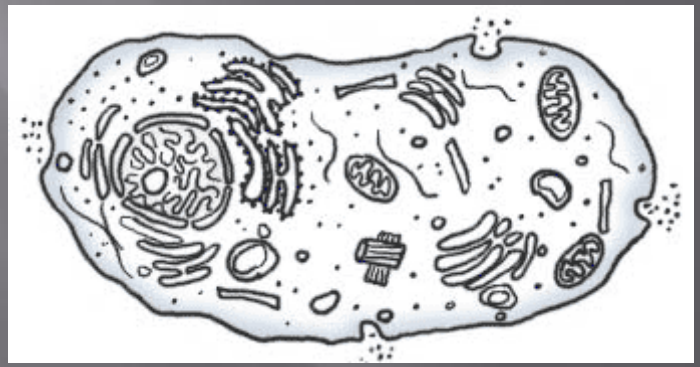
# Chemical Fate and Transport in the Environment

Garry Codling

# Aim

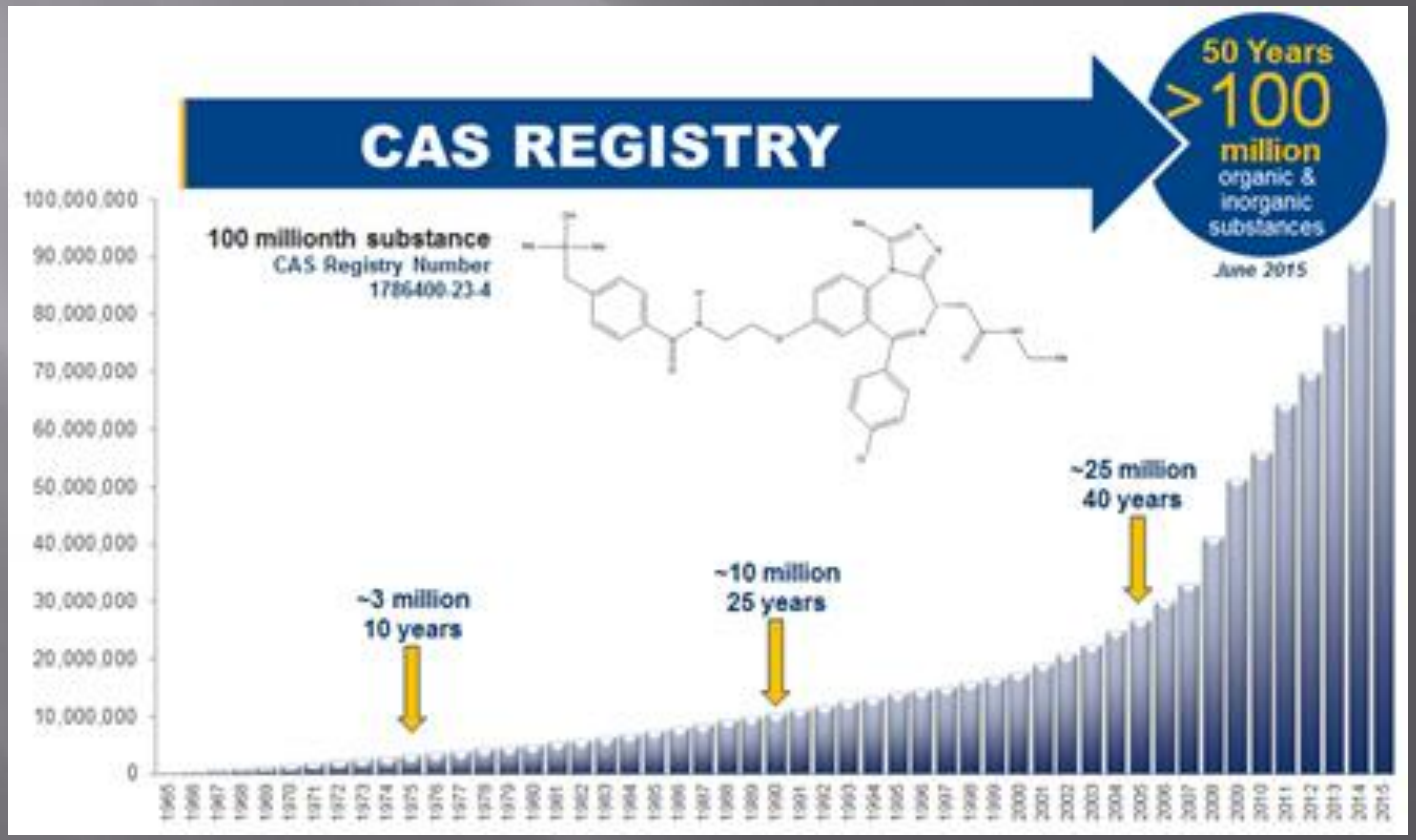
Go from the globe to you and beyond

- What
- Where
- How
- When
- Why



# Chemicals

- 102 million compounds –approx.
- 100’000 in use
- 15’000 per day are added



# Units of measurement

**Mass per volume**

Air –$m^3$

Water –$L^{-1}$

Soil –$g^{-1}$

**Other Terms**

PPM, PPT, PPB

Mole ($6.02 \times 10^{23}$ atoms)

Wet weight/Dry weight

Normalized

# Scientific Theory

- Observation
- Experimentation
- Theory
- Simulation/Model
- Observation

# POPs (Persistent Organic Pollutants)

- Stockholm convention 2001
  - The Dirty Dozen
    - Alrin
    - Chlordane
    - DDT
    - Dieldrin
    - Endrin
    - Heptachlor
    - Hexachlorobenzene (HCB)
    - Mirex
    - Toxaphene
    - Polychlorinated Biphenols (PCBs)
    - Polychlorinated dibenzo-p-dioxins (PCDD)
    - Polychlorinated dibenzofurans (PCDF)

# POPs

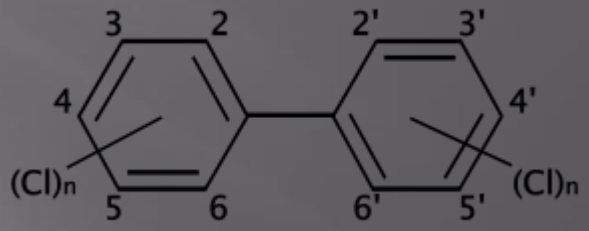
- Stockholm Convention 2011
  - The naughty 9
    - chlordecone
    - alpha hexachlorocyclohexane, beta hexachlorocyclohexane, lindane, (α- β- γ- HCHs)
    - pentachlorobenzene
    - hexabromobiphenyl
    - hexabromodiphenyl ether, heptabromodiphenyl ether
    - pentachlorobenzene
    - perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (PFOS)
    - tetrabromodiphenyl ether and pentabromodiphenyl ether
    - alpha hexachlorocyclohexane, beta hexachlorocyclohexane and pentachlorobenzene

# What makes a POP

- Bioaccumulation
- Long range transport
- Toxicity

# Half-Lives

- PCBs
  - Atmosphere -USEPA
    - Mono- 12.5 days
    - Hepta 1.31 years




Soil/Sediment

Arochlor 1254 -940 days Hsieh et al. (1994).

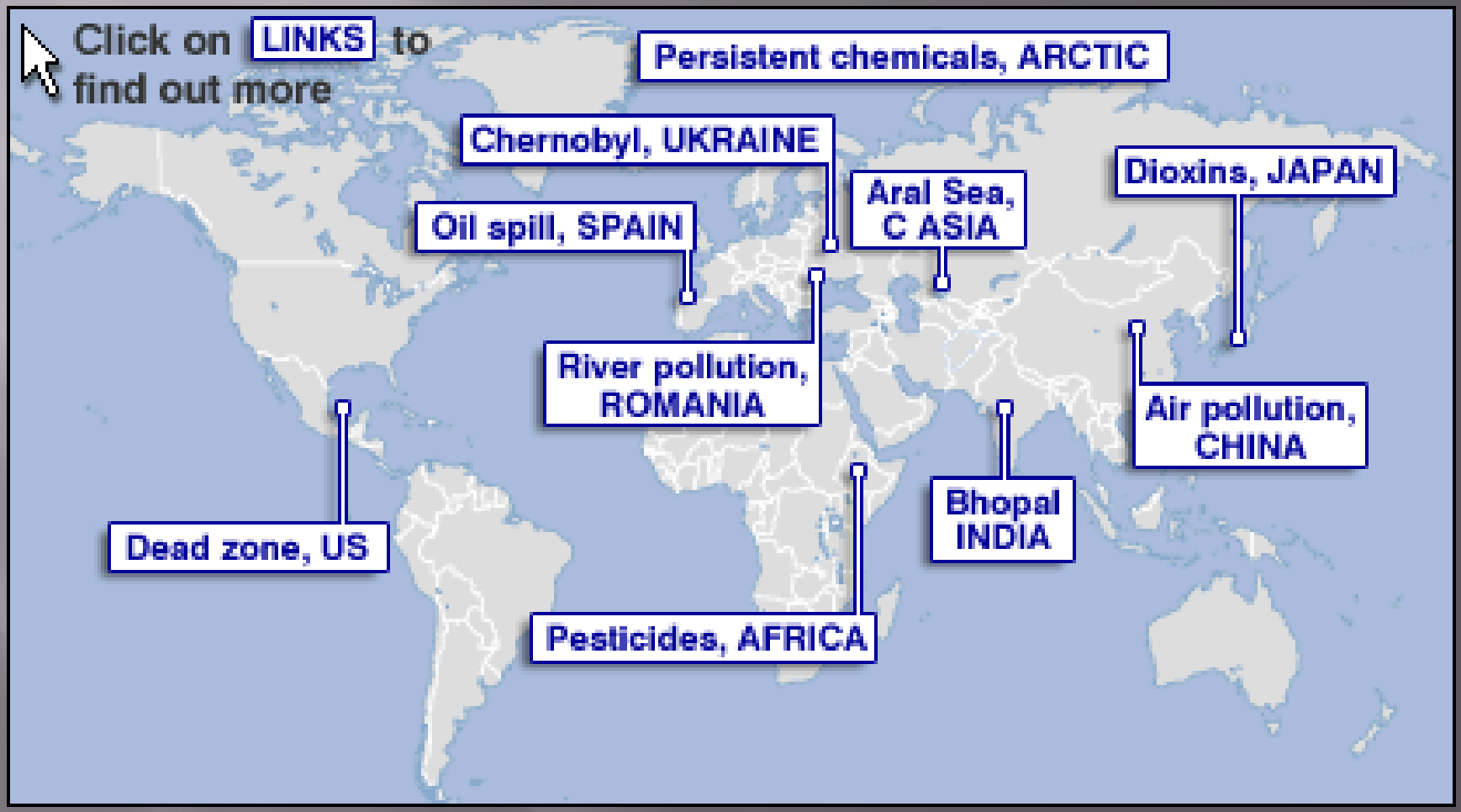
2.9-37 year (Sinkkonen and Passivirta, 2000)

Water

Mono-0.17 years

Hepta 23.4 years

# Example of issues




BBC News

# Individual

# Point sources

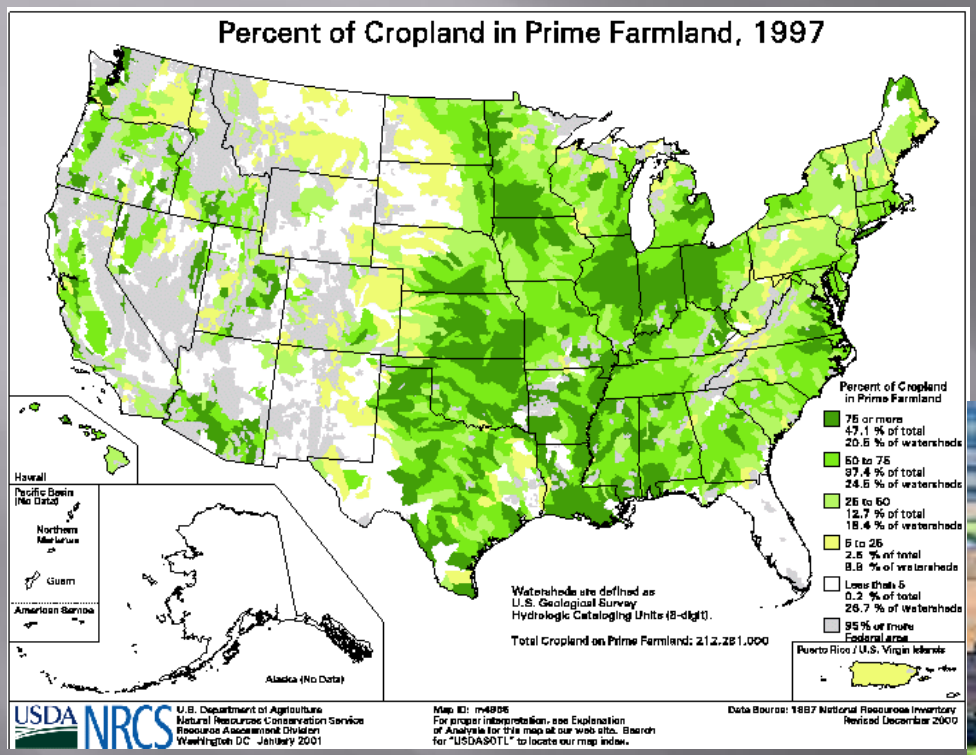
Industrial

# Diffuse Sources

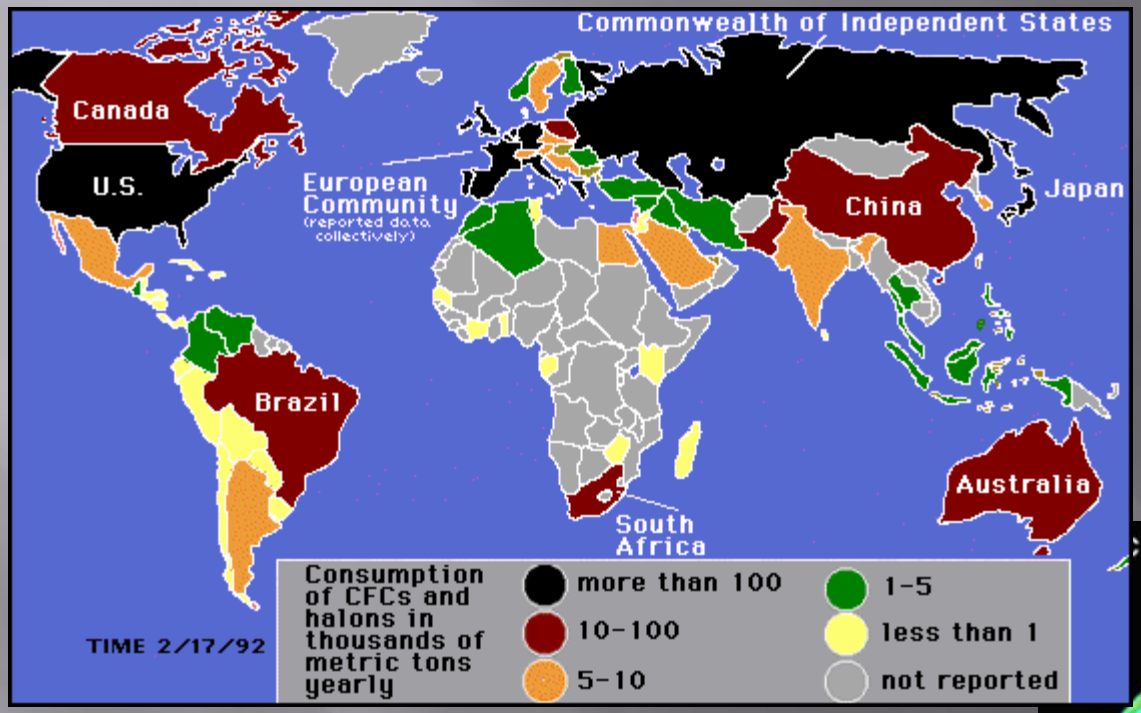


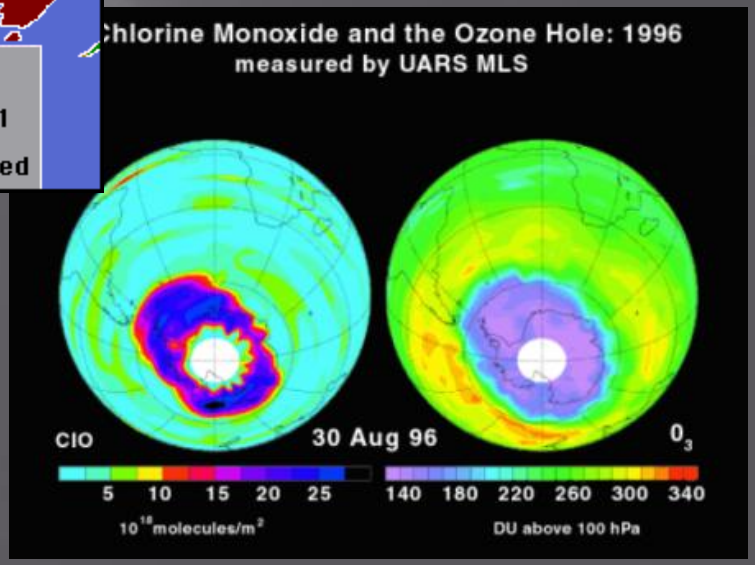

Mexico City

# Regional Sources




# Global



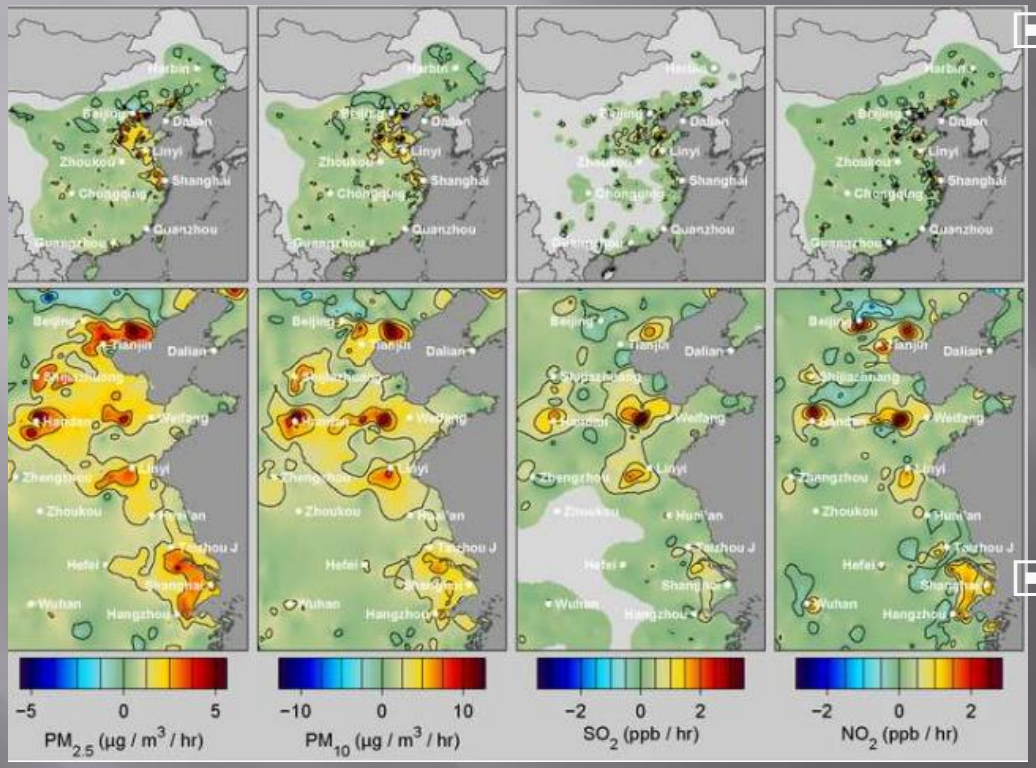

- E.g. CFC

# Lakes and Rivers

# Transport Routes

- Atmospheric Transport
- Water Transport
- Biovectors

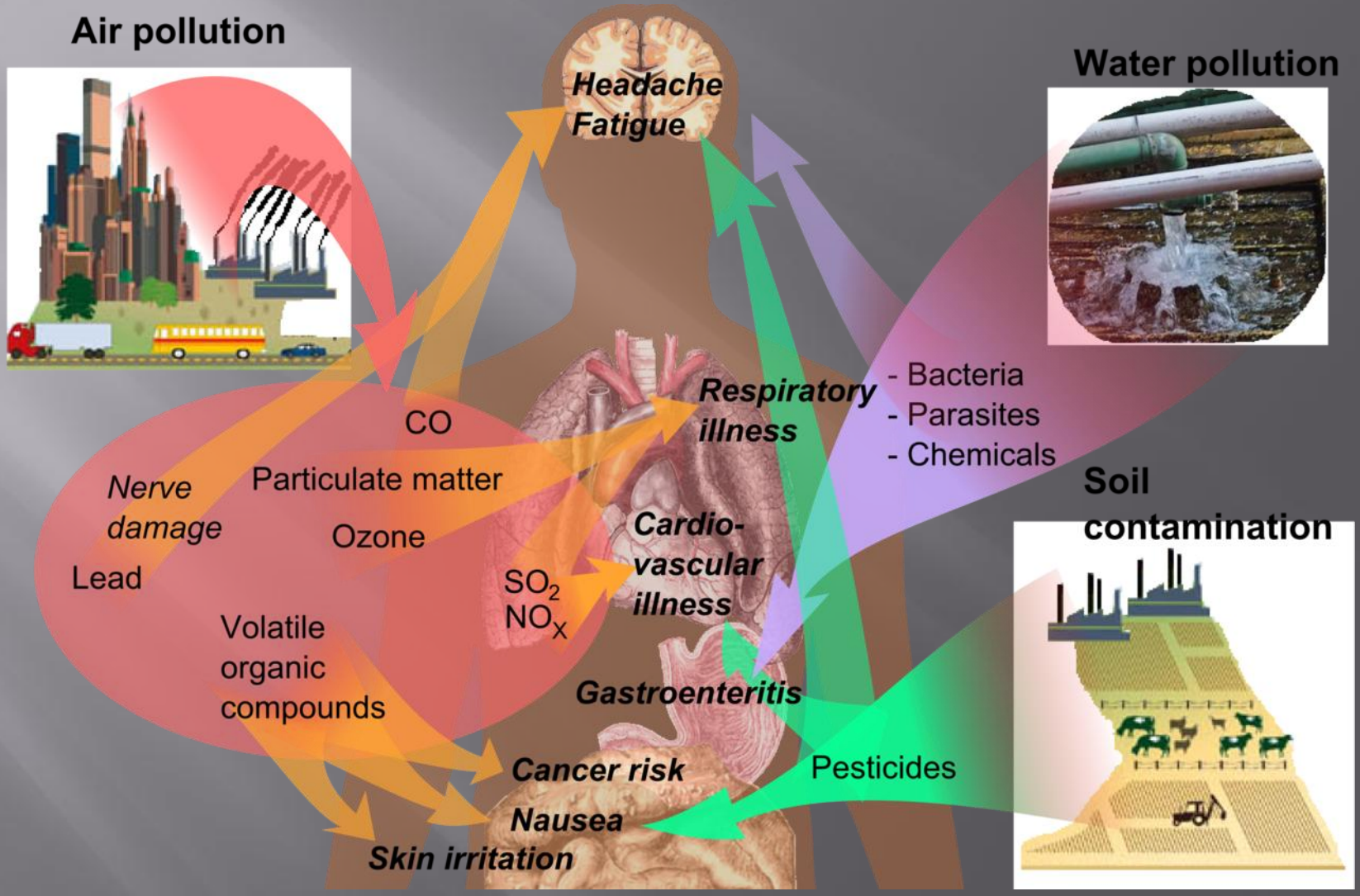

# Why Bother with all this?




- Air pollution in China kills 1.6 million per year
  - That's 4400 a day or 3 per minute
- UK 1952 'Great Smog' killed 4000 people in London >100'000 ill

