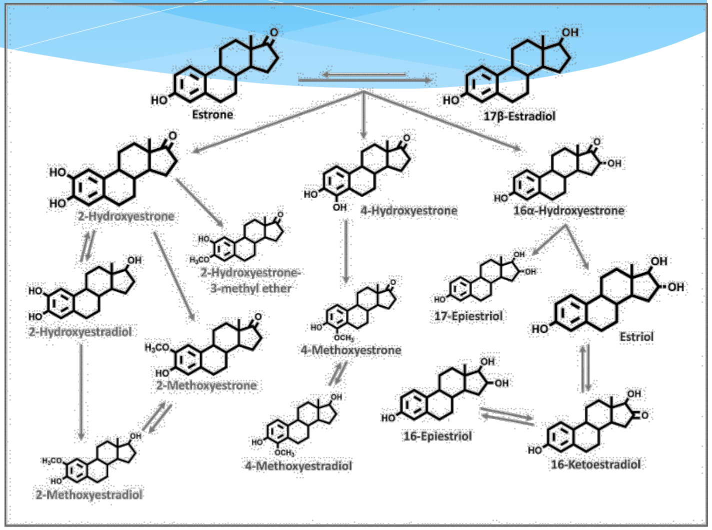
PFCs and Airports



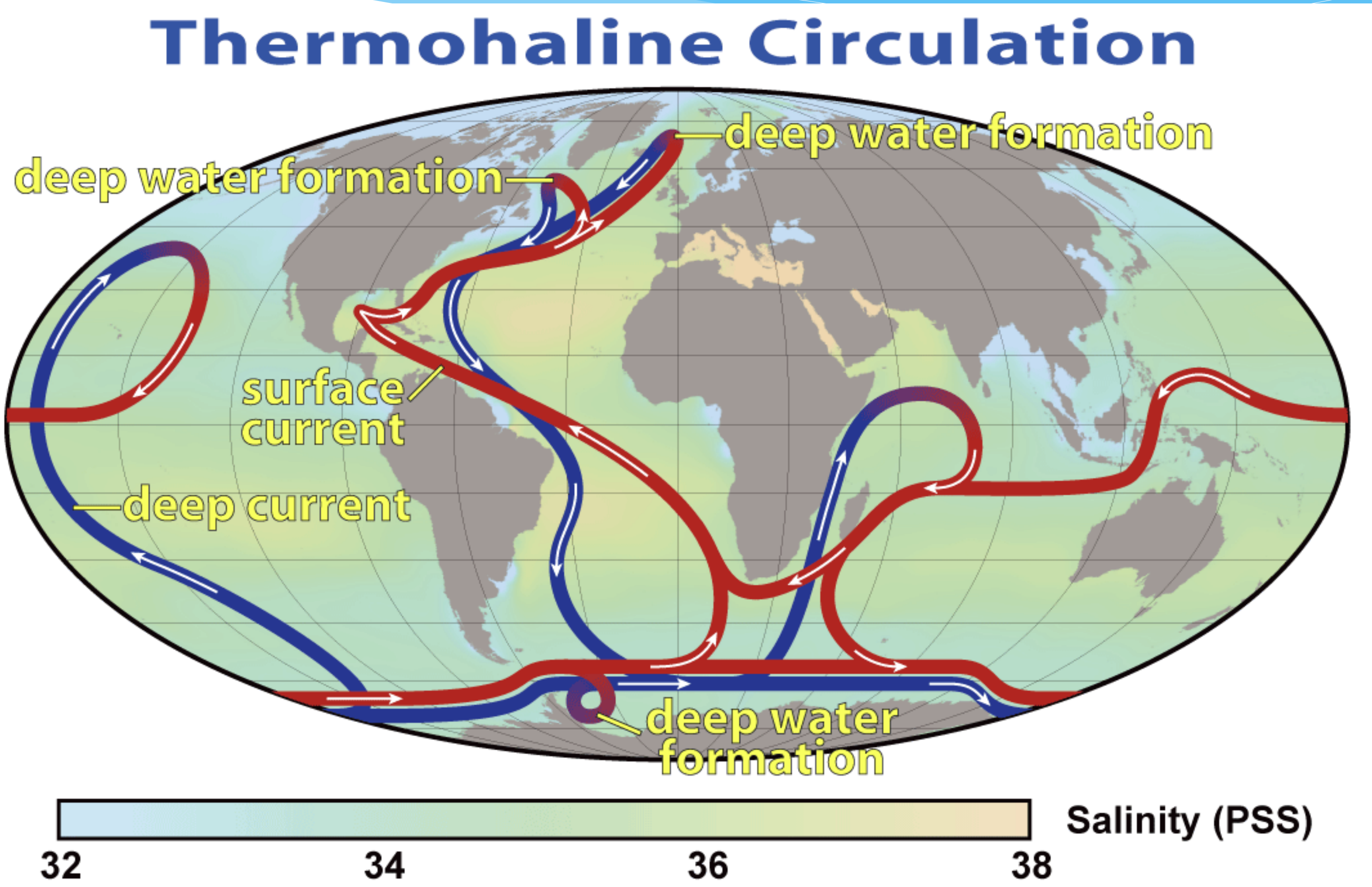


Fate

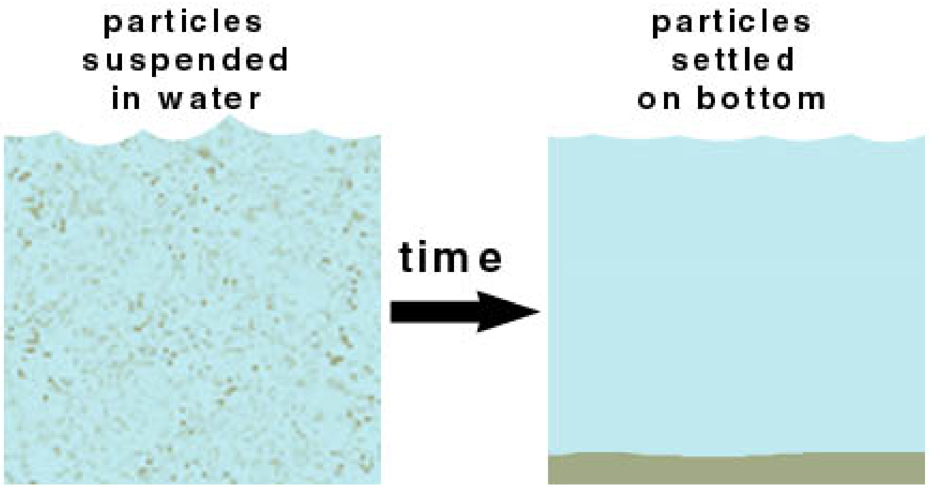
* Breakdown
  * Photolysis
  * Metabolites
  * Degradation
* Storage in soil and sediment
* Deep ocean water
* Storage in ice/snow
* Biological uptake



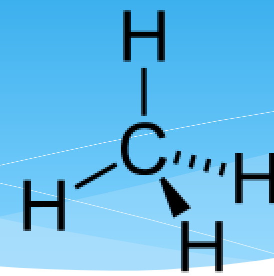
Deep ocean water

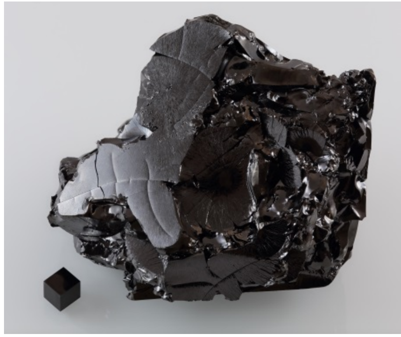


Sedimentation



Carbon

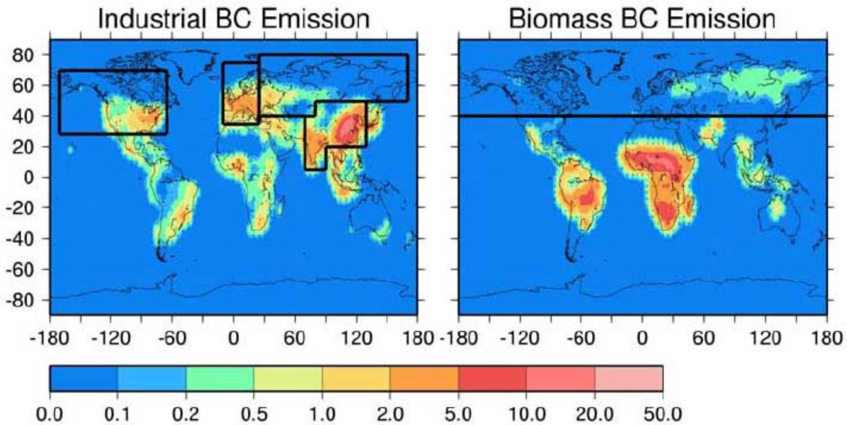




* Symbol C
* Atomic mass 12.0107
* Atomic number 6
* CAS 7440-44-0
* Naturally found as
  * anthracite (coal)
  * Graphite
  * Diamond
* Discovery date…. Considered prehistoric

Carbon

- Total Carbon (TC)
  - Inorganic Carbon (IC)
    - Particulate
    - Dissolved
  - Organic Carbon (OC)
    - Volatile Organic Carbon (VOC)
    - Particulate
    - Dissolved



Black carbon

* Strongest light absorber of atmospheric particulates
* Fine particles ($PM_{2.5}$)
* Absorbs 1 million times more solar energy that CO2
* Major soot component
* Transport vector for many compounds including PAHs
* In soil and sediment may be primary sink of organic contaminants and heavy metals

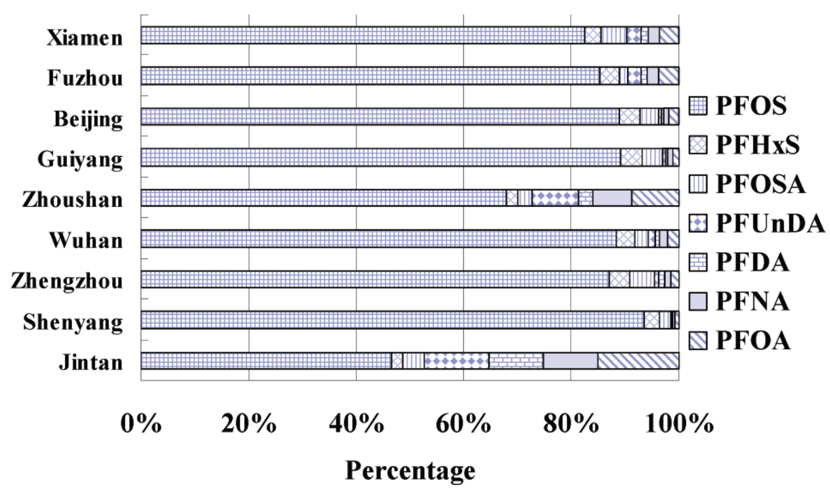
By air or by sea

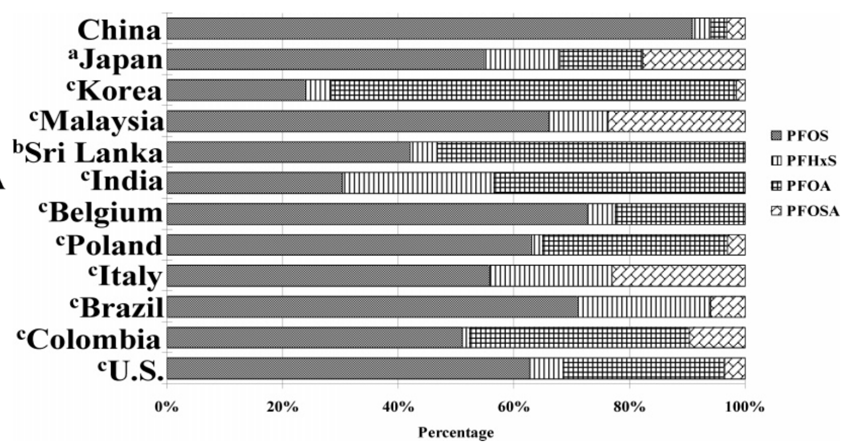
Perfluorinated compounds

Uses

PFC humans

country	PFOS	PFHxS	PFOA	PFOSA
	(ng/mL)			
USA	43.2	4	19.1	4.14
Colombia	8.28	0.2	6.16	1.57
Brazil	11.7	3.77	<20	1
Italy	4.32	1.64	<3	1.78
Poland	42.1	1.3	21.3	2.06
Belgium	15.7	1.04	4.82	<3
India	1.85	1.6	2.64	<3
Sri Lanca	5.03	0.57	6.38	N.A
Malaysia	12.7	1.98	<10	4.57
Korea	21.1	3.95	61.8	1.3
Japan	24.6	5.92	6.4	7.92
China	52.7	1.88	1.59	1.82