Air Pollution in China: Mapping of Concentrations and Sources Robert A. Rohde , Richard A. Muller

# Heath Effects




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

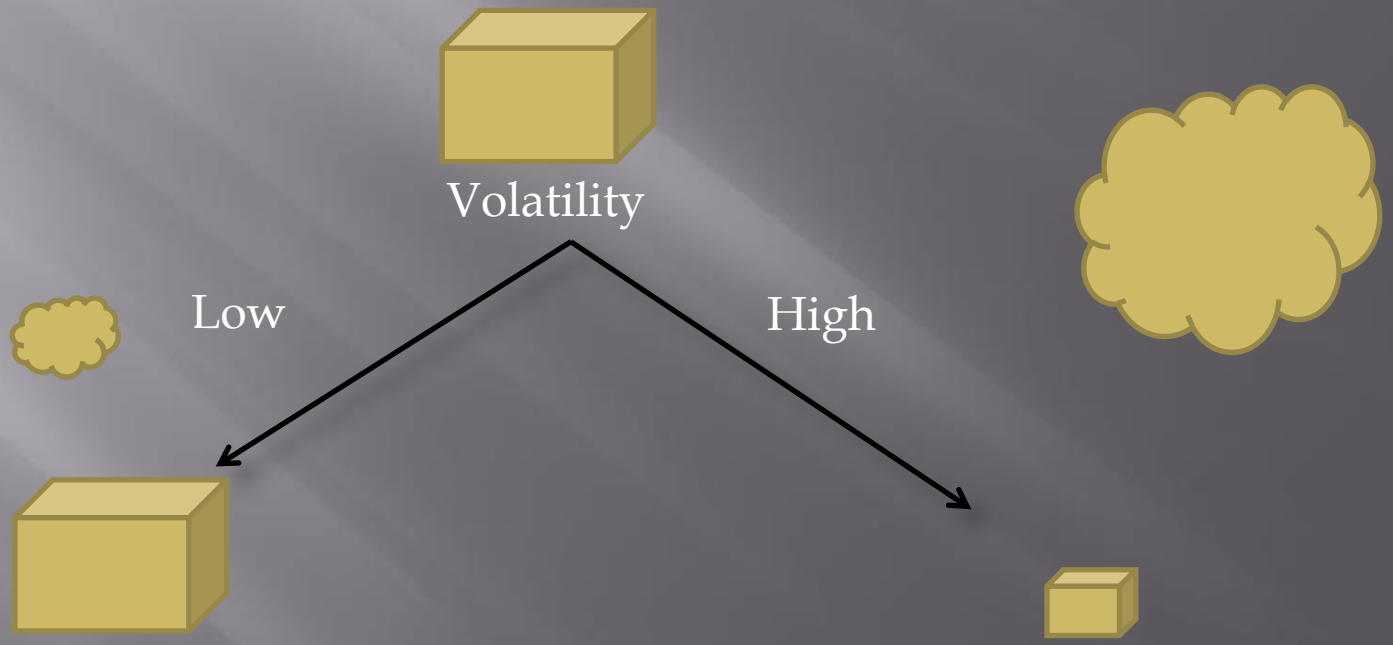
# Chemical Factors

- 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

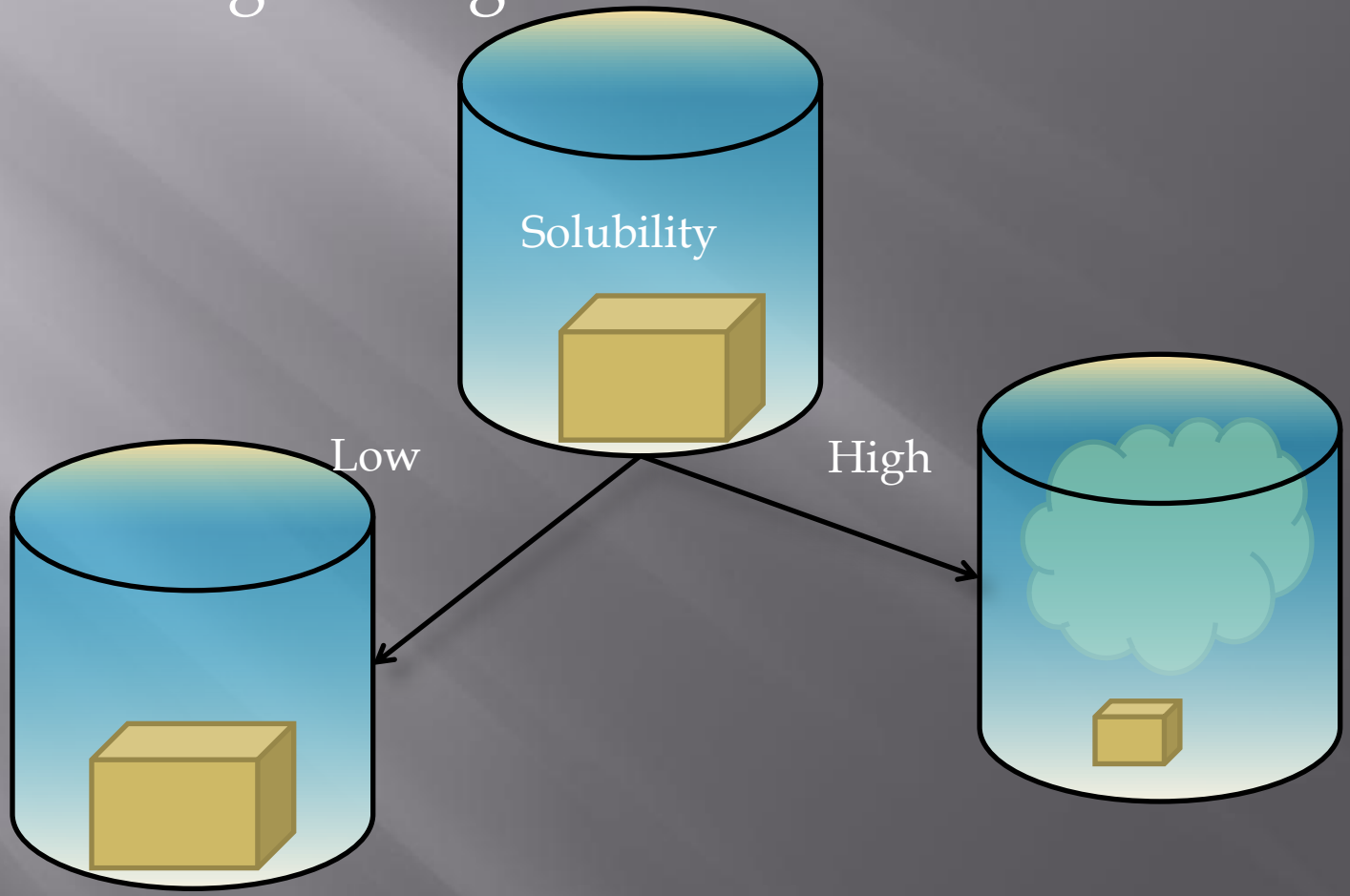
# Mass Balance

- What goes in goes where

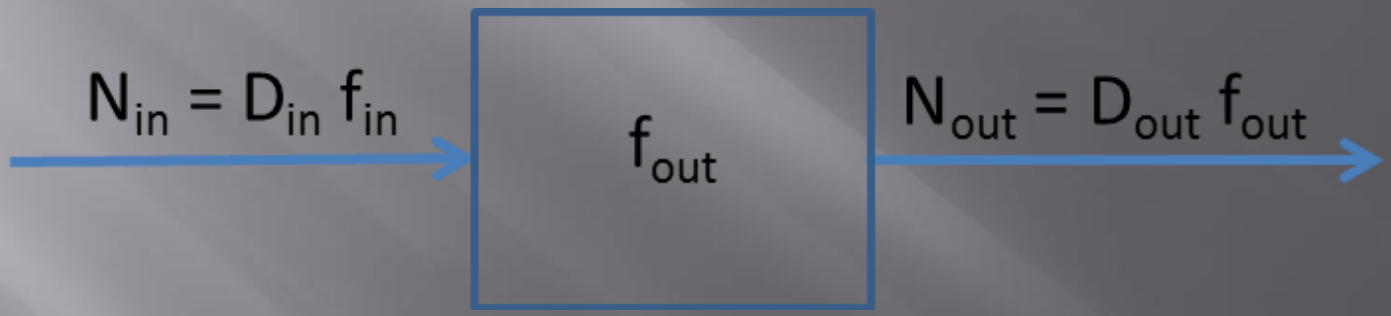


# Mass Balance

- What goes in goes where



# Fugacity Models



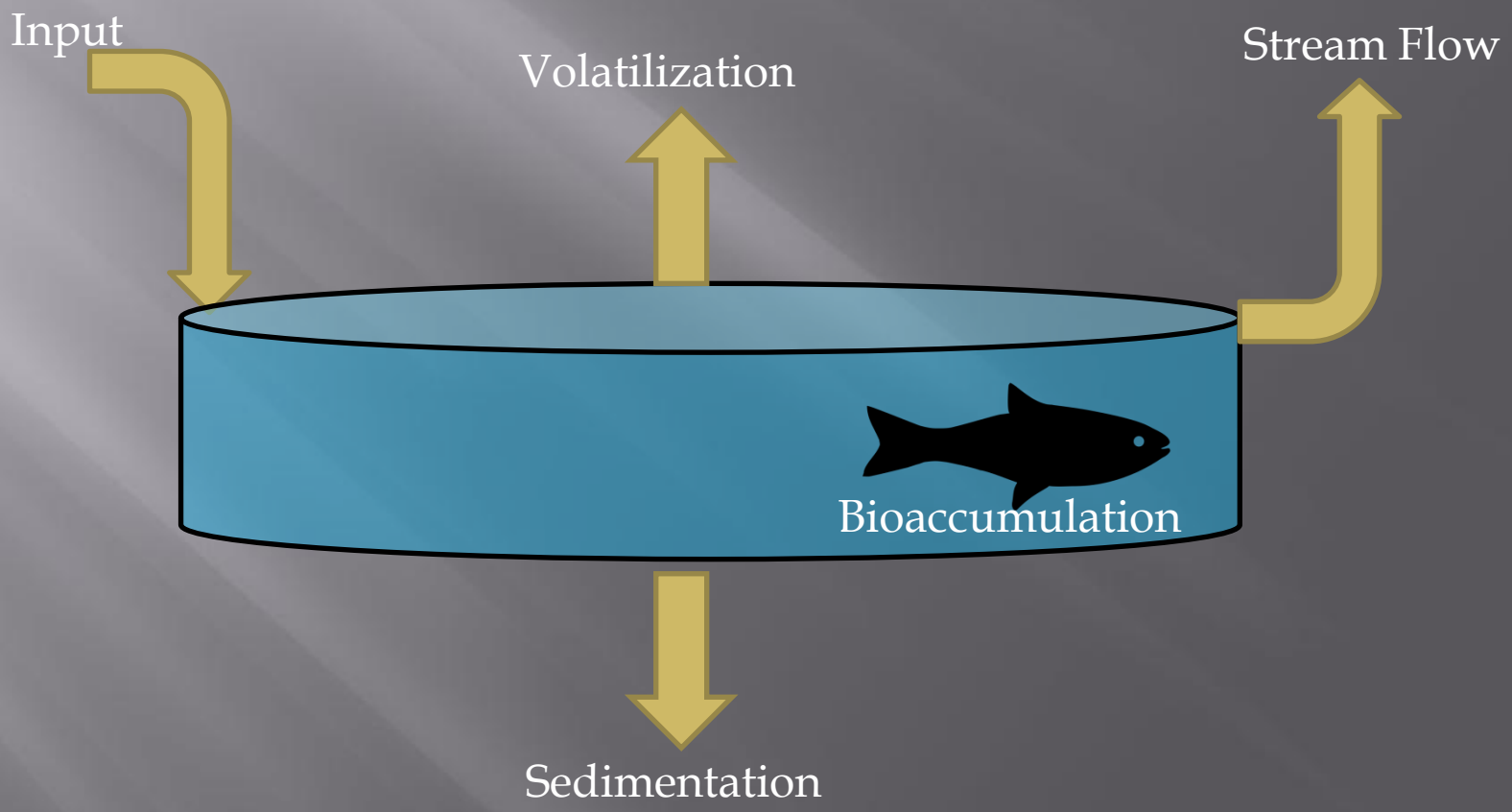

- D is a transport parameter based on rate of flow or diffusion (mol $Pa^{-1}$ $h^{-1}$)
- f is the fugacity (Pa) of the chemical in question

Macdonald et al, 2002, Wania 1999

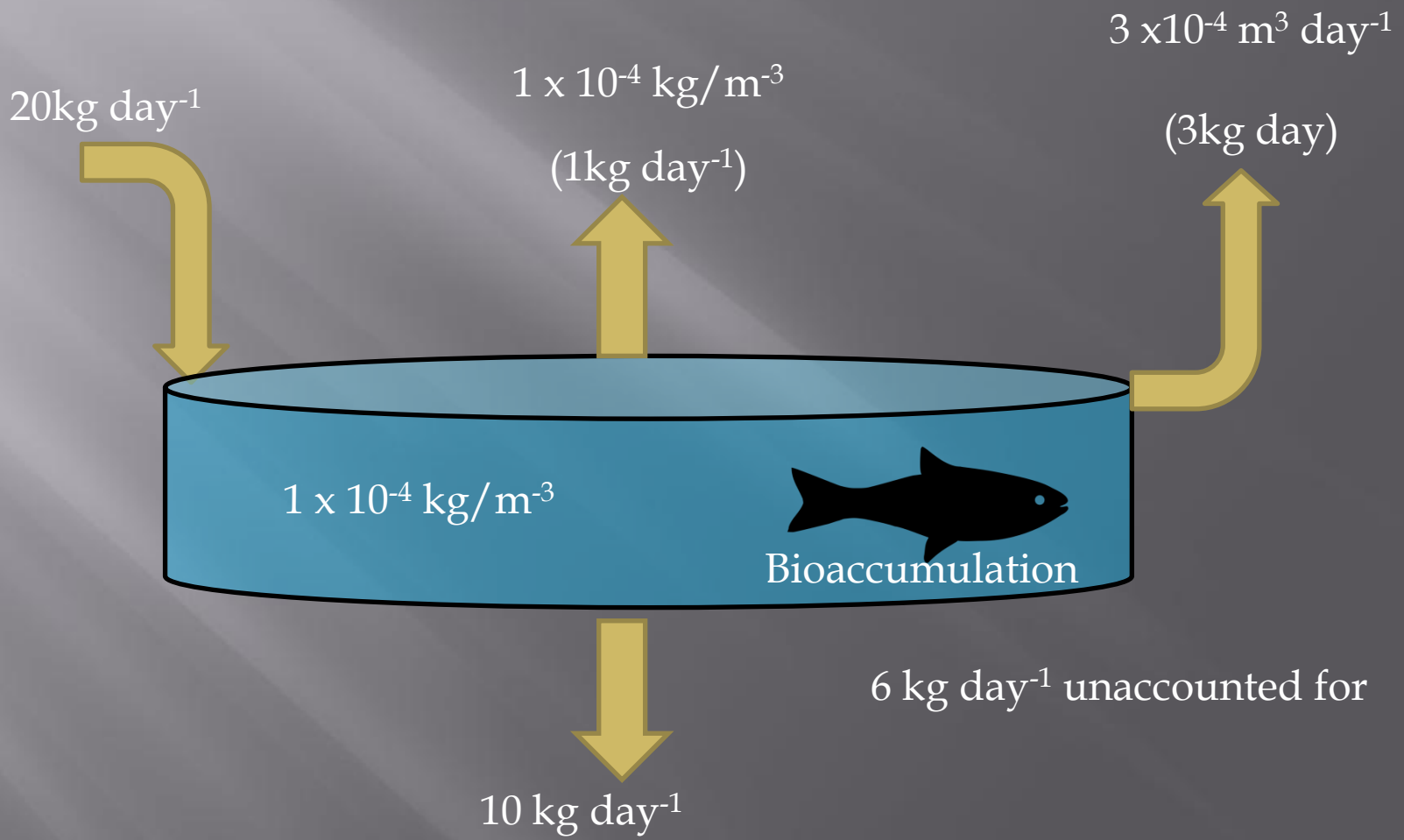
# Example

- Rate of change in a system =
  - + Mass of compound in
  - -Mass Transport out
  - -Breakdown