Yeung et al 2006

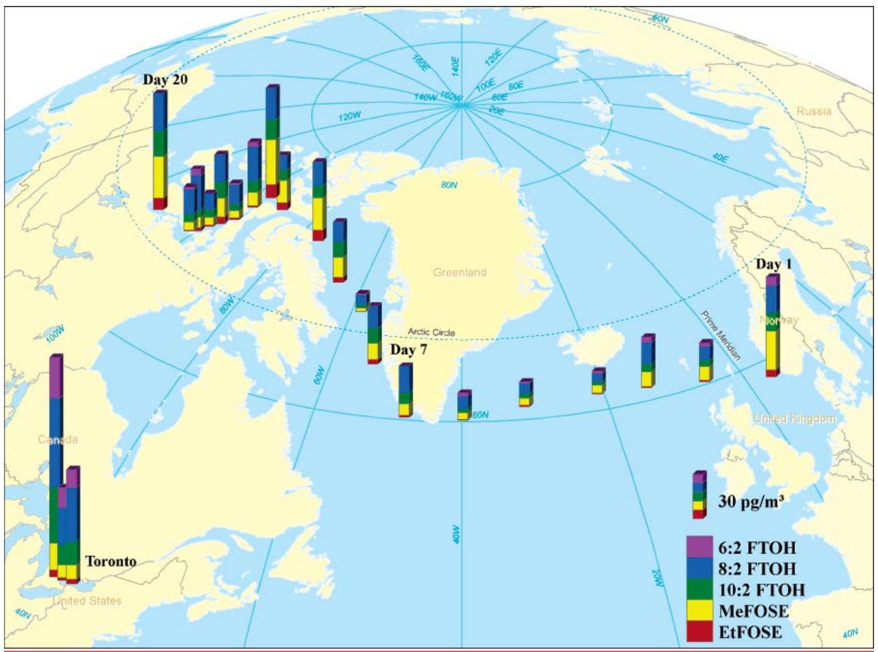
PFCs

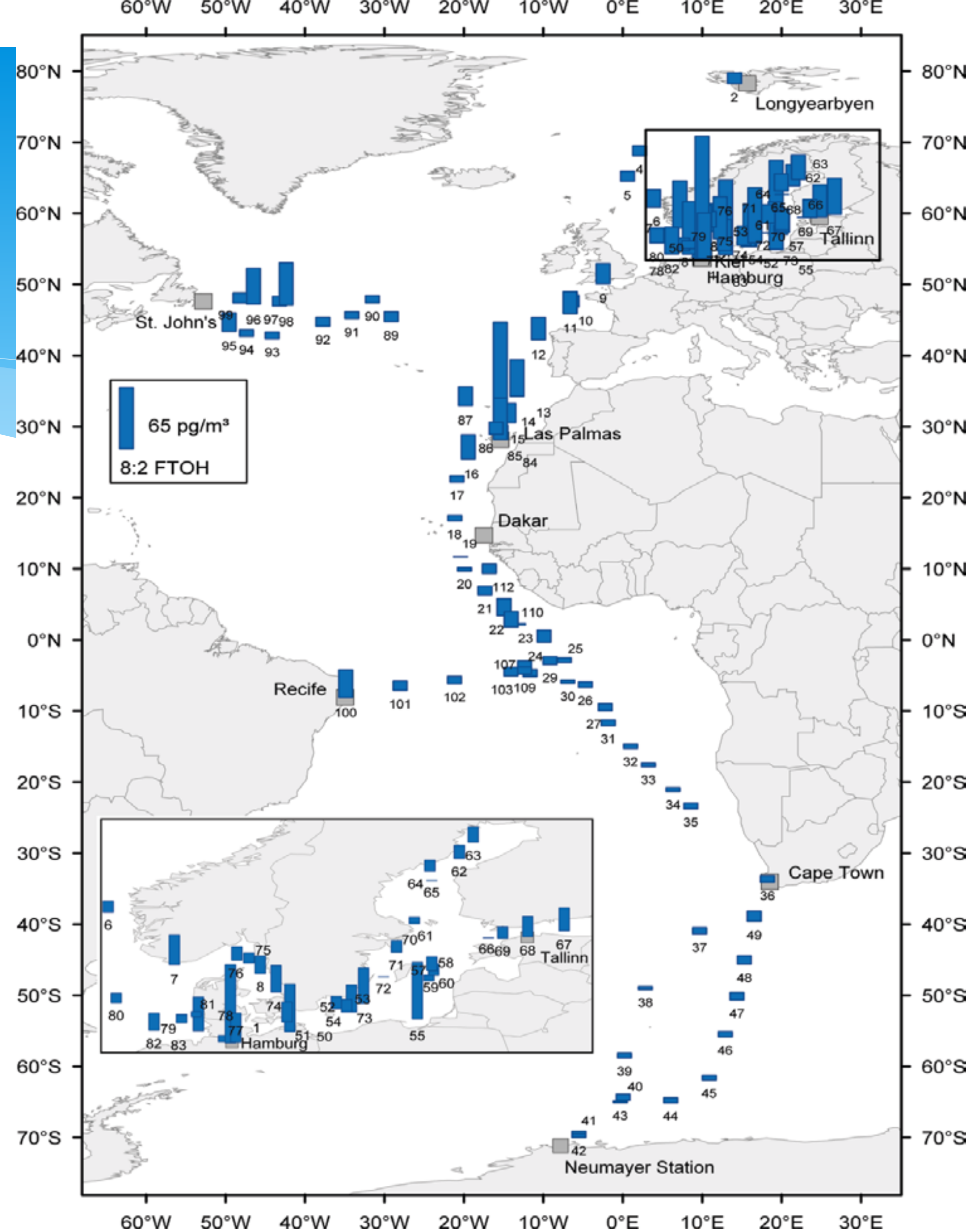
- So in the Arctic are they transported from the air to the water
- Or is the water the transport

How would we test this?

Is it important to know?

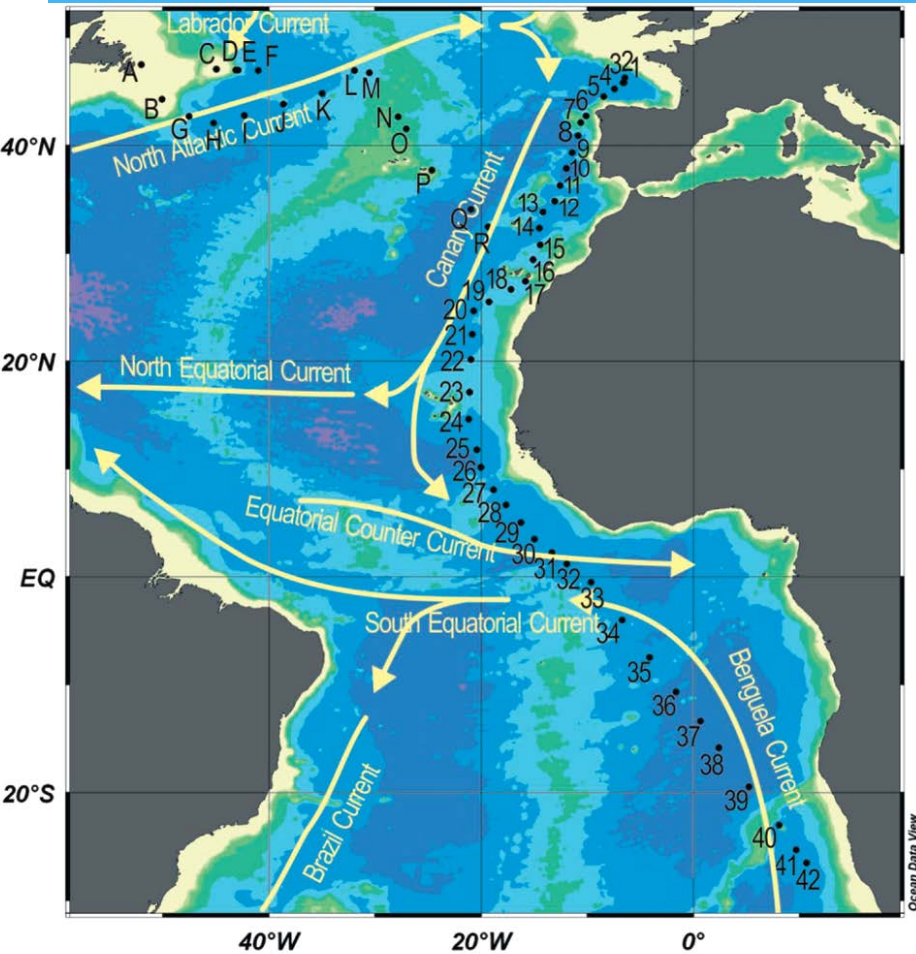
Evidence of Atmospheric

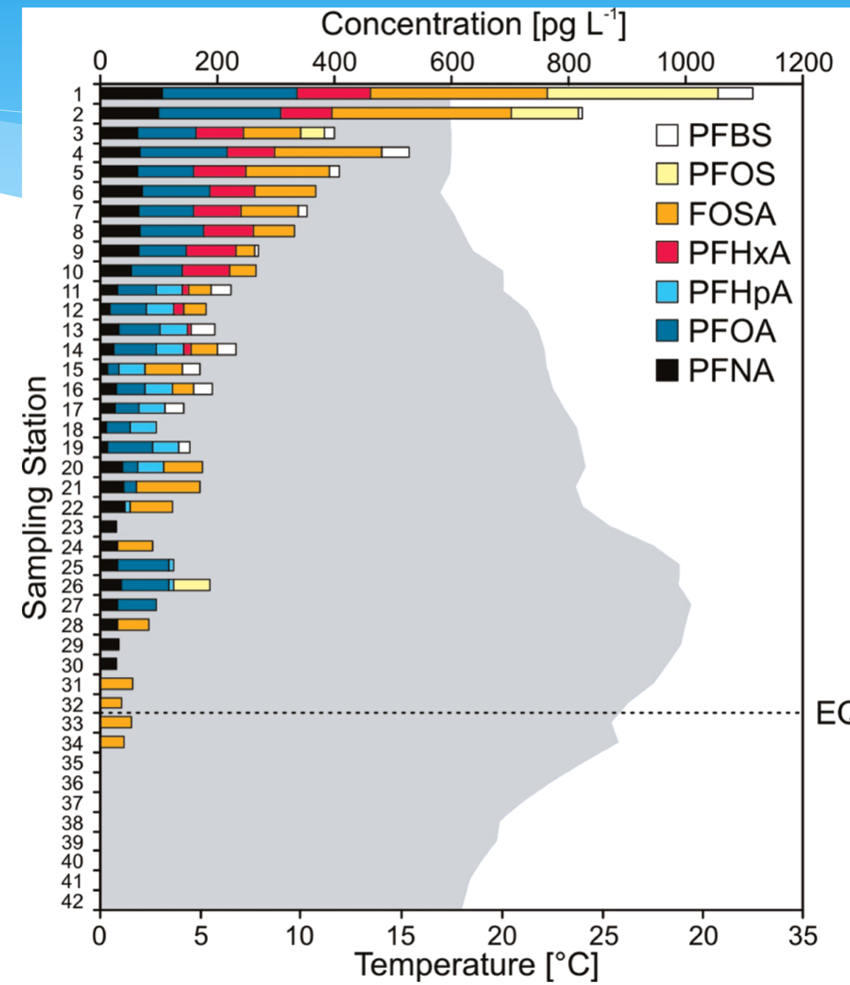




Dryer et al 2010 Shoeib and Harner 2006

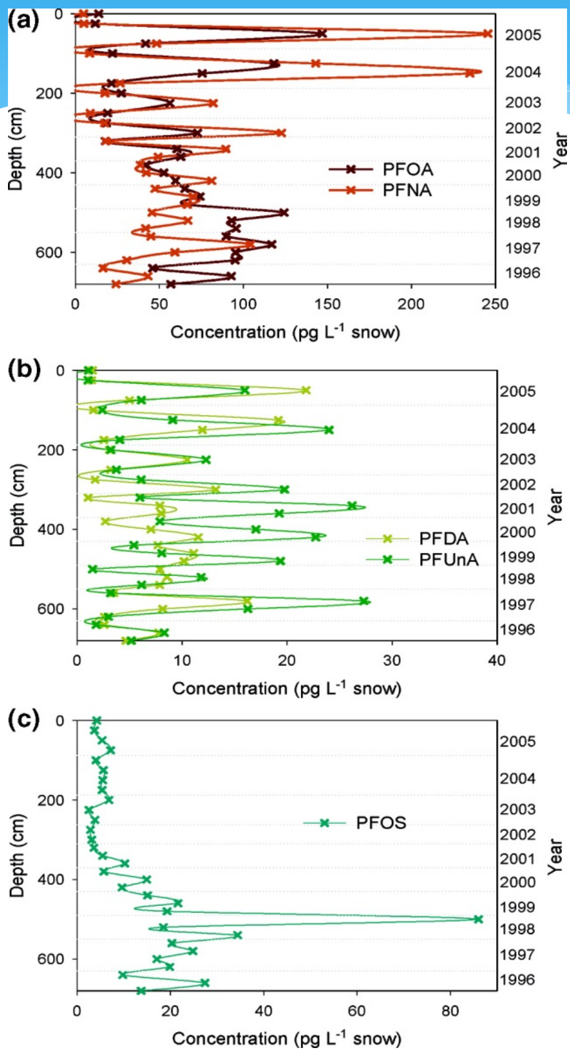
Ocean Water PFCs

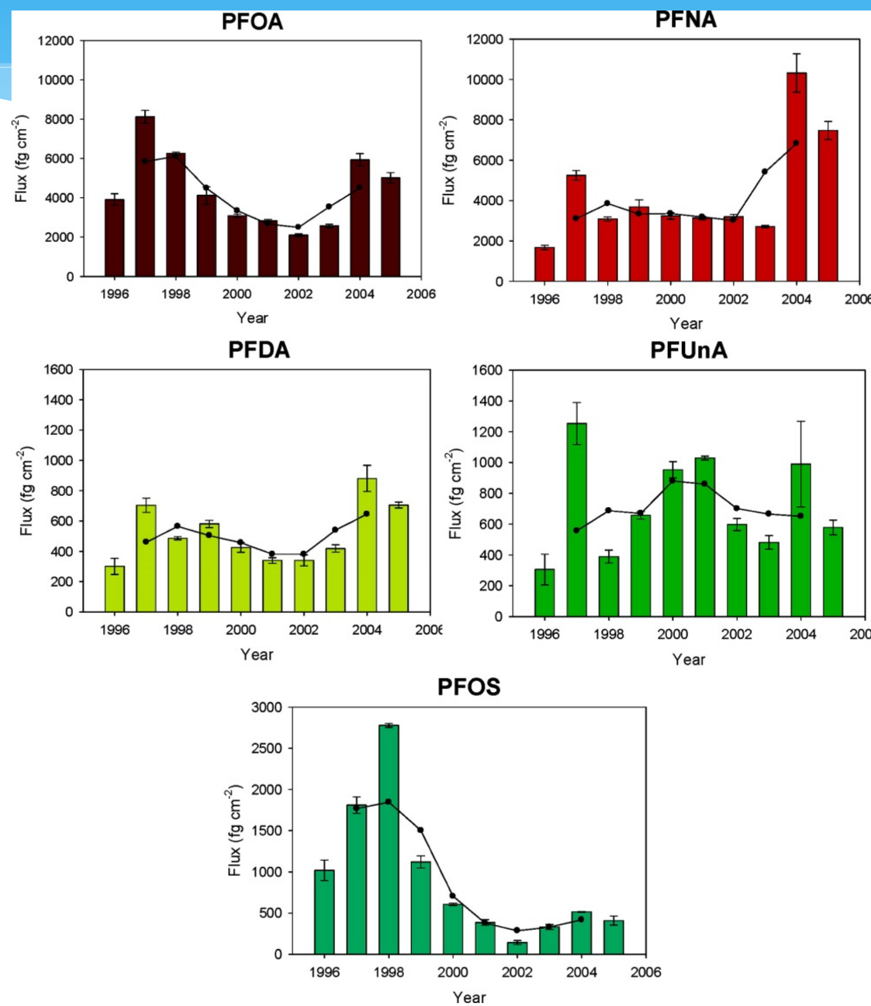




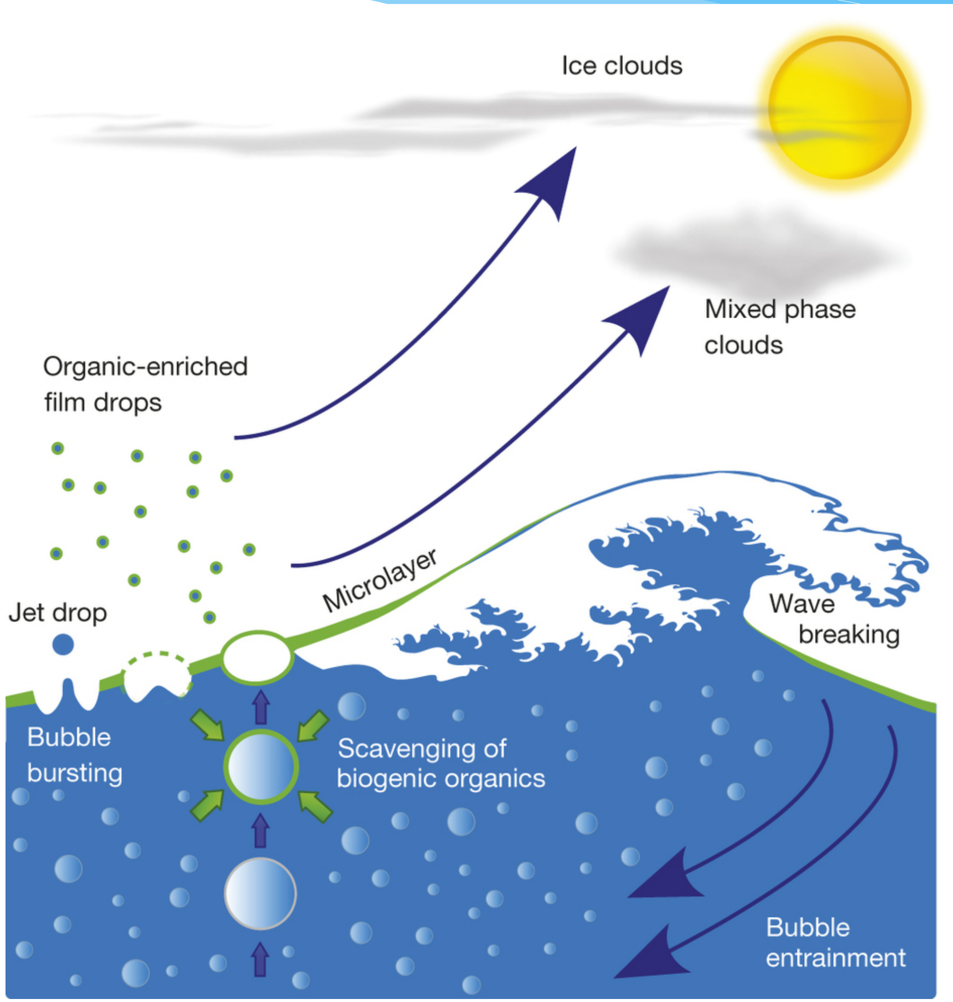
Ahrens Et al

Devon Ice Cap





The Sea may still be a source



Importance