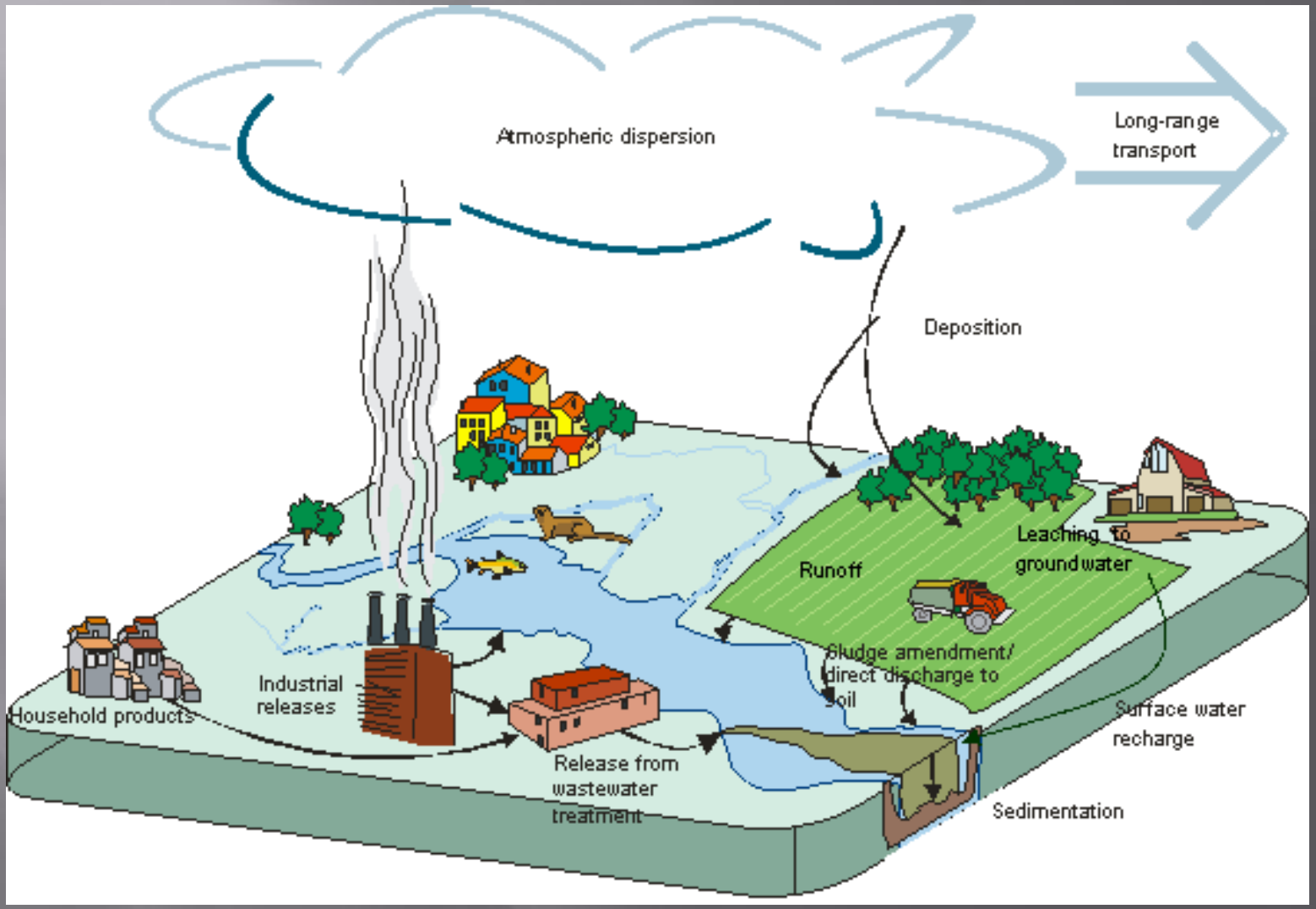
# So for an Lake system



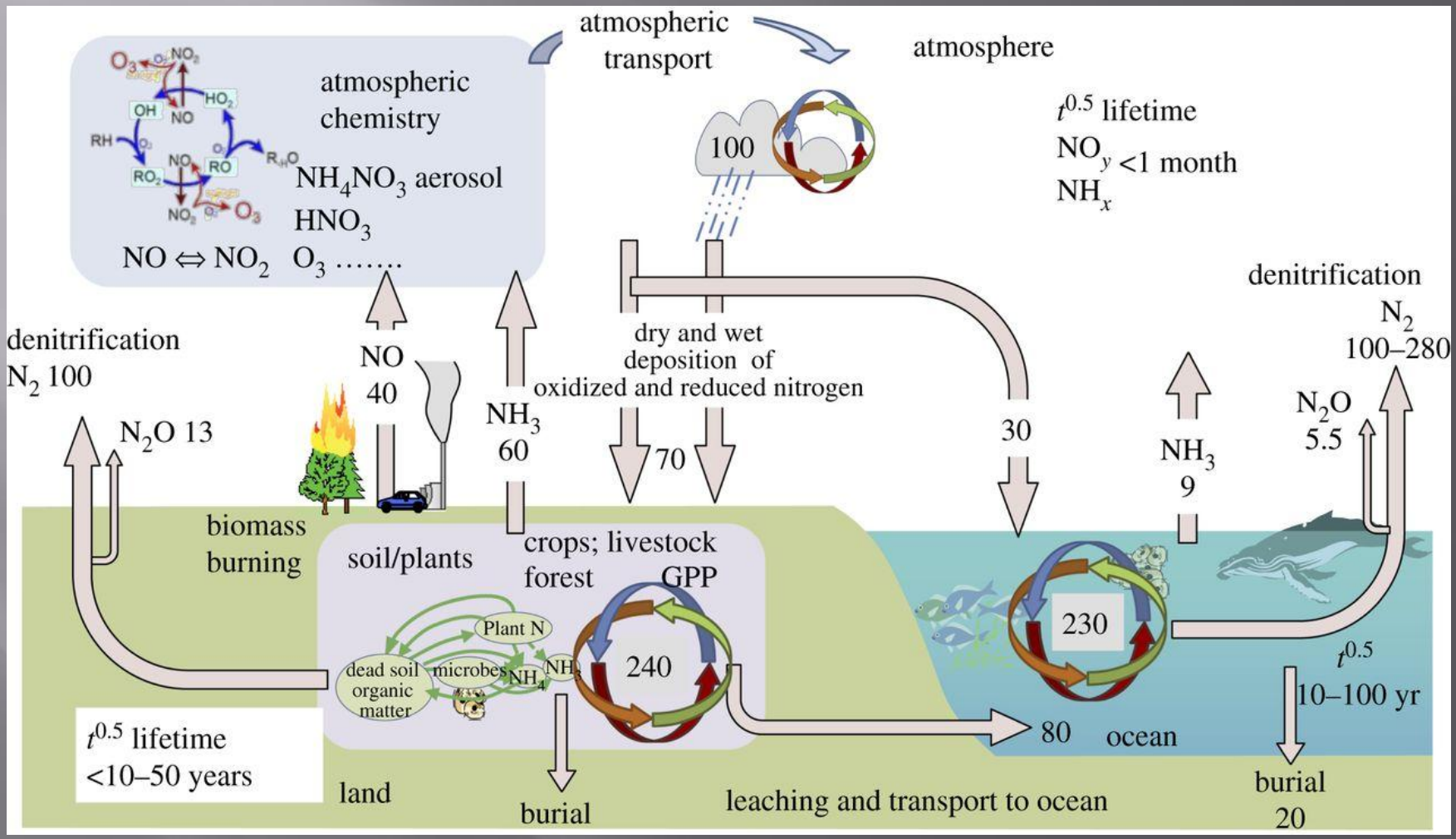
# So for an Lake system



# It's a bit more complicated

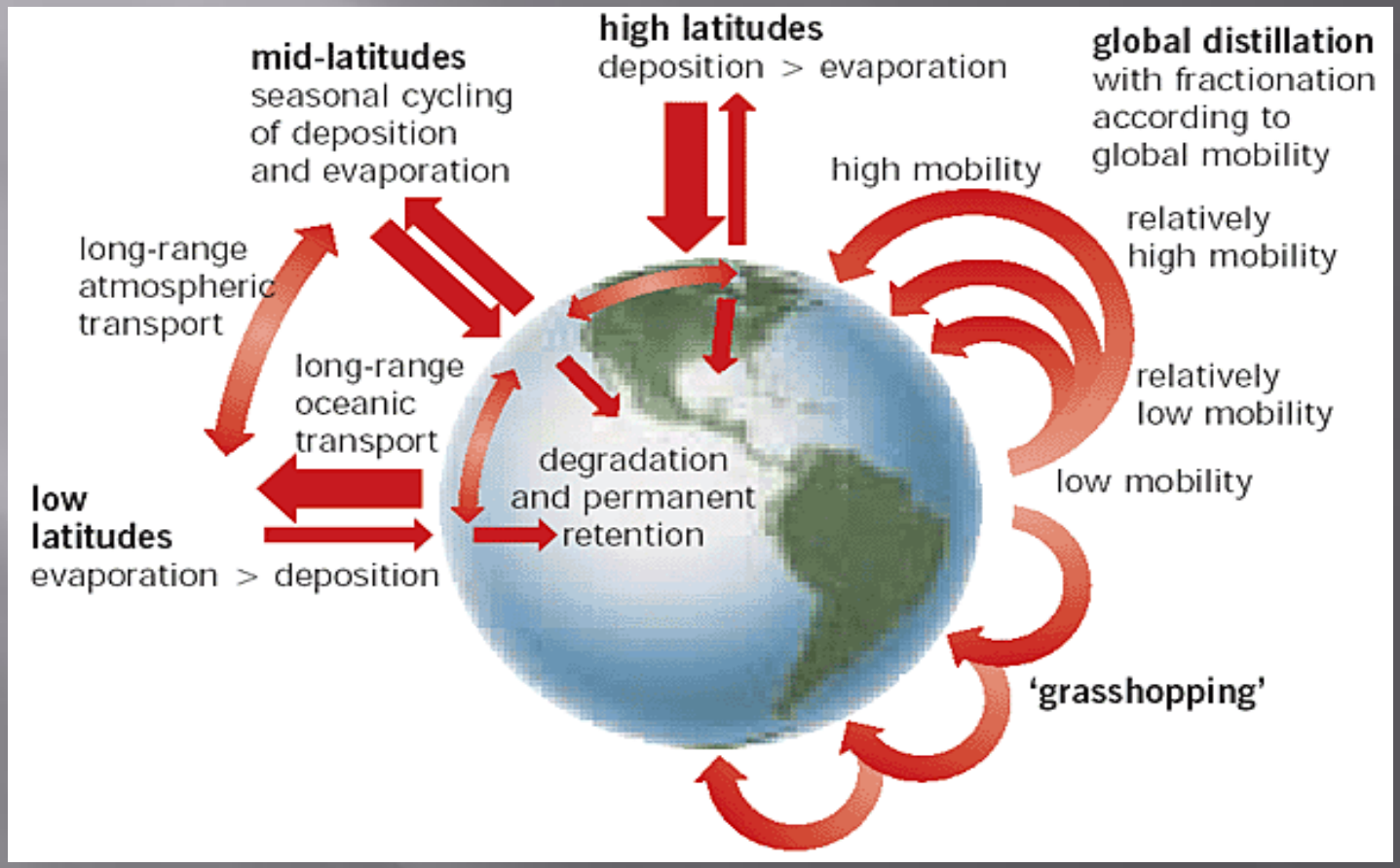


# NO global model

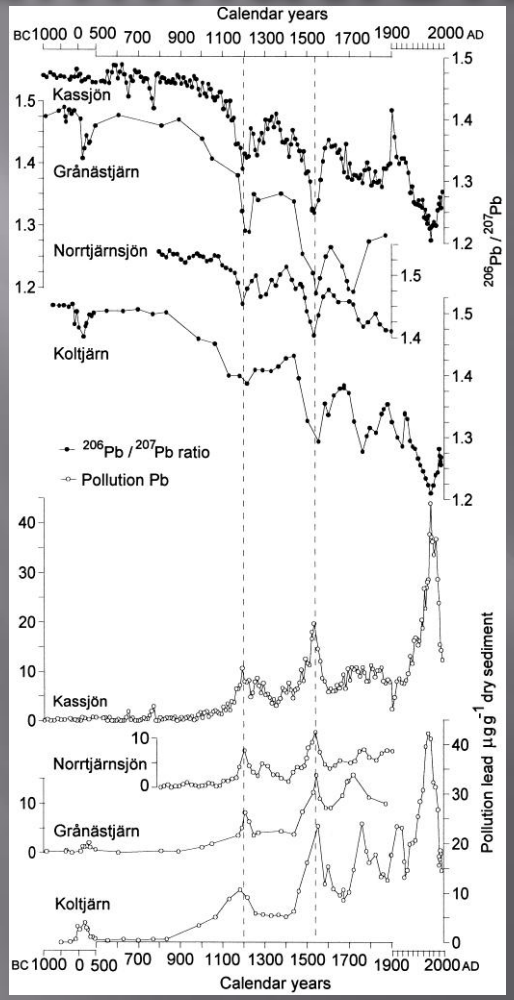


# Environmental Air Transport


# Atmospheric Transport



# Air Contamination is not new



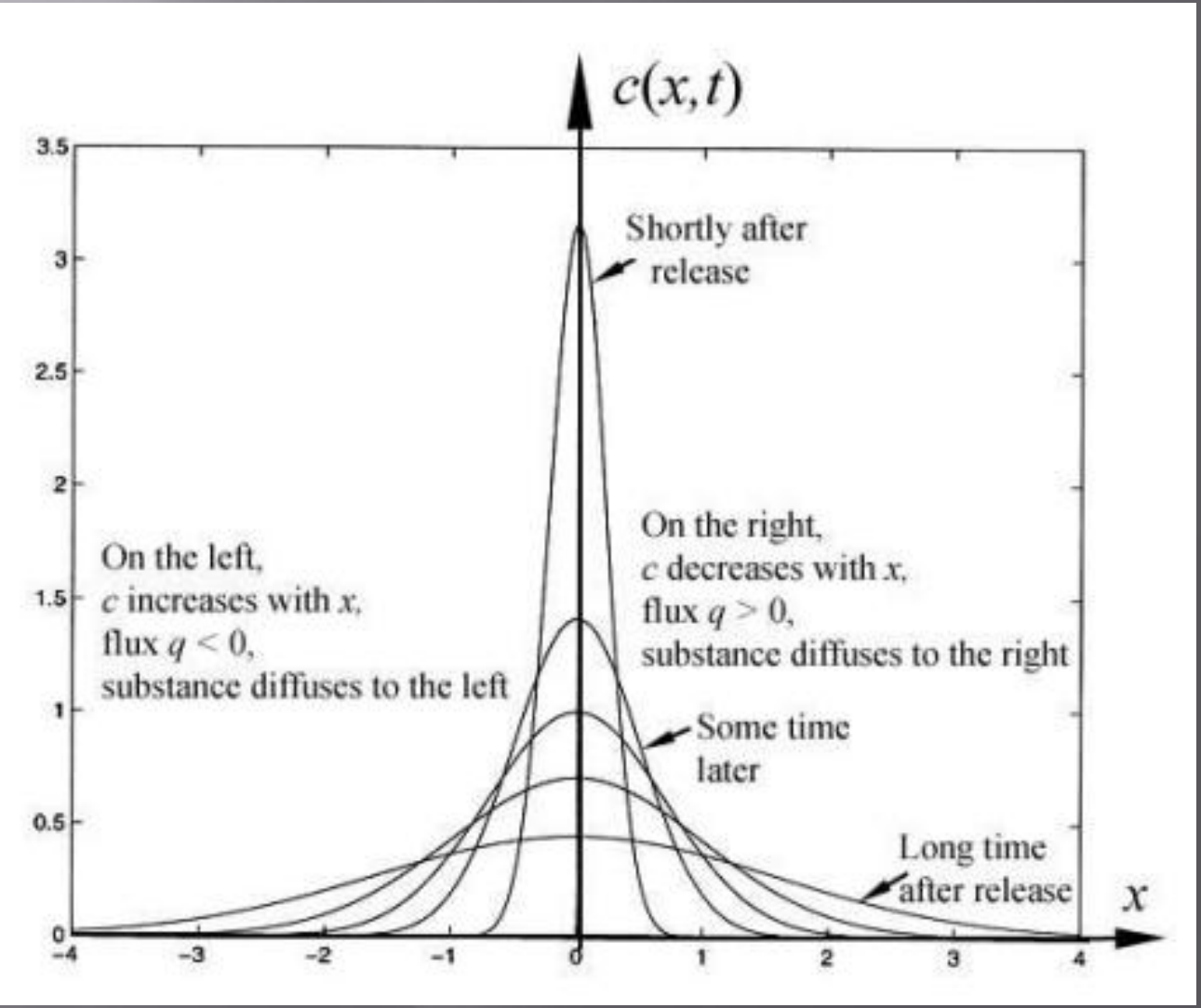

Published in: Maja-Lena Brännvall; Richard Bindler; Ingemar Renberg; Published in: Ove Emteryd; Published in: Jerzy Bartnicki; Published in: Kjell Billström;
*Environ. Sci. Technol.* **1999,** 33, 4391-4395.
DOI: 10.1021/es990279n

# National Air Quality Standards

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

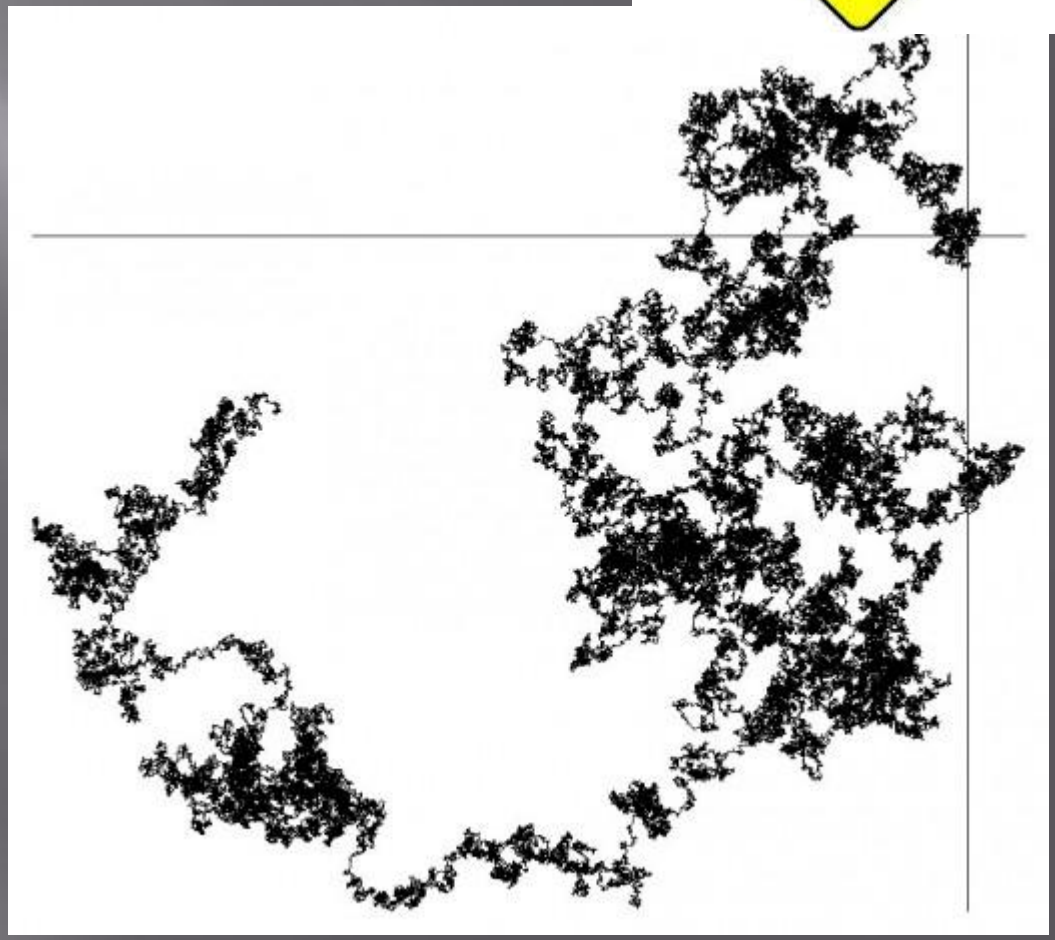
The six chemicals designated as criteria pollutants by the US Environmental Protection Agency and the corresponding National Ambient Air Quality Standards.