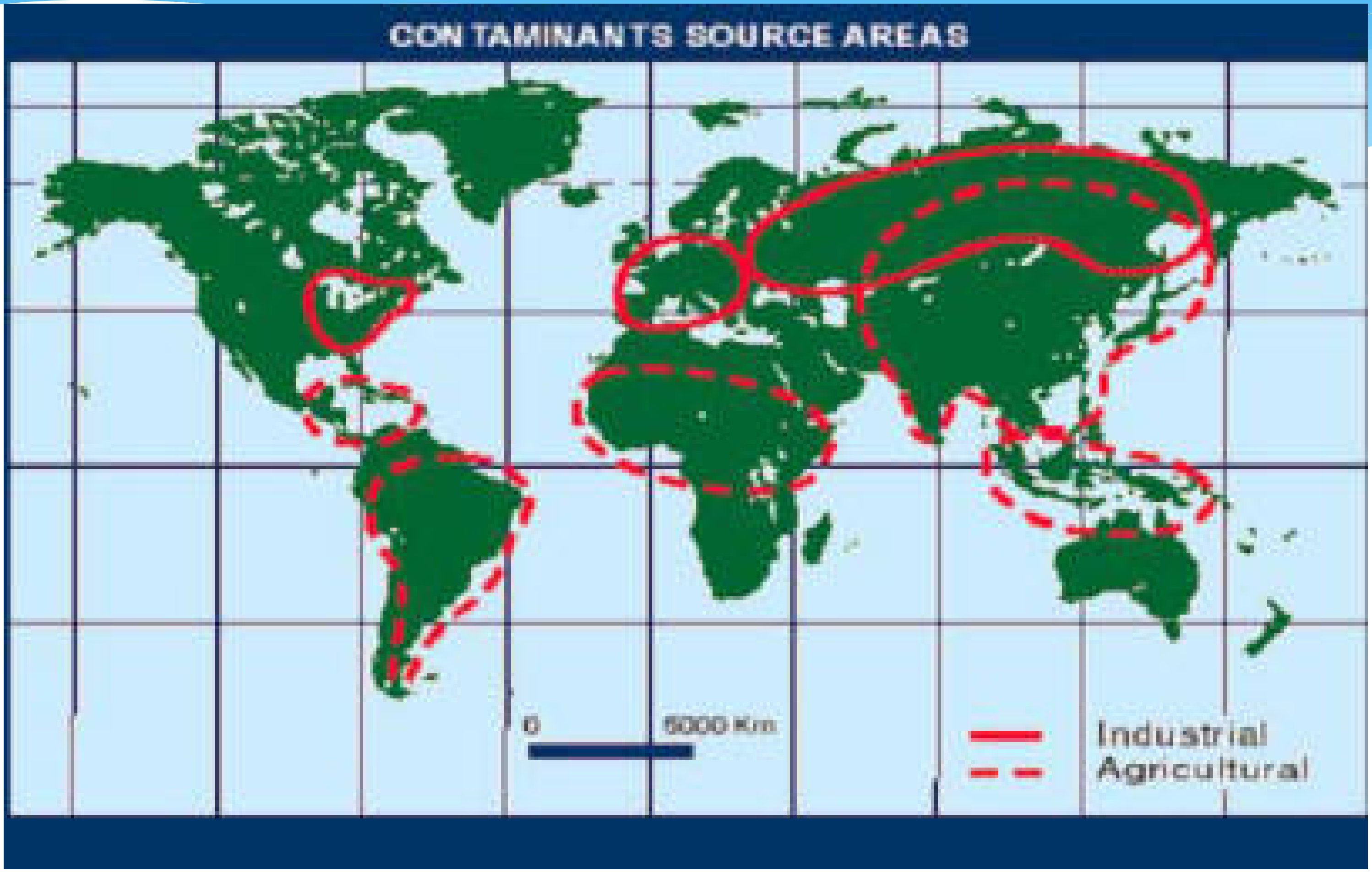
* By knowing the source we can predict the behavior
* We can also limit the emissions if possible
* Can monitor one matrix to predict others
* Identify routes of exposure

The Arctic

Why look in the Arctic

* Northern Diets
* Persistence
* Snow and Ice
* Volume
* Bioaccumulation
* 0.0008% PCB
* 21% of γ-HCH
* 12% of DDT

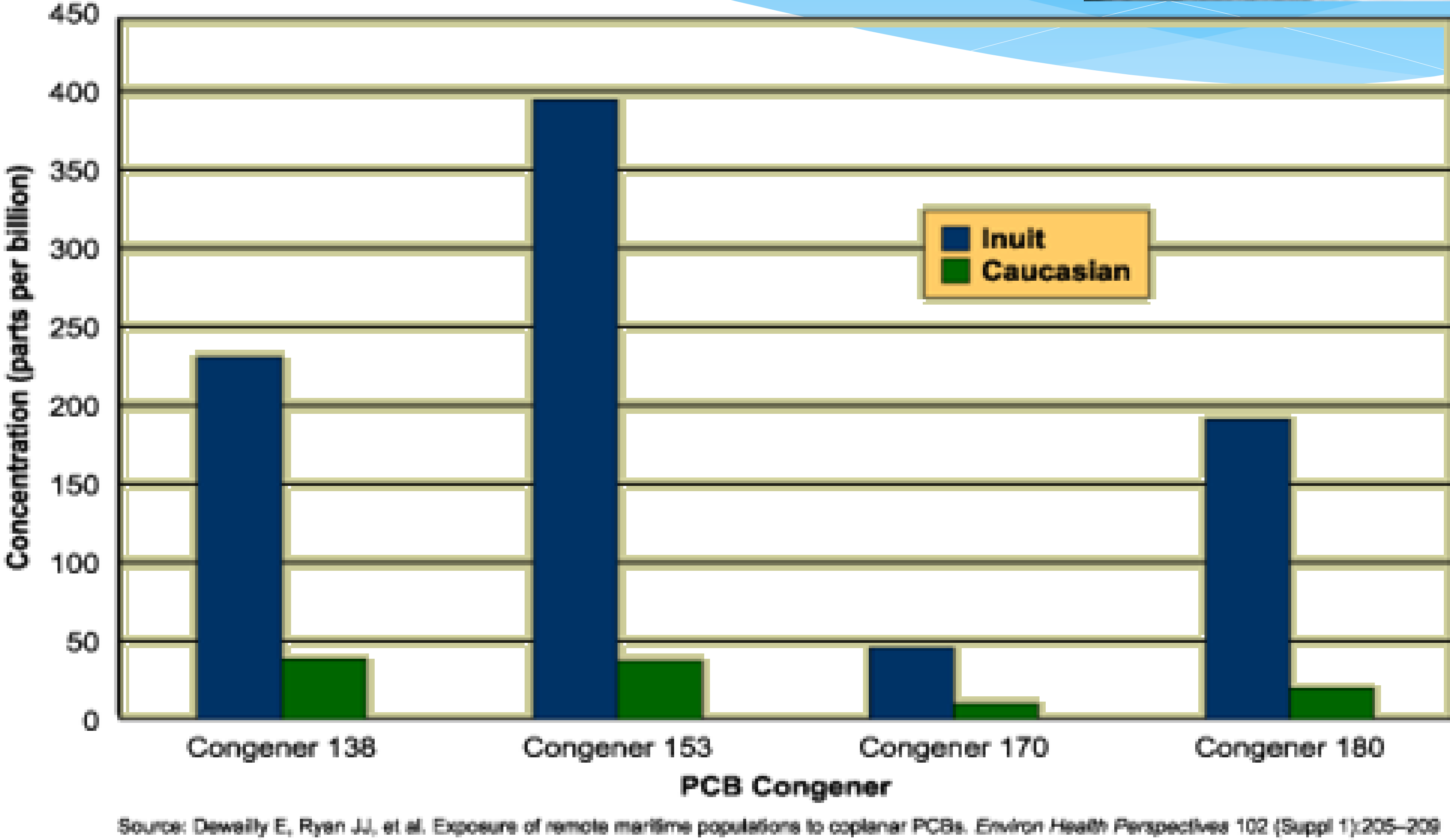
Sources

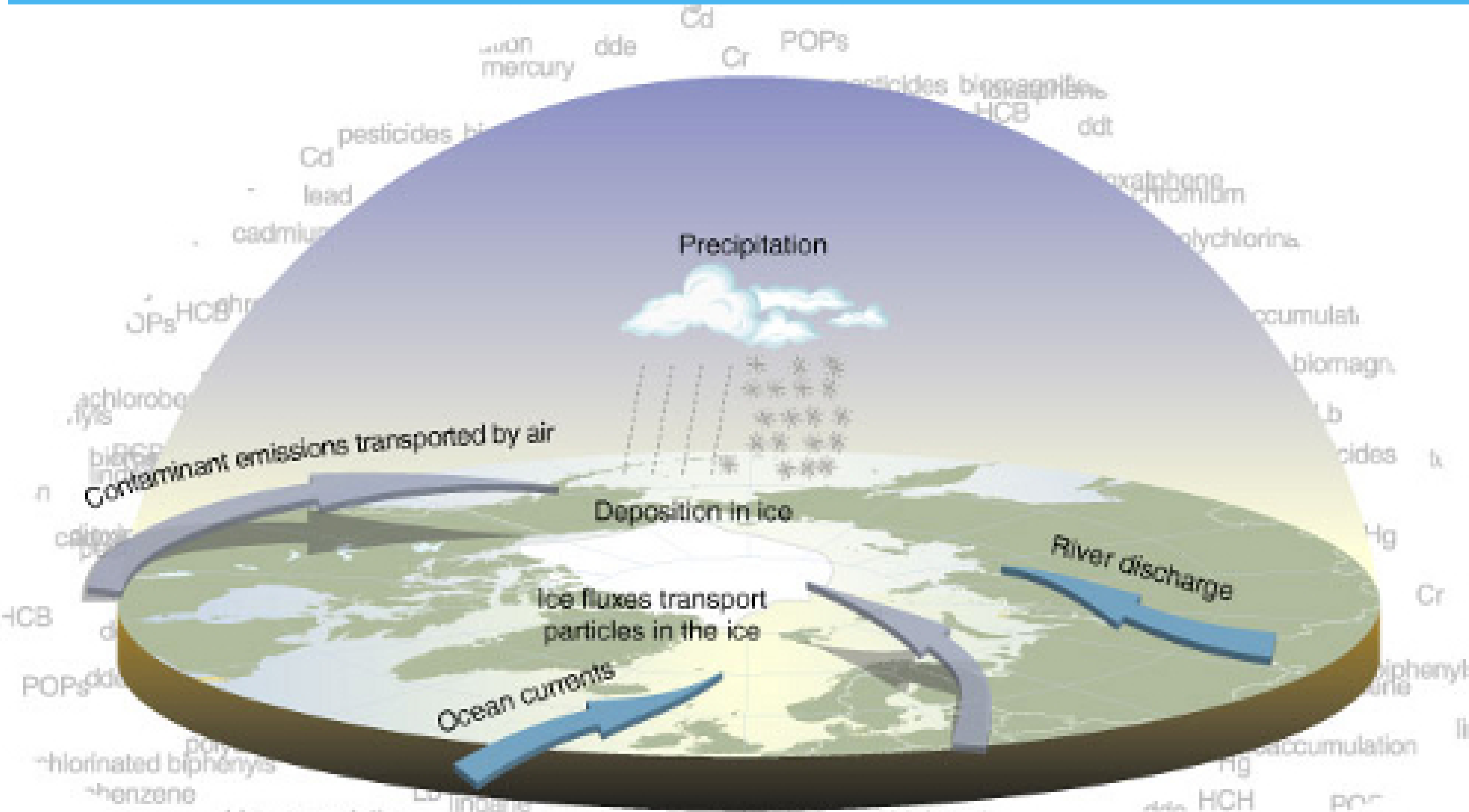

CONTAMINANTS SOURCE AREAS
0
5000 Km
Industrial
Agricultural

Canada

Yukon
Whitehorse
Northwest Territories
Yellowknife
Nunavut
Iqaluit
Newfoundland and Labrador
St. John's
British Columbia
Victoria
Alberta
Edmonton
Saskatchewan
Regina
Manitoba
Winnipeg
Ontario
Ottawa
Toronto
Quebec
Québec
Charlottetown
Prince Edward Island
Fredericton
New Brunswick
Halifax
Nova Scotia
CANADA – Political
International boundary
Provincial/territorial boundary
Alberta Province/territory
Ottawa National capital
Regina Provincial/territorial capital
Scale
0 250 500 750 1 000 km