# Diffusion


c(x,t)
3.5
3
2.5
2
1.5
1
0.5
0
−4
−3
−2
−1
0
1
2
3
4
x
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

# 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

# Simple Example

25%

25%

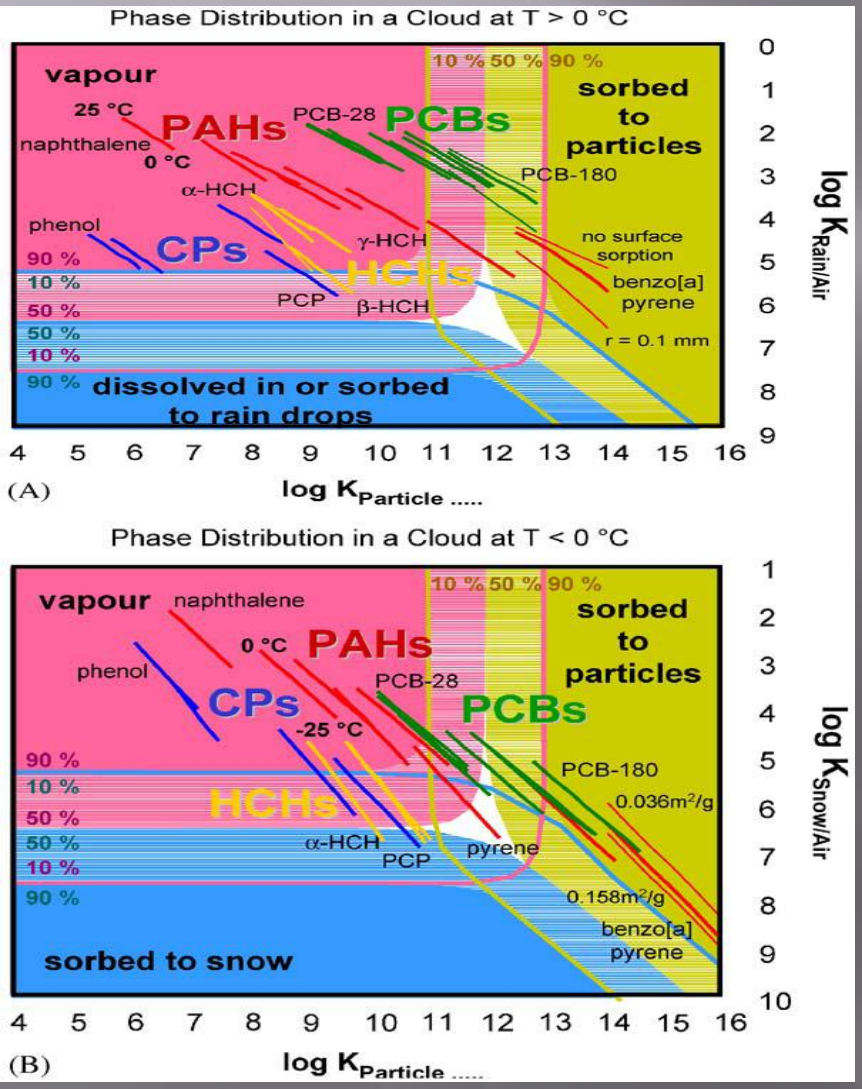
50%

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

# 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 |

# Snow/Rain Partitioning

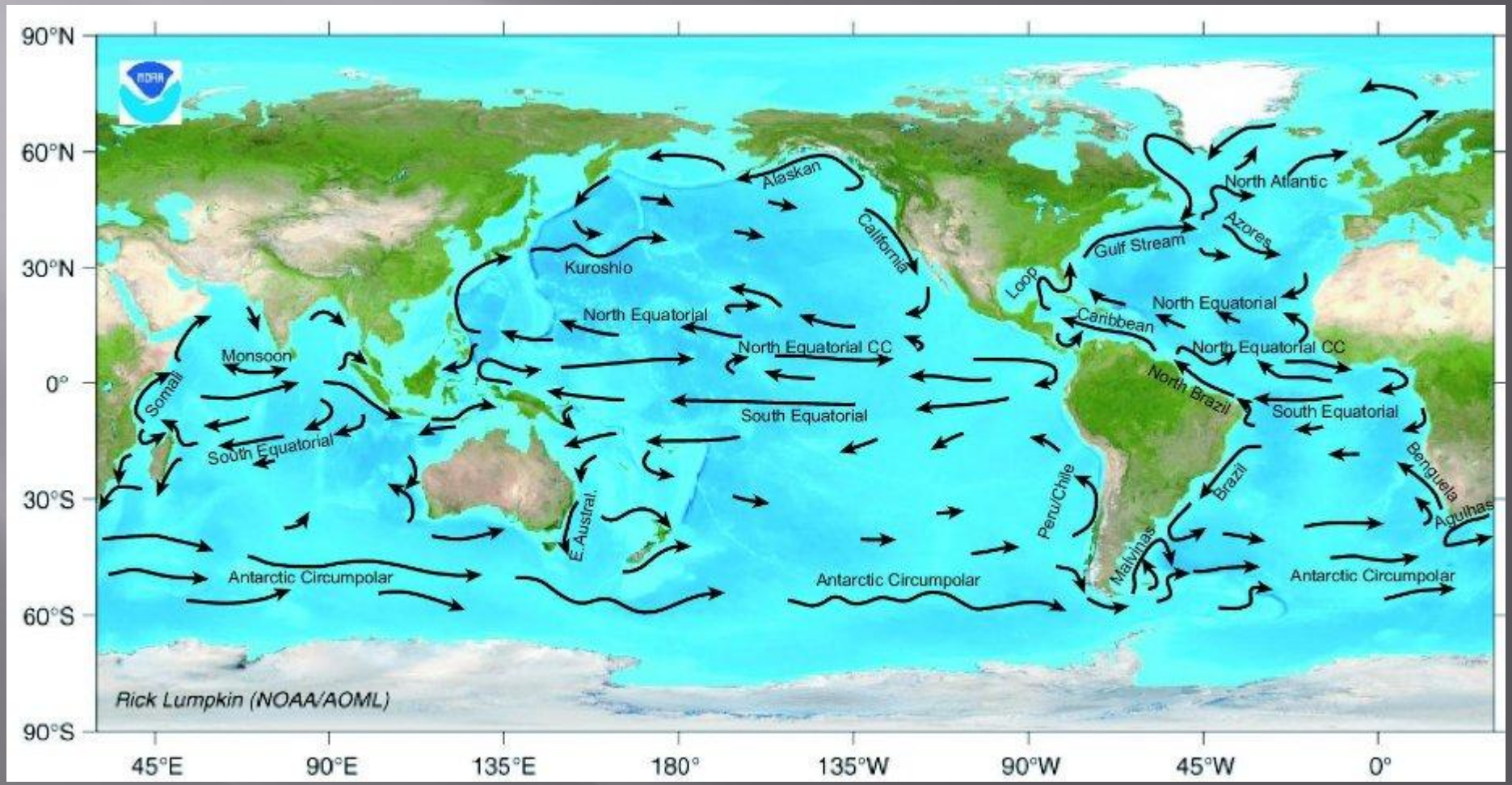



- Different chemicals disperse into different phases
- Rain and Snow generate different partitioning
- How chemicals will fall out will change with seasonality

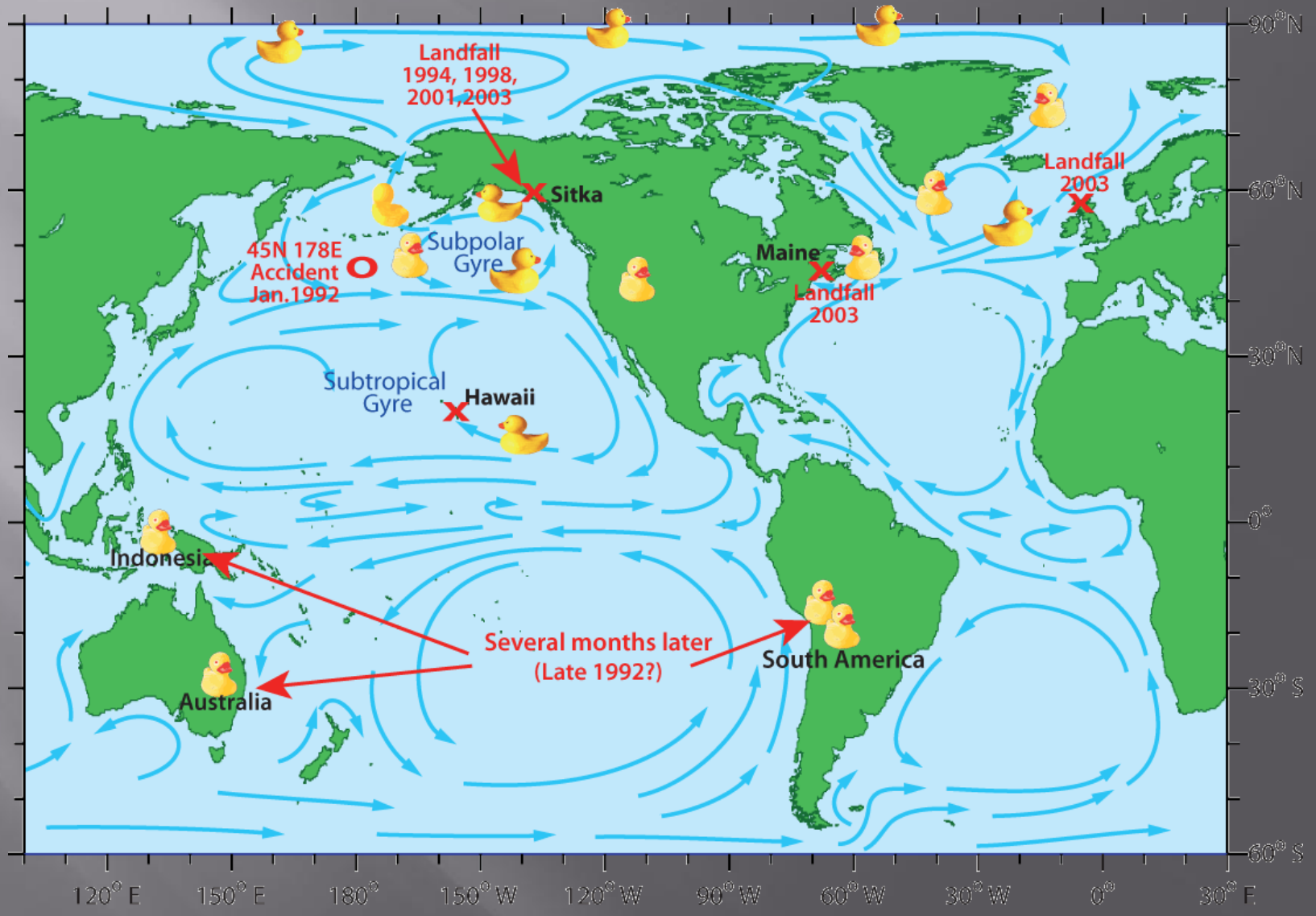
Lei and Wania 2004

# Water Transport

# Surface Circulation



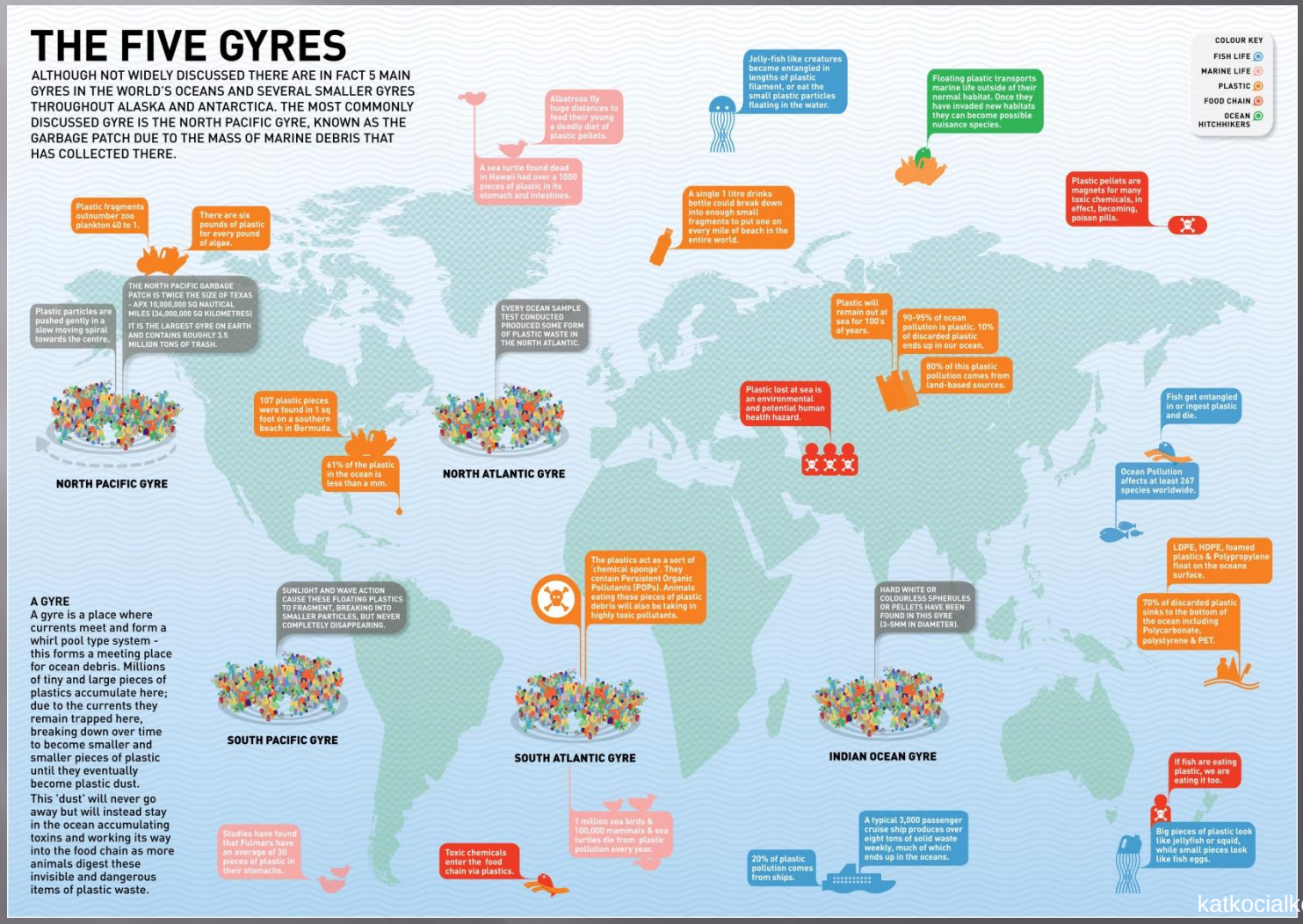
# The Great Rubber Duck Escape



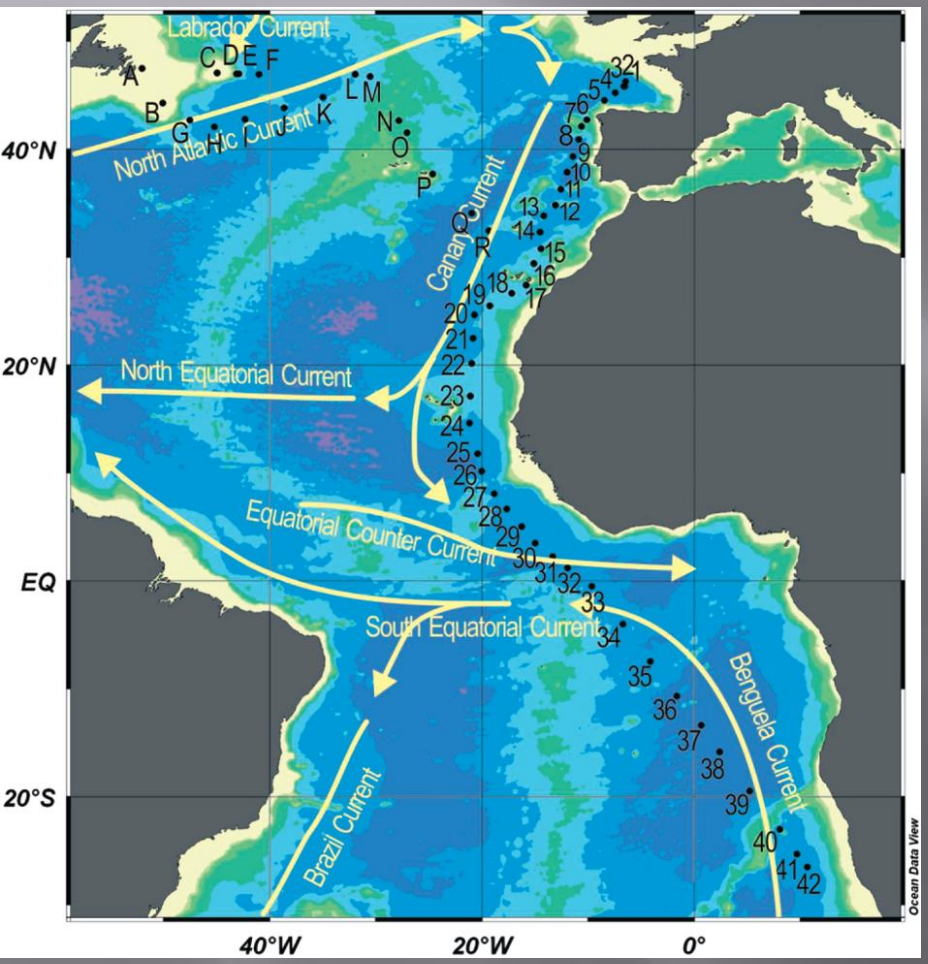
# The Nike Run

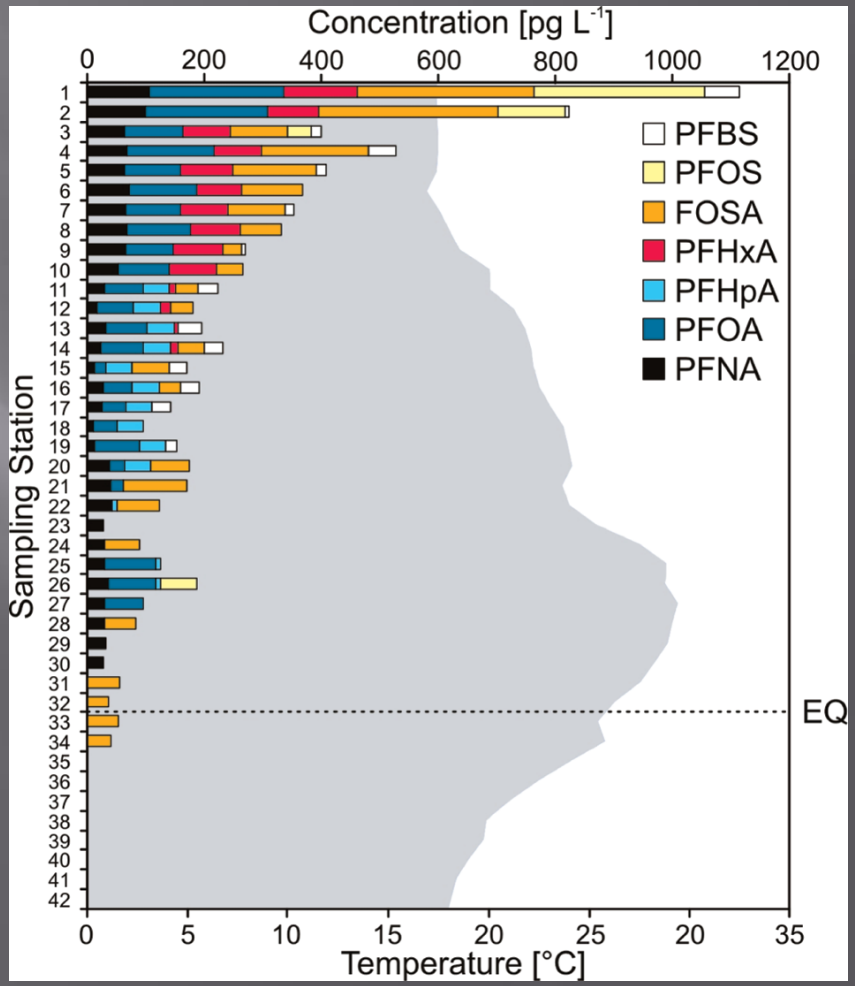

Alaska Current
Queen Charlotte Island
Vancouver Island
OREGON
Accident May 1990
Landfall New Year 1991
North Pacific Current
NORTH PACIFIC OCEAN
California Current
Landfall Summer 1992
Hawaii
North Equatorial Current
60° N
30° N
0°
180° W
150° W
120° W