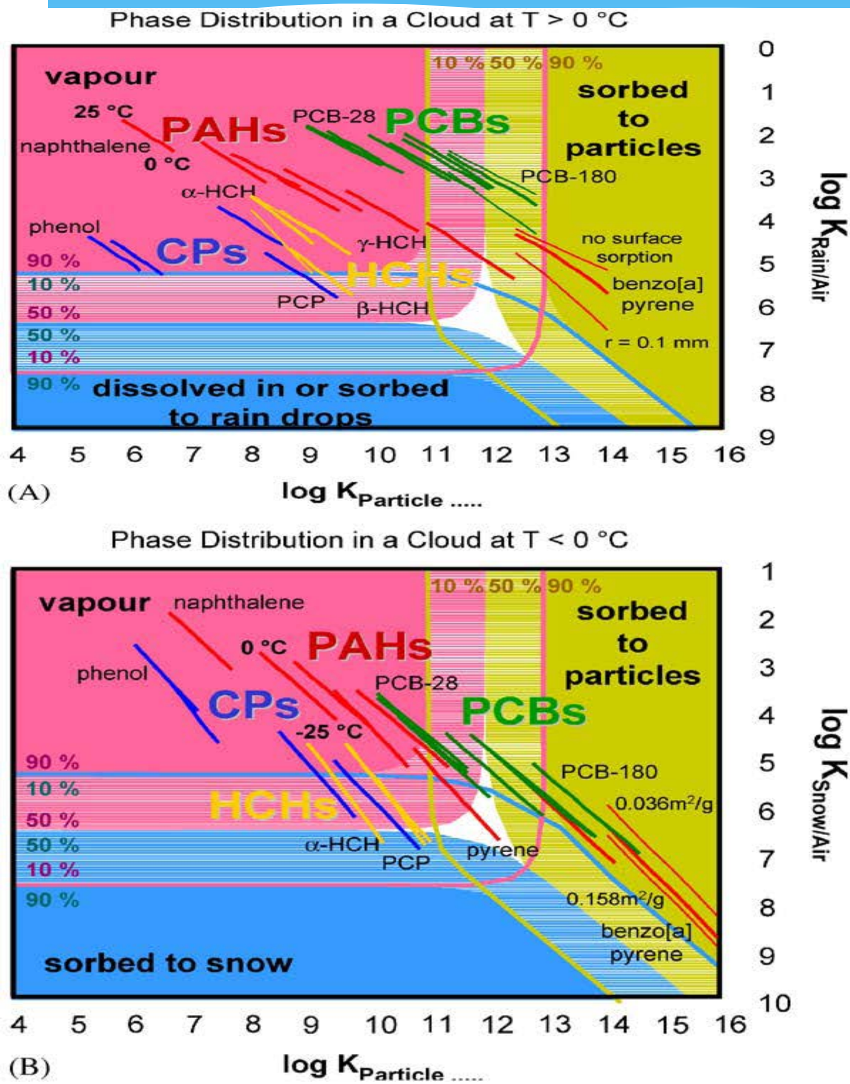
PCBs


450
400
350
300
250
200
150
100
50
0
Concentration (parts per billion)
Inuit
Caucasian
Congener 138
Congener 153
Congener 170
Congener 180
PCB Congener
Source: Dewailly E, Ryan JJ, et al. Exposure of remote maritime populations to coplanar PCBs. Environ Health Perspectives 102 (Suppl 1):205–209