# Macro Contaminants



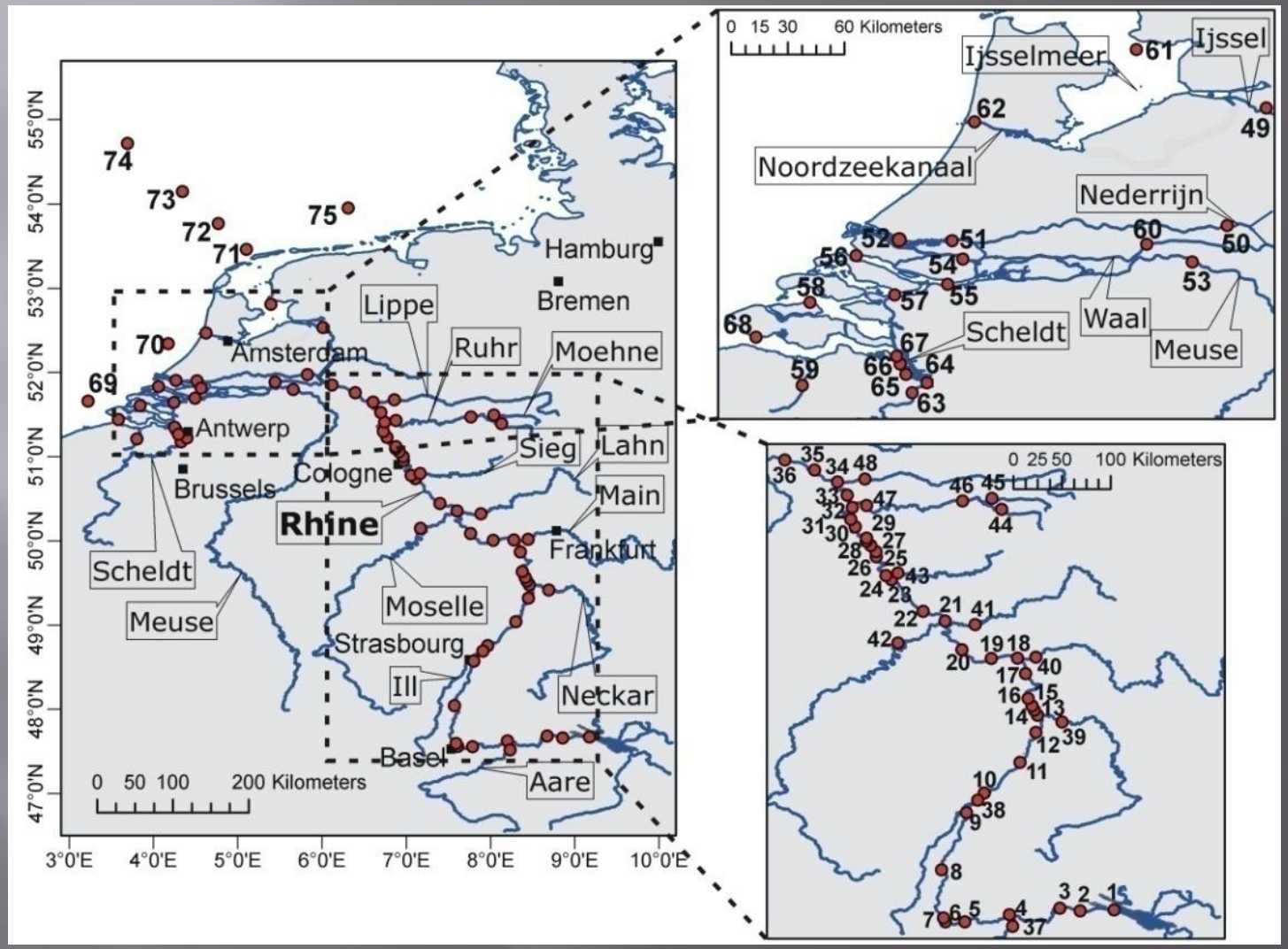
# Ocean Water PFCs



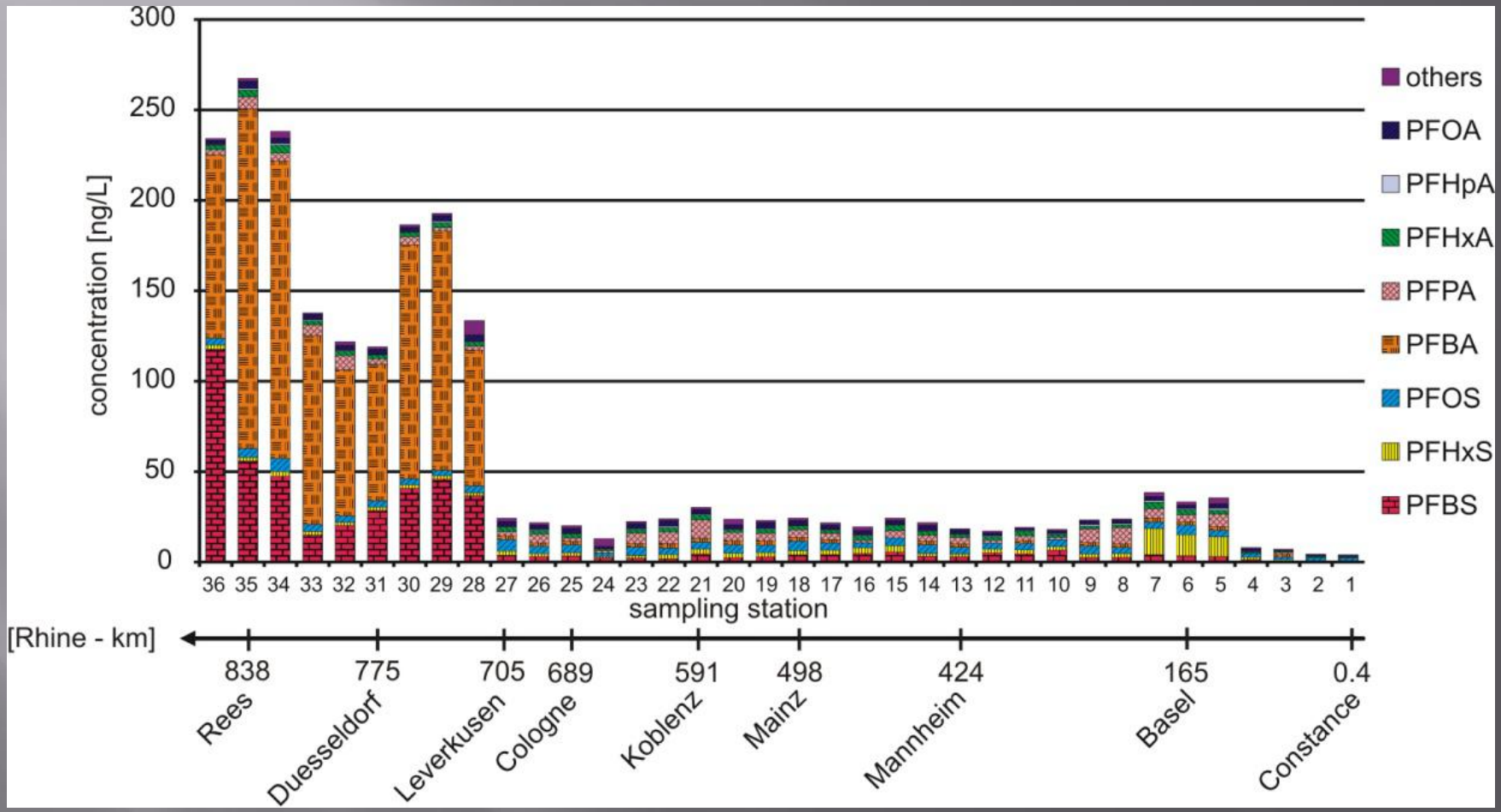

Ahrens Et al

# Rivers




Moller et al 2011

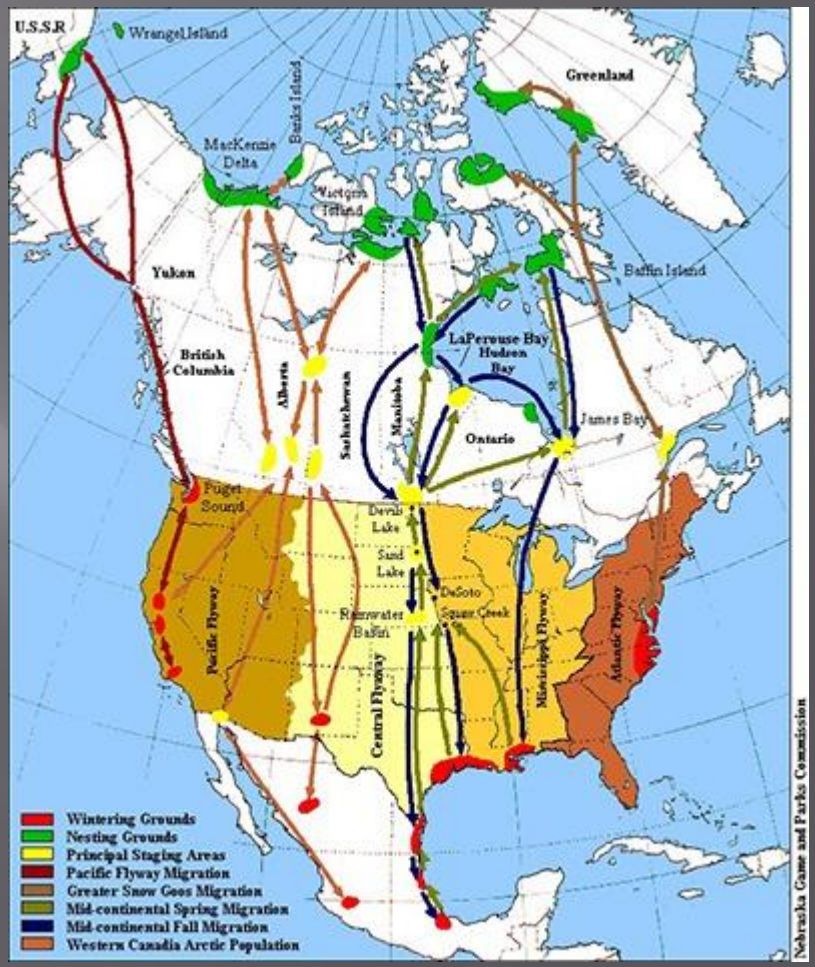
# Rivers




Moller et al 2011

# 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

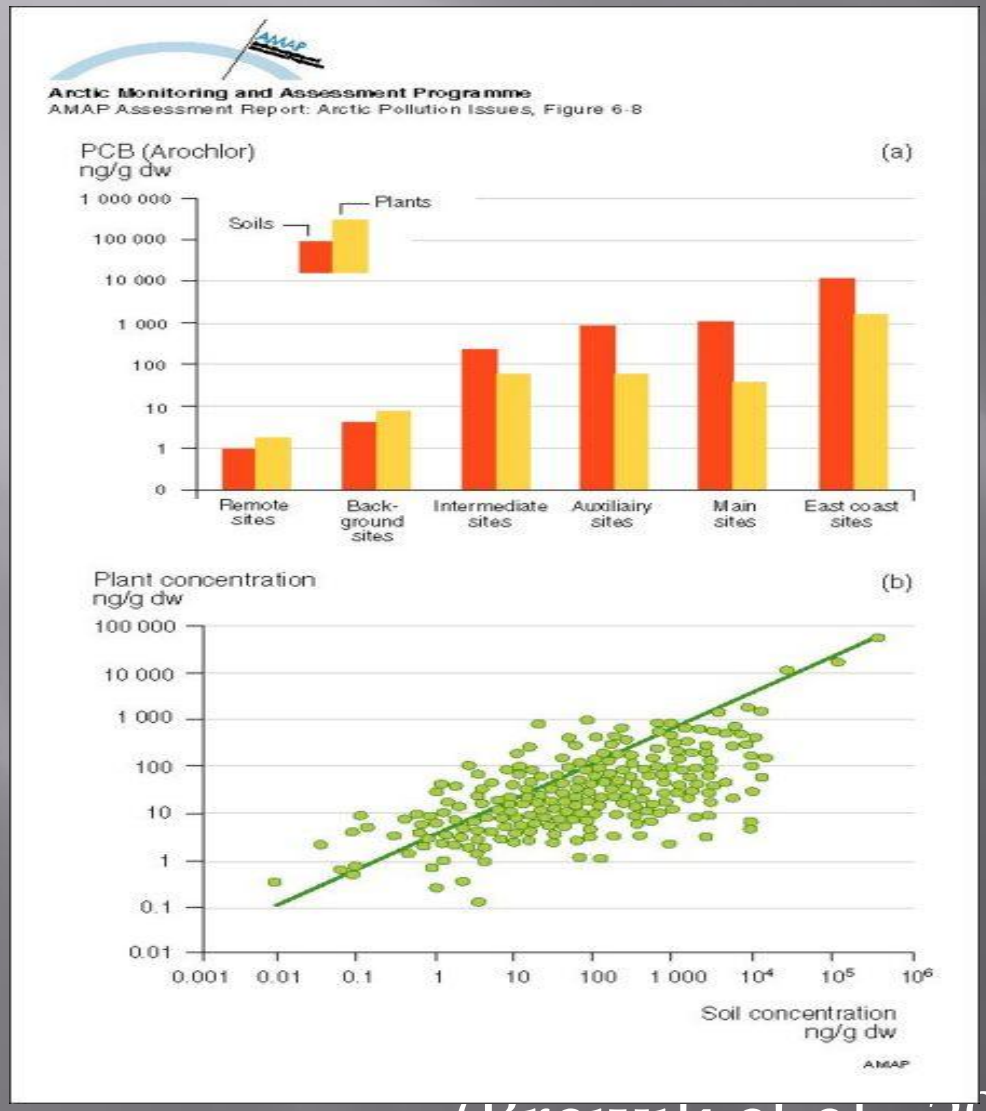
- Annually 20’000 Chinook salmon (*Oncorhynchus tshawytscha*) spawn and die in the Credit River,
- Passive water monitoring devices (SPMDs, (semi-permeable membranes devices)
- ~75g of ∑PCBs and 25g of DDT to the river over a few weeks


O’Toole et al 2005

# Transport Halo

- DEW sites (distance early warning)

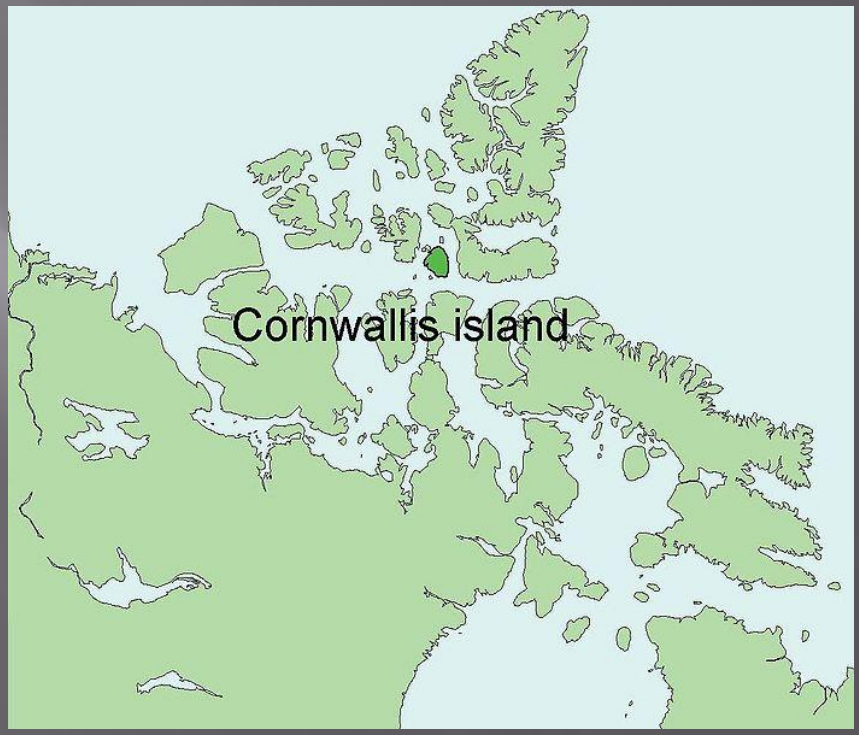
# PCB Halo

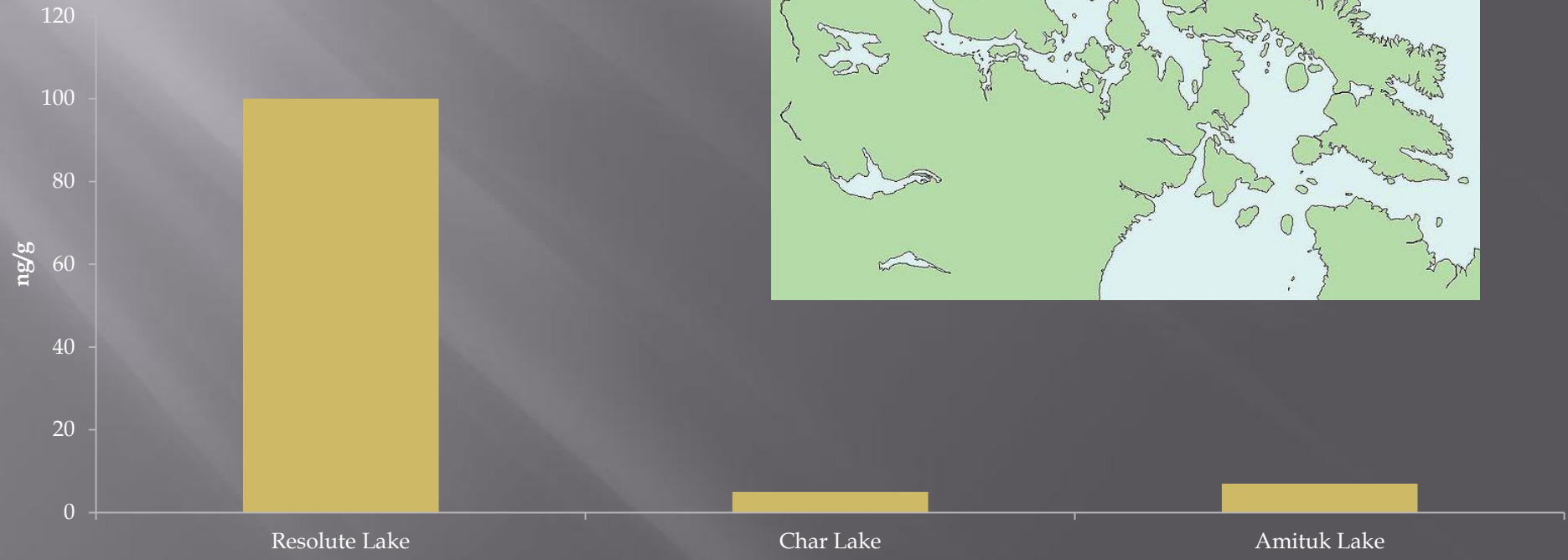



- ~119 kg of PCB waste dumped
- 42 sites


(Breivik et al., 2004 Stow et al., 2005).

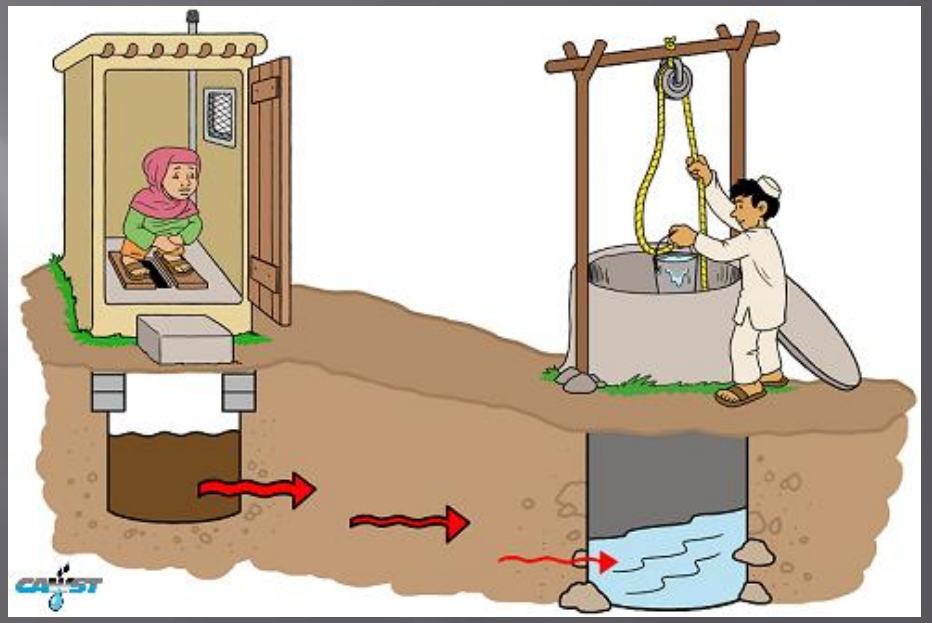
# PFCs and Airports

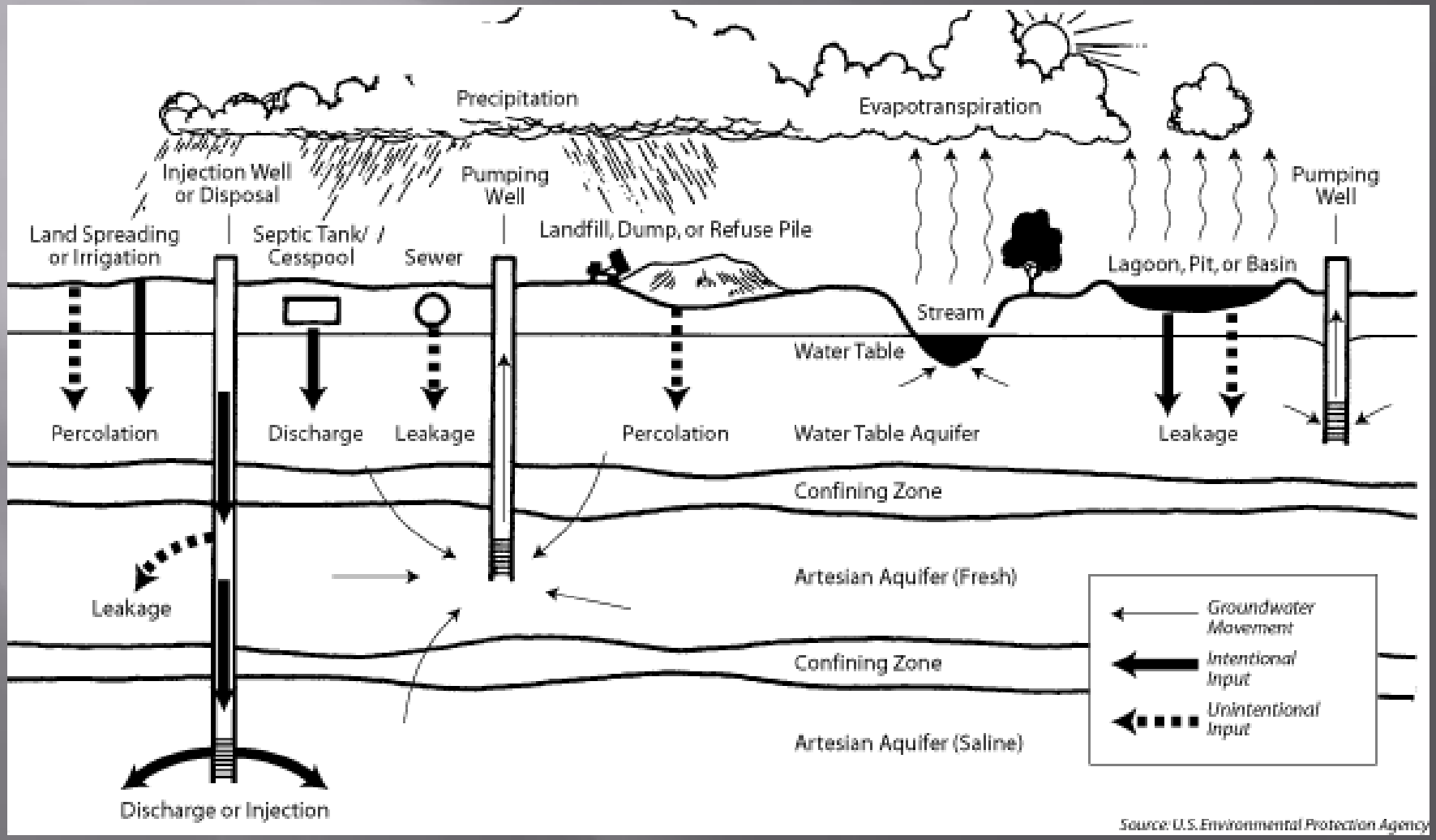



# Groundwater

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

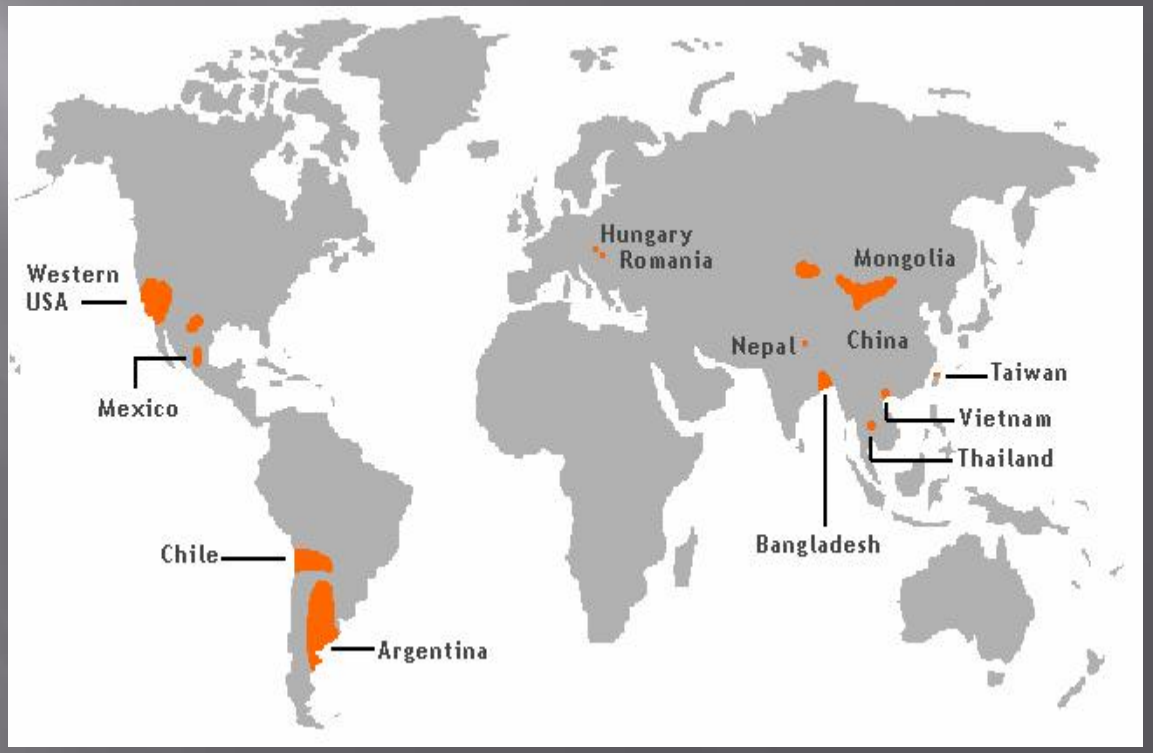


# Contamination of Groundwater



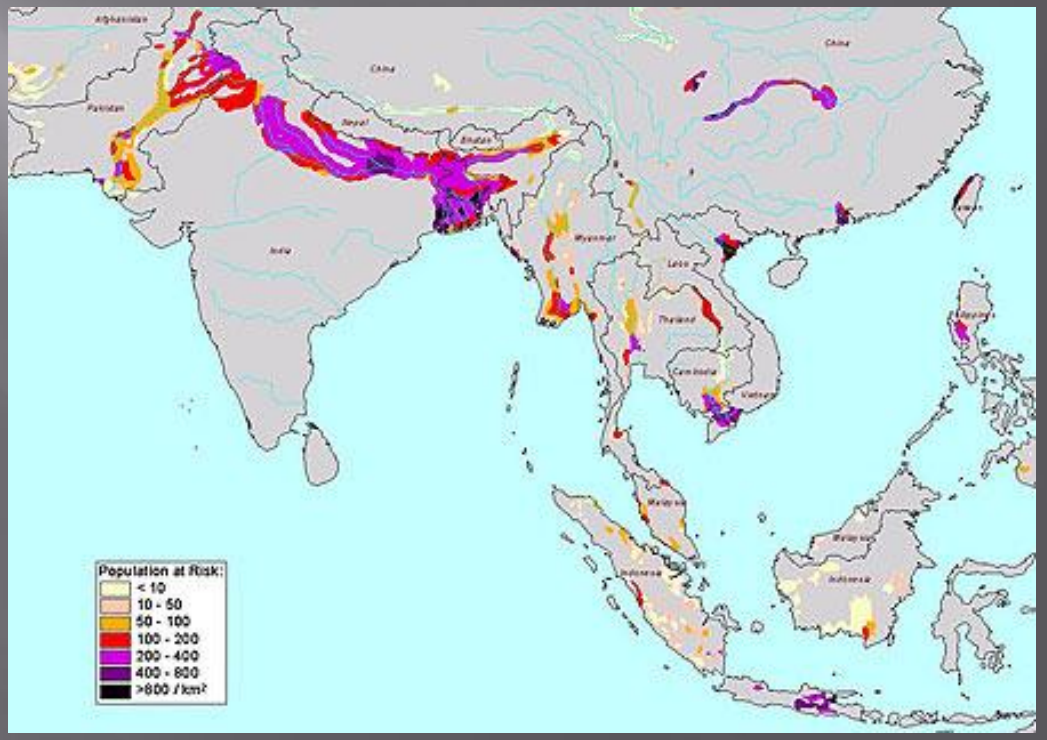
# Arsenic groundwater

- 100 million people at risk



# Bangladesh at Risk

- 95% of people in at risk



# Arsenic In India

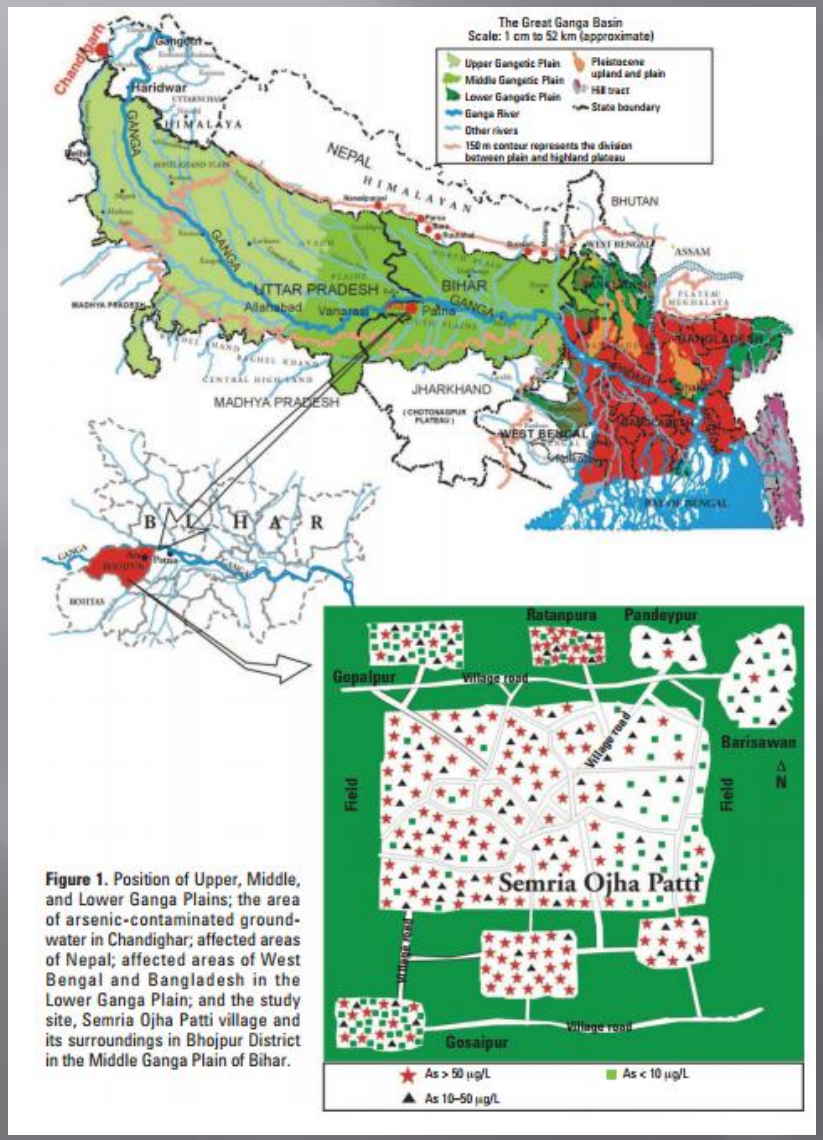



**Figure 1.** Position of Upper, Middle, and Lower Ganga Plains; the area of arsenic-contaminated groundwater in Chandighar; affected areas of Nepal; affected areas of West Bengal and Bangladesh in the Lower Ganga Plain; and the study site, Semria Ojha Patti village and its surroundings in Bhojpur District in the Middle Ganga Plain of Bihar.

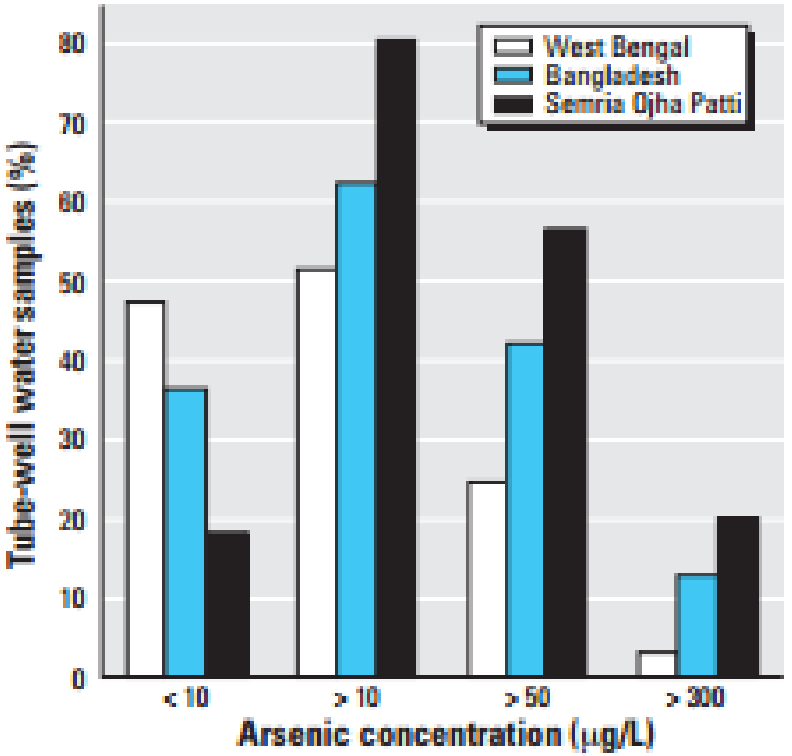



**Figure 2.** Arsenic concentrations in the tube wells of Semria Ojha Patti village ($n$ = 206) compared with the arsenic-affected areas of West Bengal ($n$ = 99,520) and Bangladesh ($n$ = 29,200).

# Effects of Arsenic

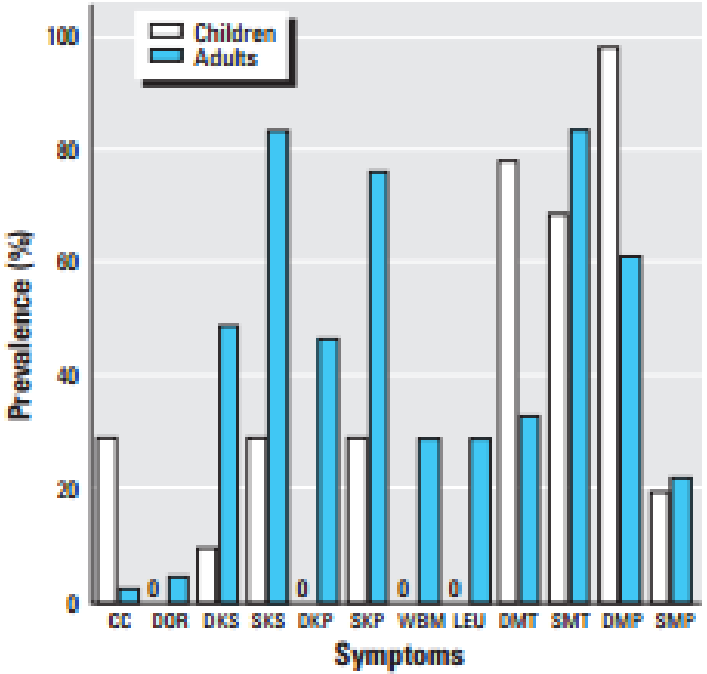



**Figure 4.** Comparative prevalence of dermatologic involvement manifested by the arsenic-affected adults ($n$ = 50) and children ($n$ = 10) of Semria Ojha Patti village. Abbreviations: CC, conjunctival congestion; DKP, diffuse keratosis on palm; DKS, diffuse keratosis on sole; DMP, diffuse melanosis on palm; DMT, diffuse melanosis on trunk; DOR, dorsal keratosis; LEU, leuco-melanosis (white spots with some black); SKP, spotted keratosis on palm; SKS, spotted keratosis on sole; SMP, spotted melanosis on palm; SMT, spotted melanosis on trunk; WBM, whole-body melanosis.

**Figure 3.** Subject from Semria Ojha Patti village with the full panoply of arsenical skin lesions, including hyperkeratosis, suspected Bowen's disease, and nonhealing ulcers (suspected cancer).

# Urine Contamination by Arsenic

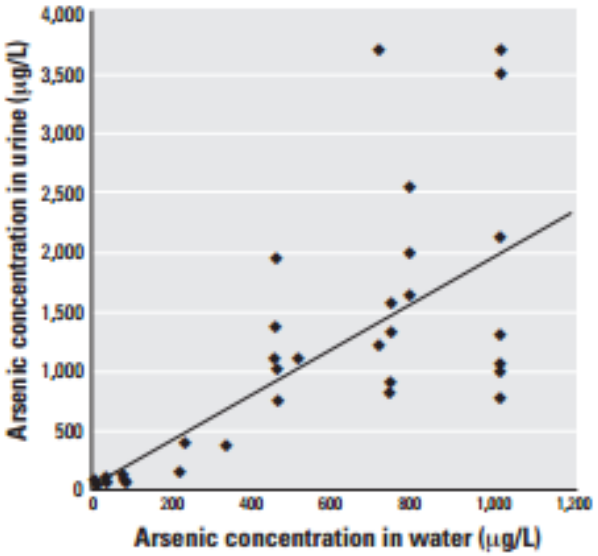



**Figure 5.** Correlation between arsenic concentrations in urine and drinking water. Mean = 798.6 µg/L; median = 387 µg/L; minimum = 24 µg/L; maximum = 3,696 µg/L; $Y = 44.3 + (1.9 \times X)$; $R = 0.774$; $n = 51$.

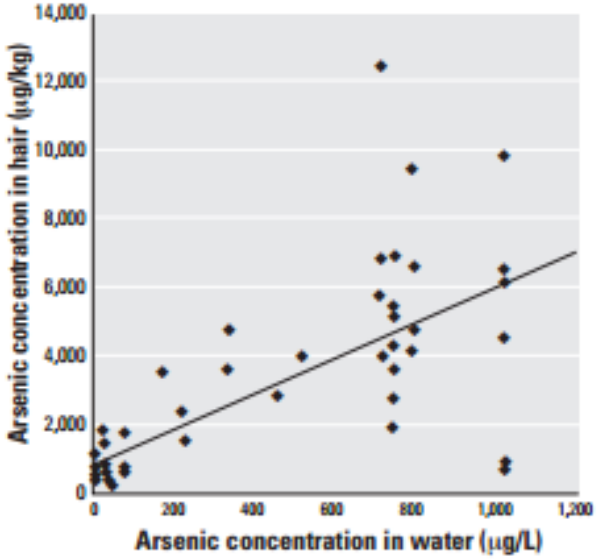



**Figure 6.** Correlation between arsenic concentrations in hair and drinking water. Mean = 2773.8 µg/kg; median = 1,470 µg/kg; minimum = 257 µg/kg; maximum = 12,404 µg/kg; $Y = 858.7 + (5.1 \times X)$; $R = 0.773$; $n = 59$.

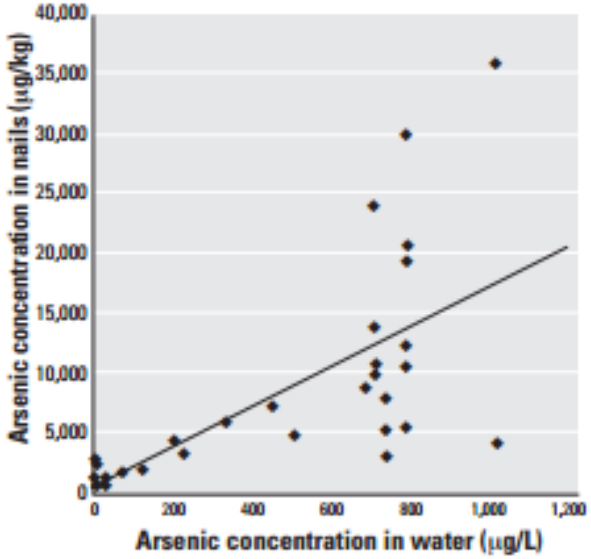



**Figure 7.** Correlation between arsenic concentrations in nails and drinking water. Mean = 6976.9 µg/kg; median = 3601.5 µg/kg; minimum = 453 µg/kg; maximum = 35,790 µg/kg; $Y = 438.4 + (16.7 \times X)$; $R = 0.719$; $n = 38$.