Source: AMAP 2002, ACIA 2004

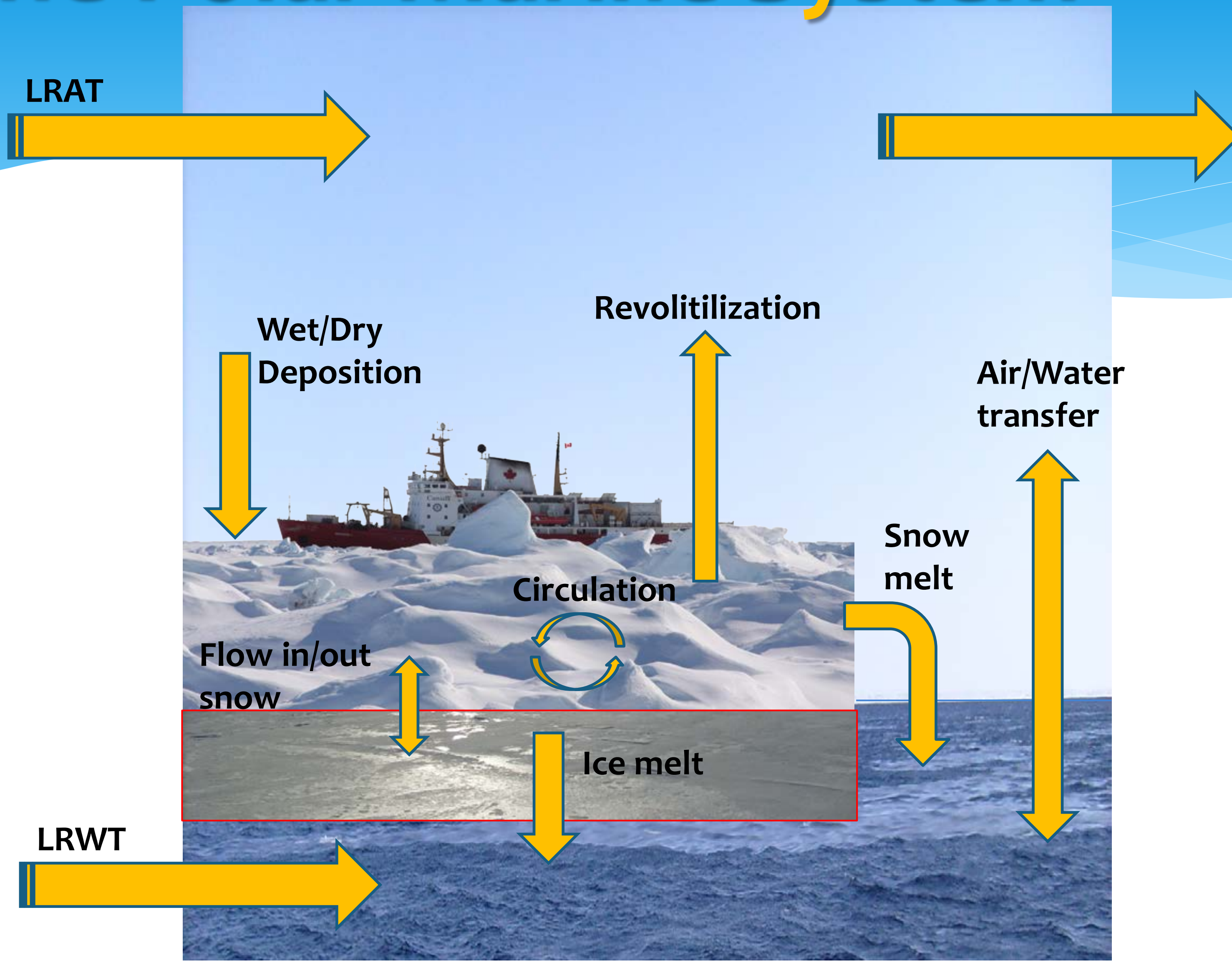
Snow/Rain Partitioning



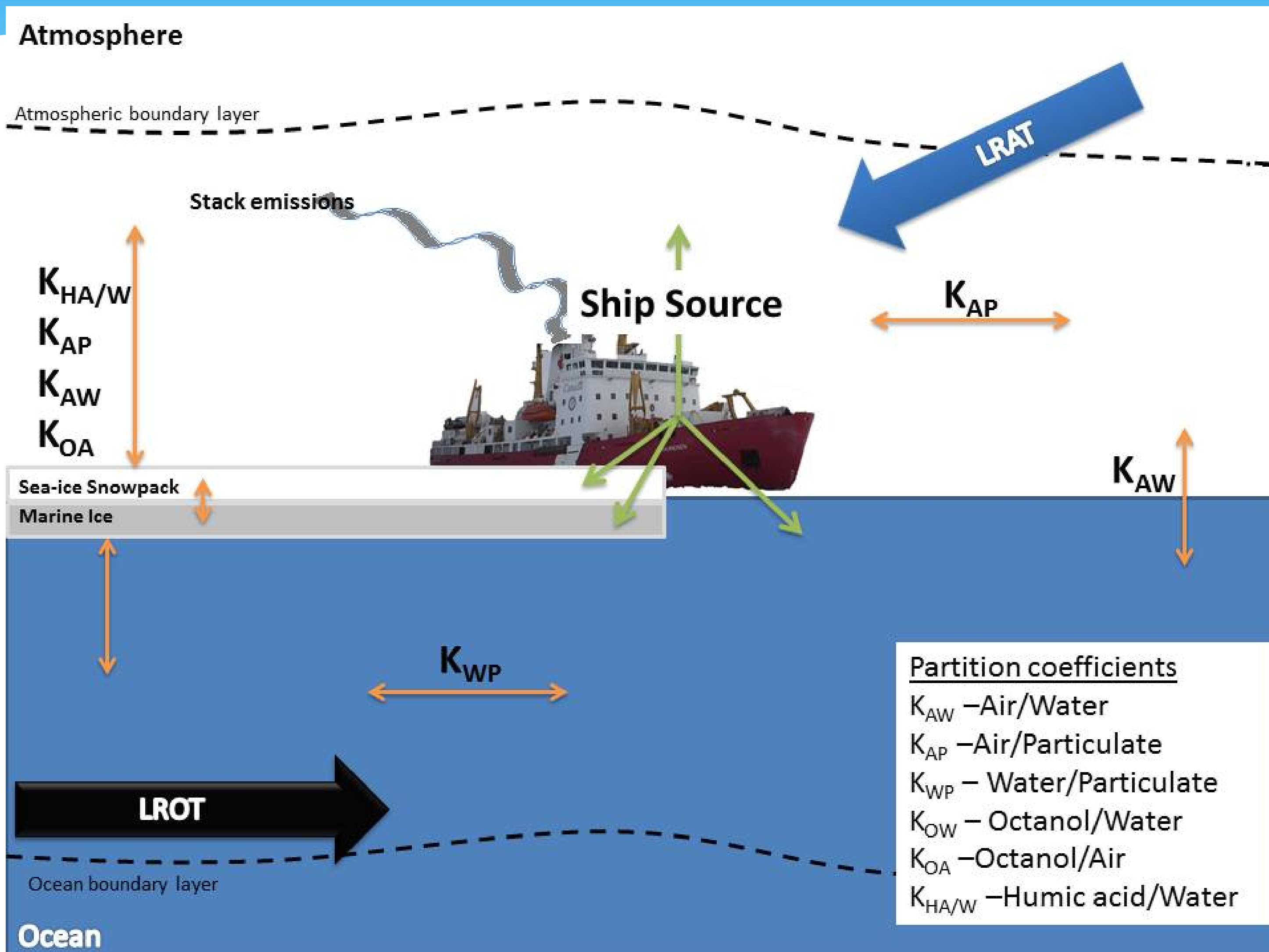
- Different chemicals disperse into different phases
- Rain and Snow generate different partitioning
- How chemicals will fall out will change with seasonality

Lei and Wania 2004

The Polar Marine System

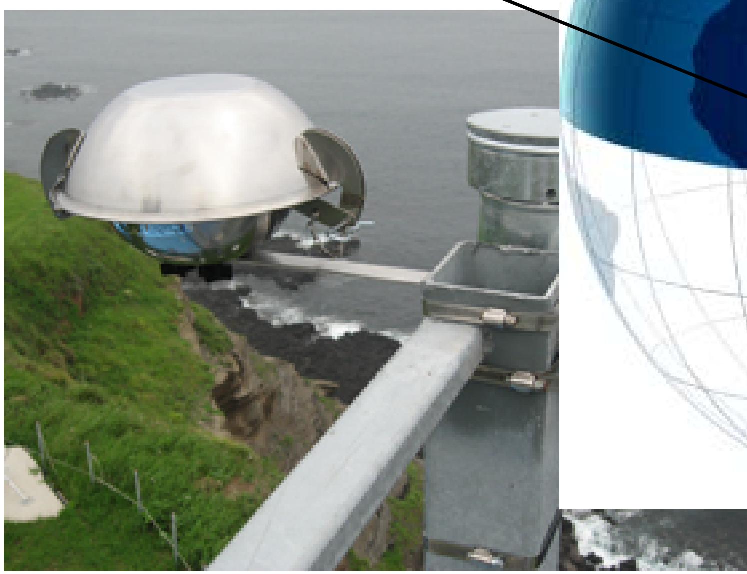


Oceanic Exchange



Concentration in the air

- $50 ng\ m^{-3}$
- 25°C



- $5 ng\ m^{-3}$
- 1°C

- **H (PCB-18) as 21.33 Pa m^3 mol^{-1}, at 298 K (or 25°C)**

Air water partition at equator

$$K_{aw} = {}^{H}/_{RT}$$

K_{aw} = 21.33 / (8.314 x 298) = 8.6 x 10^{-3} or ln K_{aw} -4.8

Concentration in water at equator

$$C_w = C_a / K_{aw}$$

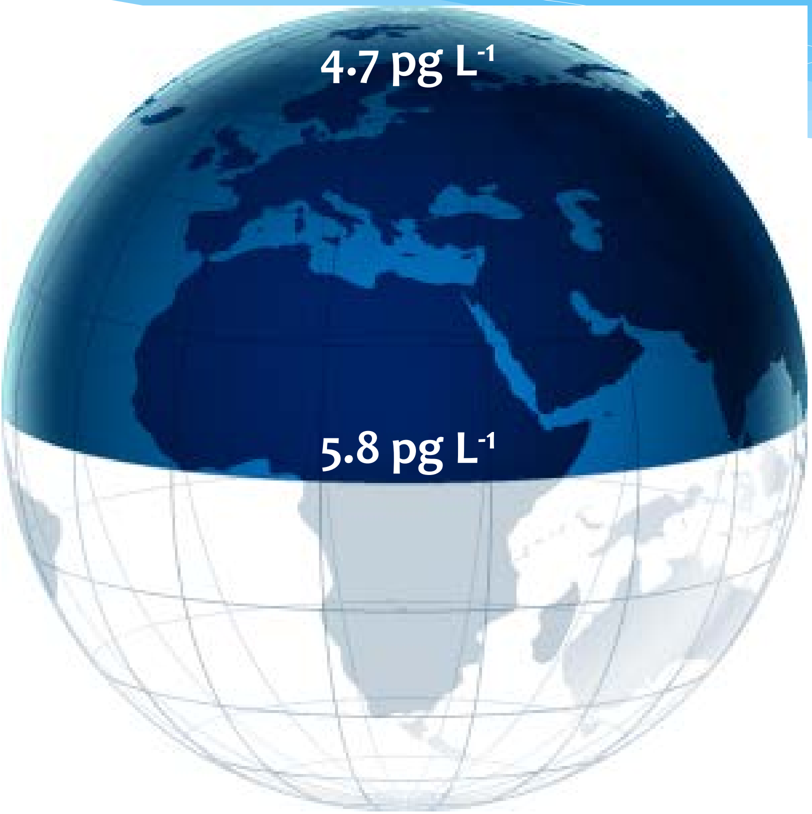
$C_w = 50 /$ g L^{-1}

For Arctic

$$\ln K_{aw}(T_2) = \ln K_{aw}(T_1) - \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

* ΔH for PCB18

Concentration



Polar bear

* 1984-2006 annual increases in PFCs
* PFOS 4.7%
* PFNA 6.1%
* PFDA 4.3%
* PFOA 2.3%
* PFCs exceed all other Organohalogen contaminants in Bears
* Based on rat and monkey tests by 2014-2024 will exceed NOAEL and LOAEL estimates

Conclusions

- Three major routes of contamination
  - Atmospheric
  - Water
  - Biovectors
- Persistence
- Toxicity
- Many factors affect the transport