# Impact Effects

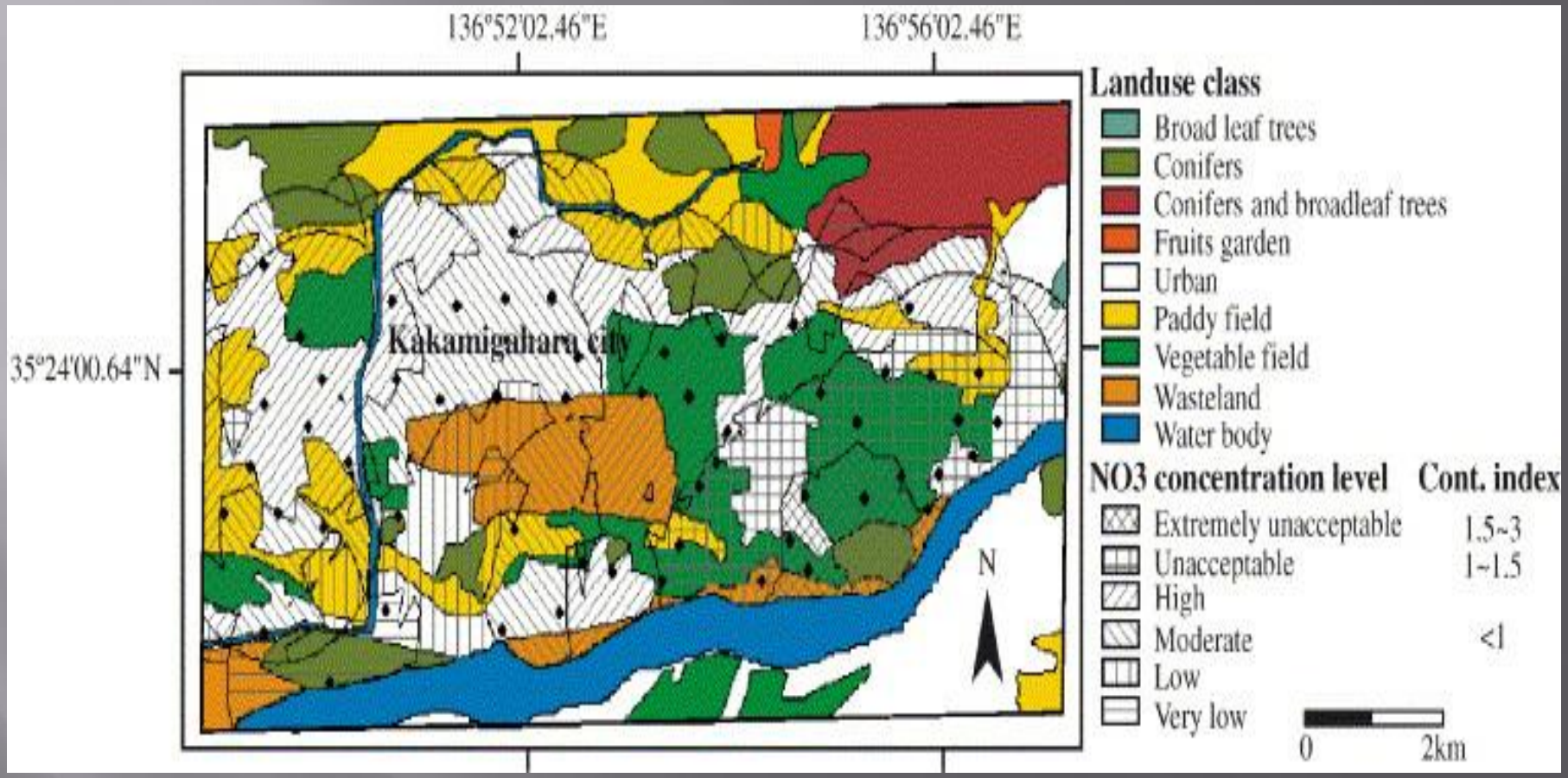
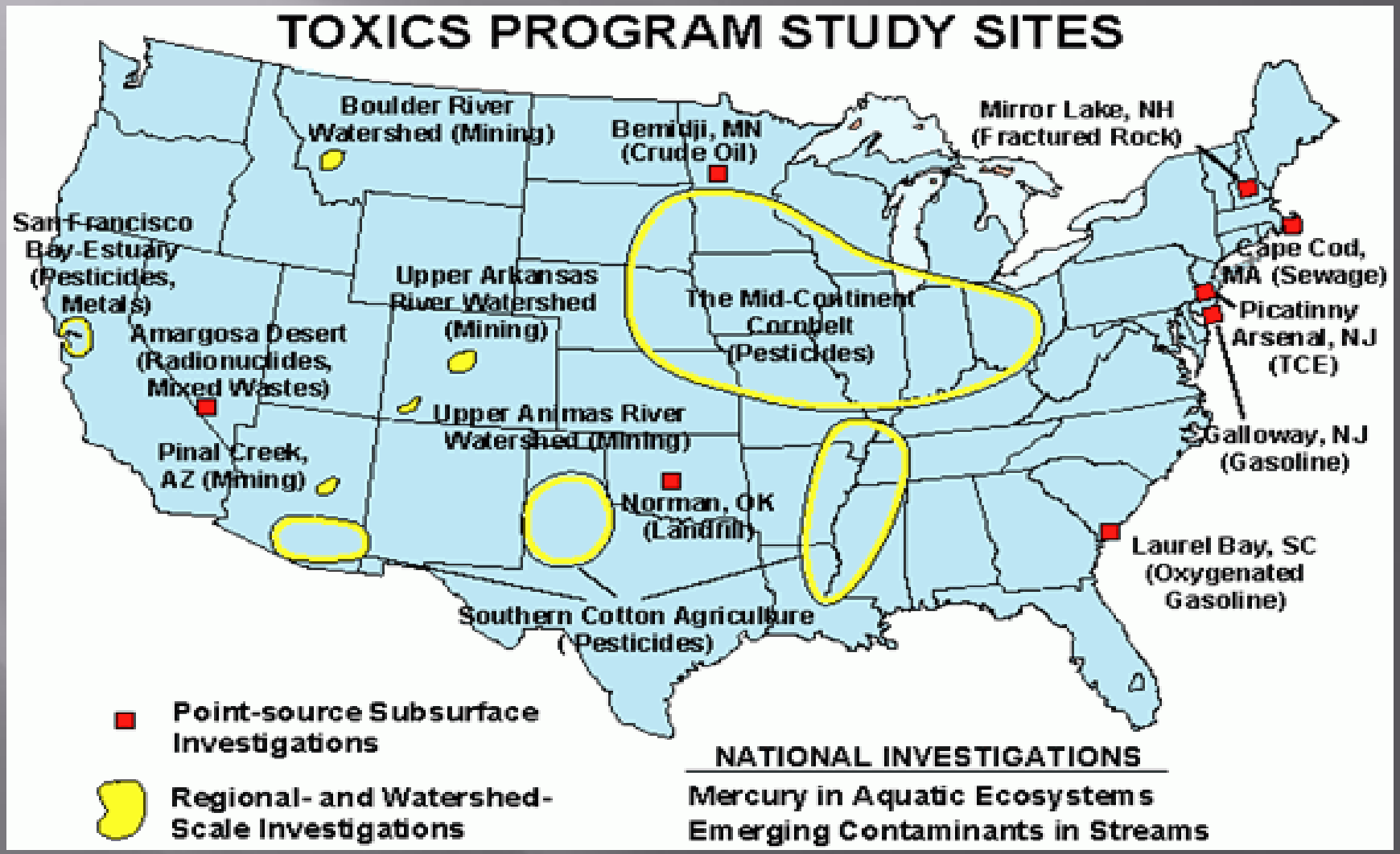


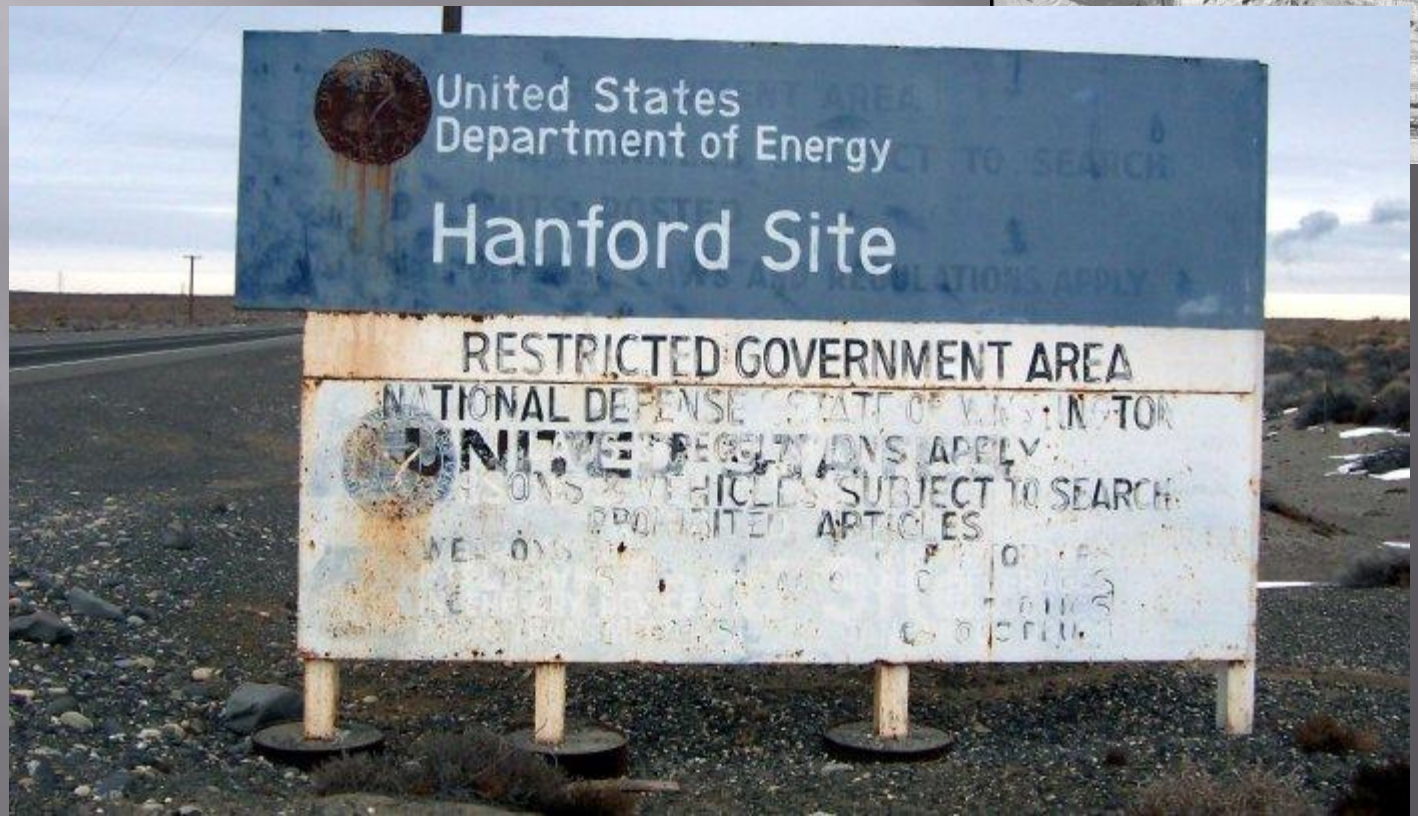

Fig. 7. Impact map showing the spatial association between land use and nitrate (NO3−) contamination defined by level of nitrate concentration and contamination index.

**Assessment of groundwater contamination by nitrate leaching from intensive vegetable cultivation using geographical information system**
Environment International, Volume 29, Issue 8, 2004, 1009–1017

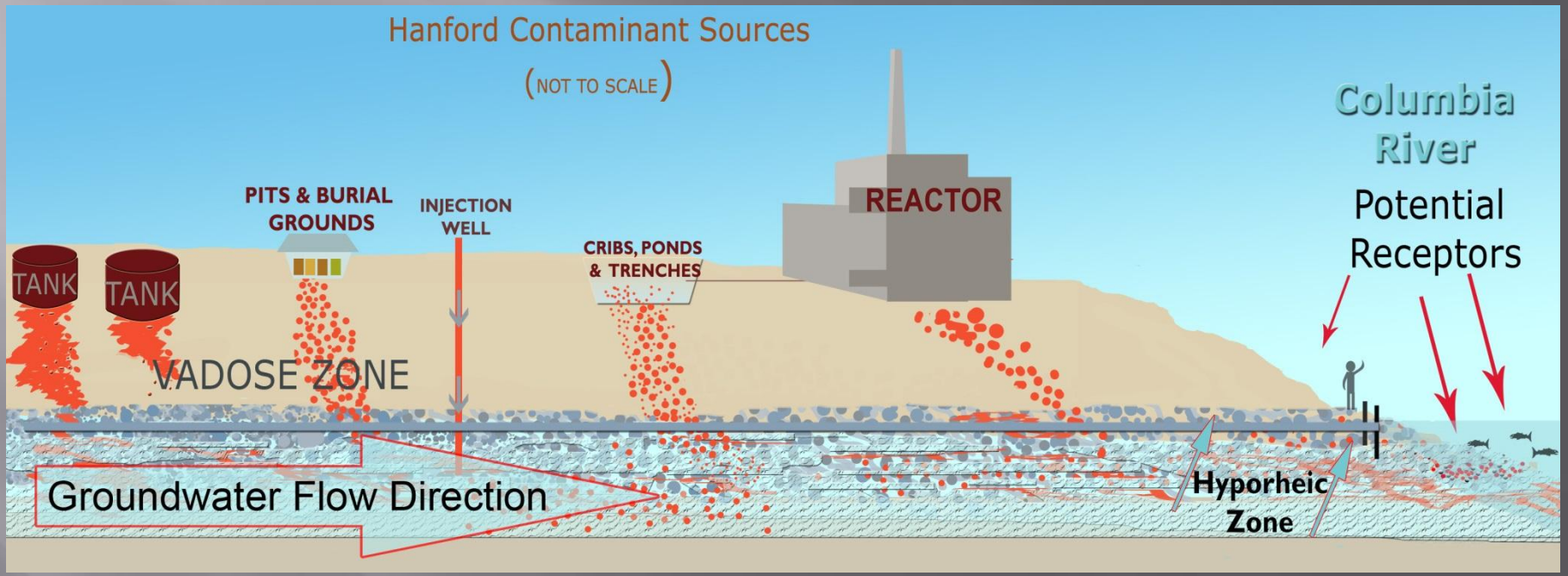



USGS Groundwater Contamination

# Radioactive Contamination



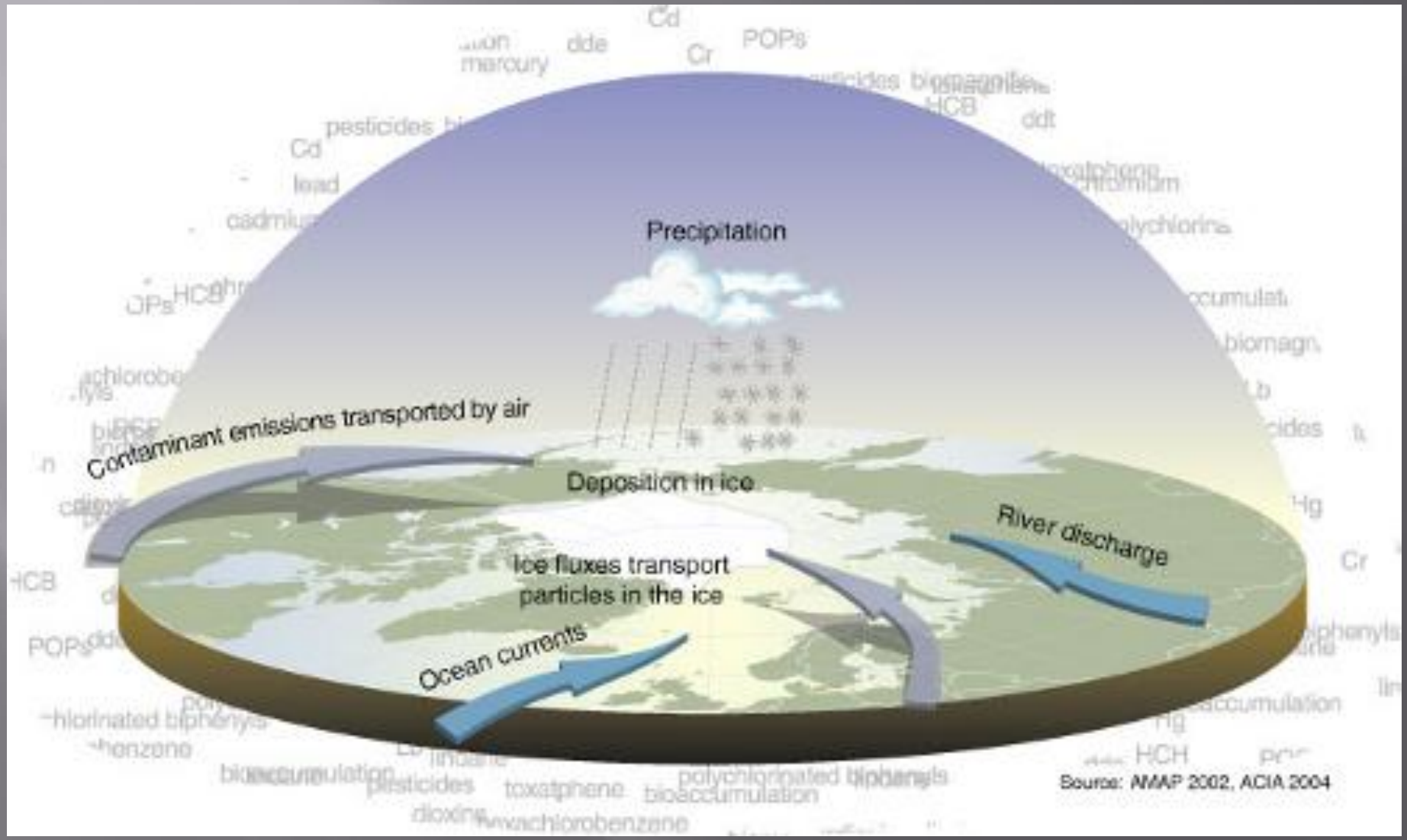
# Hanford



Hanford Contaminant Sources
(NOT TO SCALE)
Columbia River
Potential Receptors
PITS & BURIAL GROUNDS
INJECTION WELL
CRIBS, PONDS & TRENCHES
REACTOR
TANK
TANK
VADOSE ZONE
Groundwater Flow Direction
Hyporheic Zone

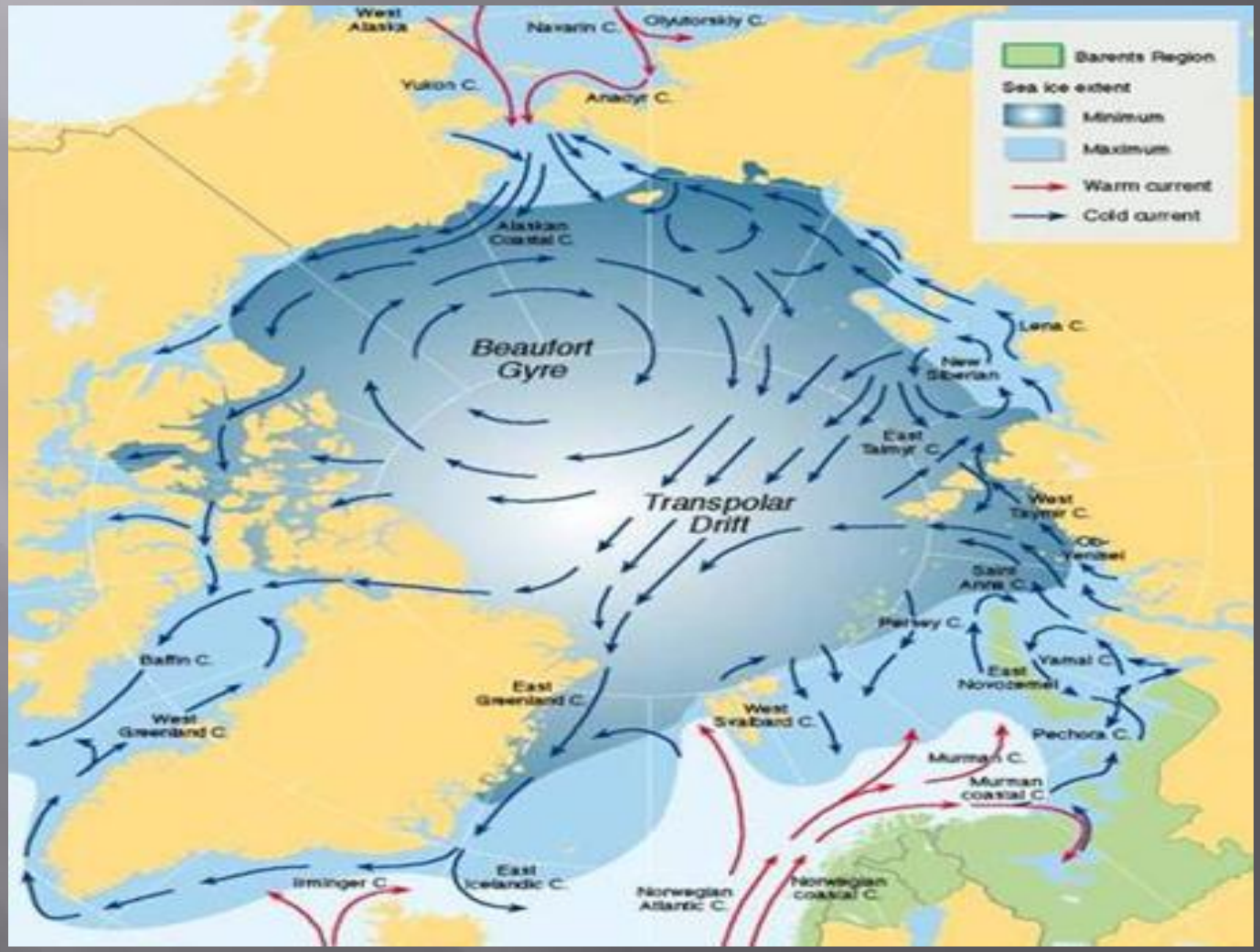
# The Arctic

# Why look in the Arctic

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


Precipitation
Contaminant emissions transported by air
Deposition in ice
River discharge
Ice fluxes transport particles in the ice
Ocean currents
Source: AMAP 2002, ACIA 2004

# Arctic Circulation



# Air masses

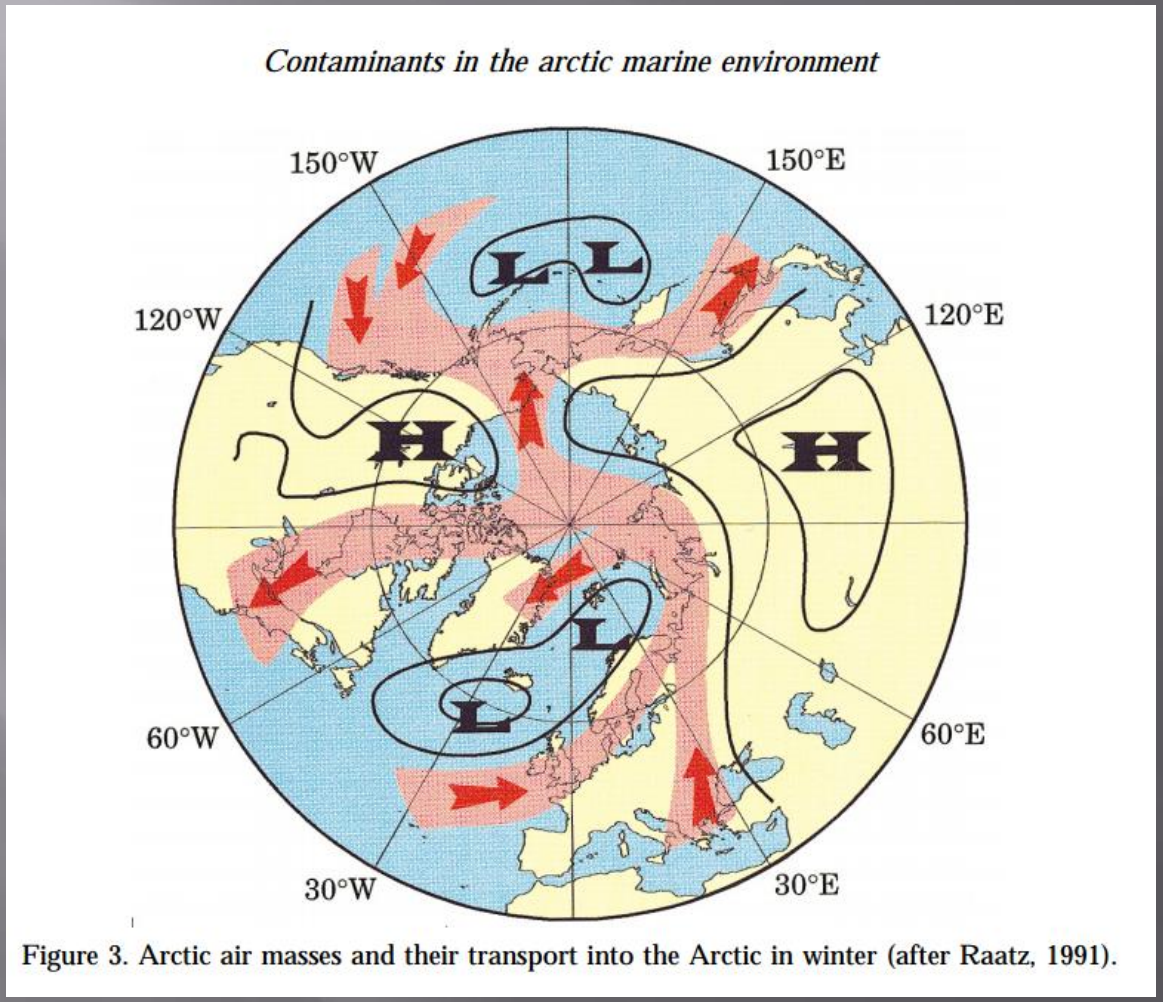
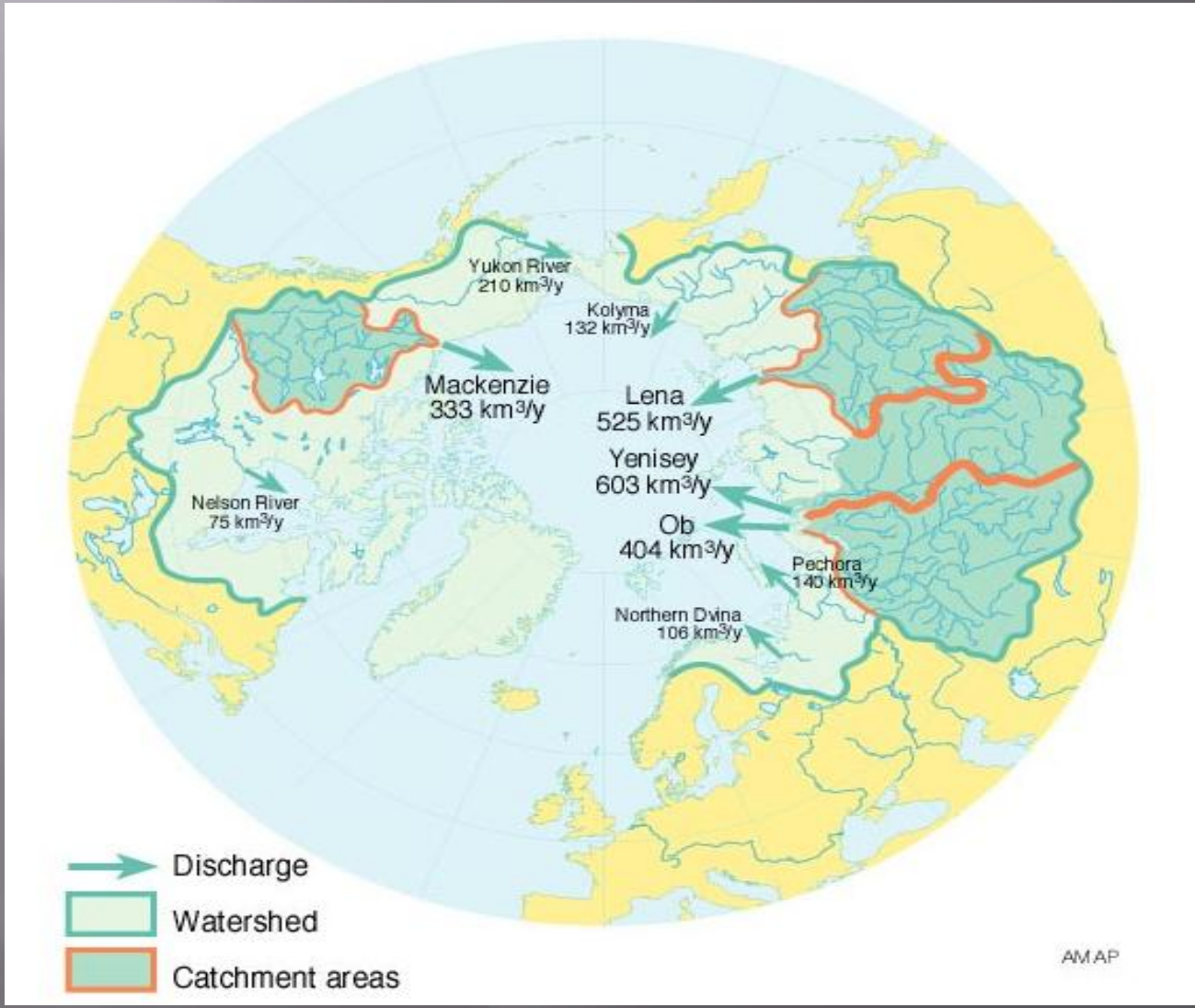
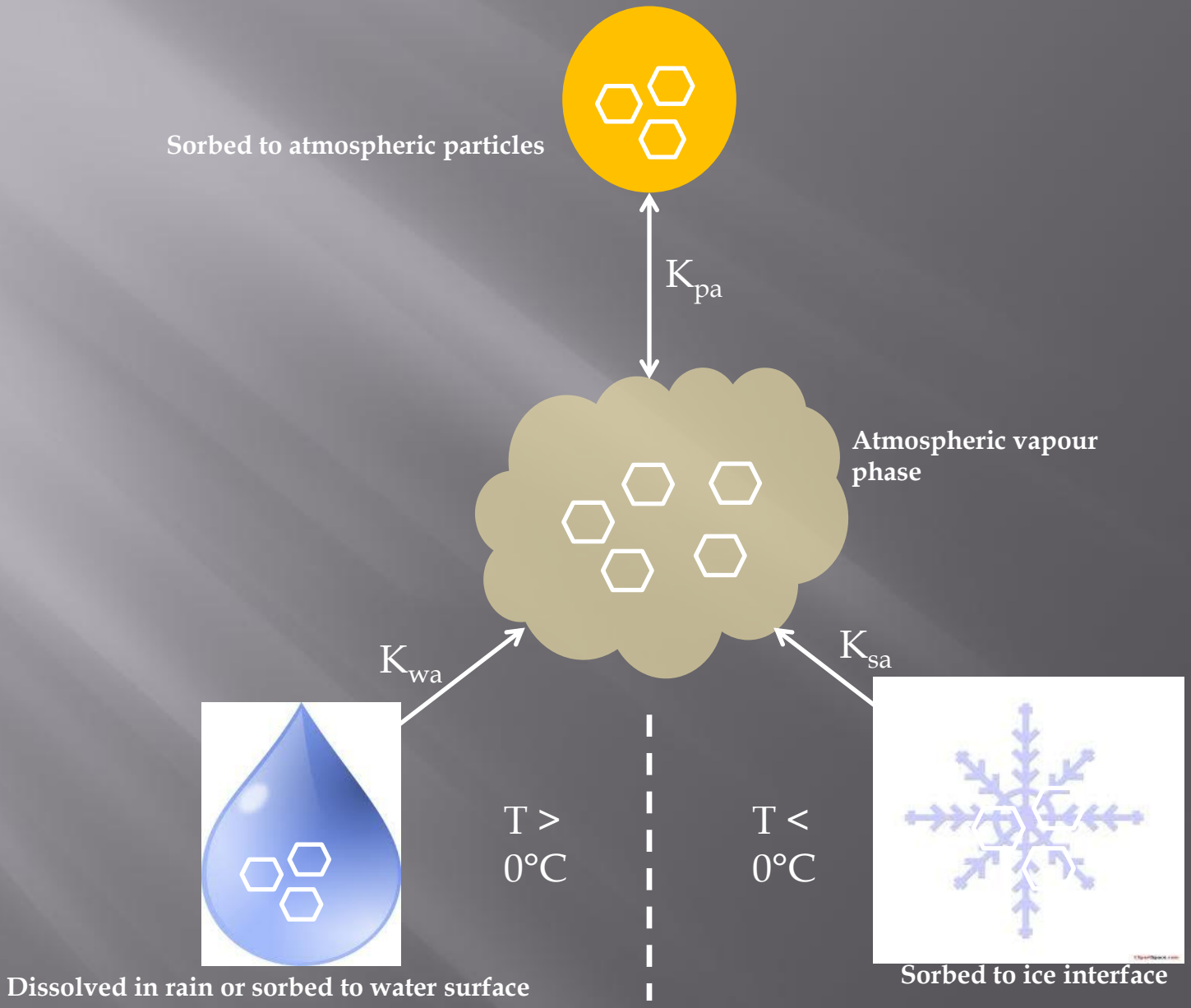


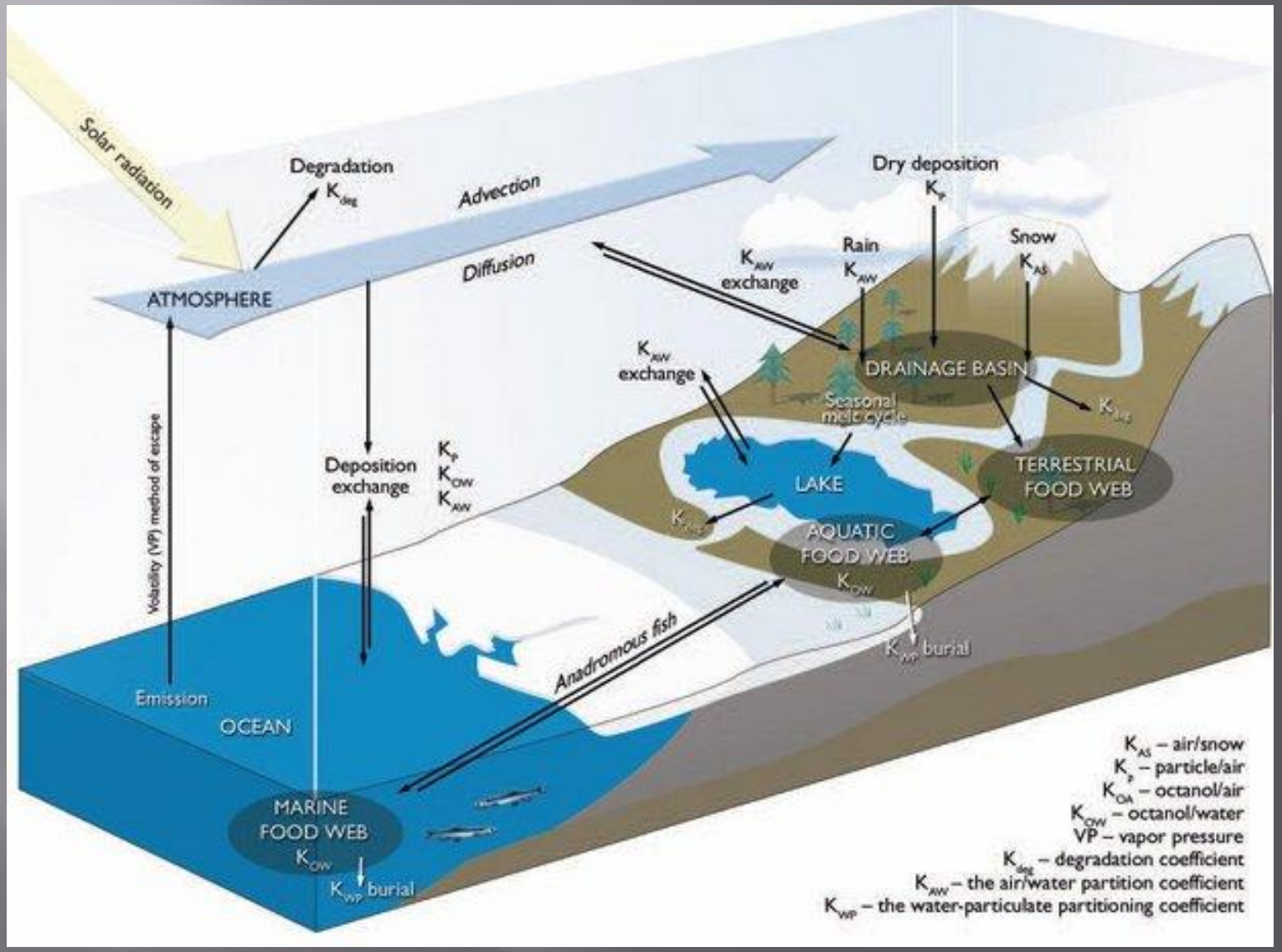

Figure 3. Arctic air masses and their transport into the Arctic in winter (after Raatz, 1991).

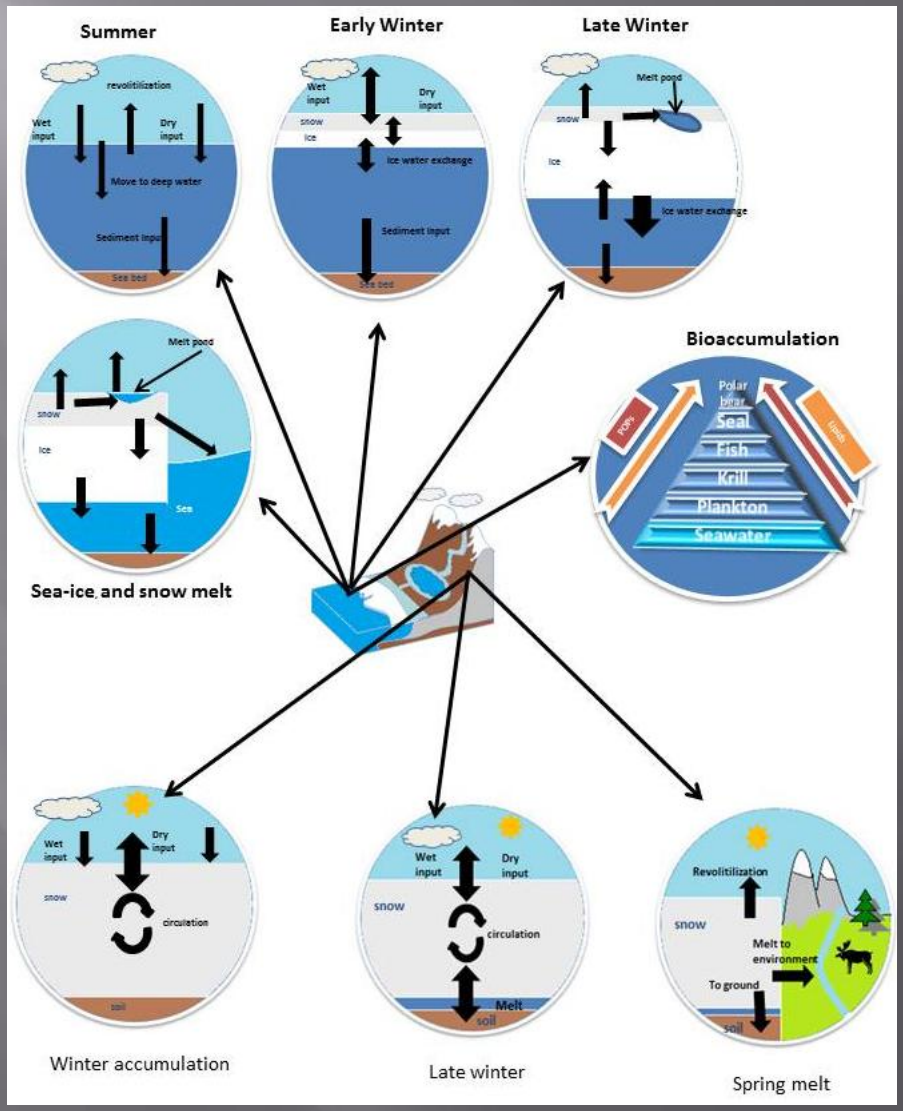
Moller et al 2011

# Rivers

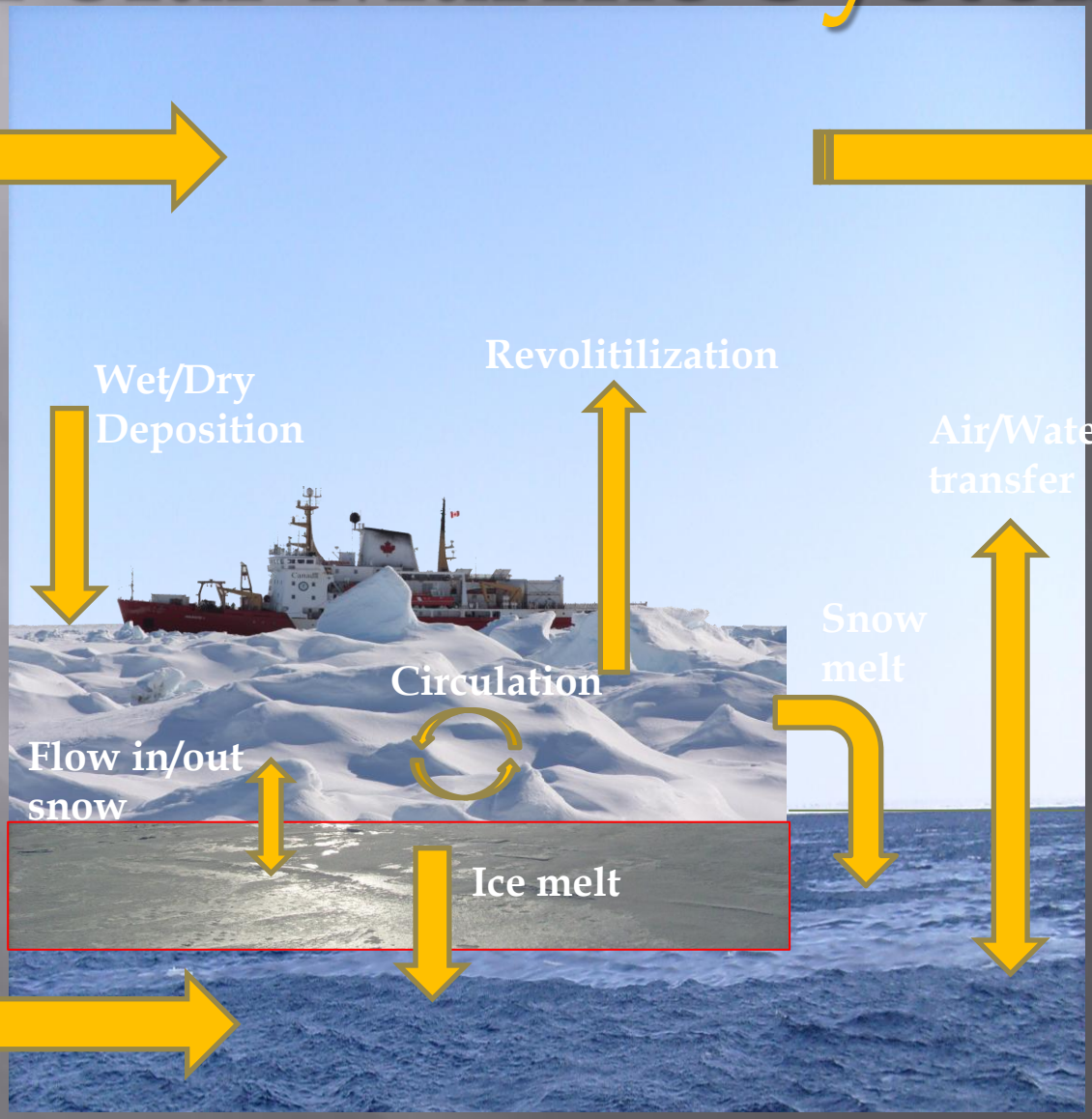

Yukon River
210 km³/y
Kolyma
132 km³/y
Mackenzie
333 km³/y
Lena
525 km³/y
Yenisey
603 km³/y
Nelson River
75 km³/y
Ob
404 km³/y
Pechora
140 km³/y
Northern Dvina
106 km³/y
Discharge
Watershed
Catchment areas
AMAP


Sorbed to atmospheric particles
$K_{pa}$
Atmospheric vapour phase
$K_{wa}$
$K_{sa}$
T > 0°C
T < 0°C
Dissolved in rain or sorbed to water surface
Sorbed to ice interface

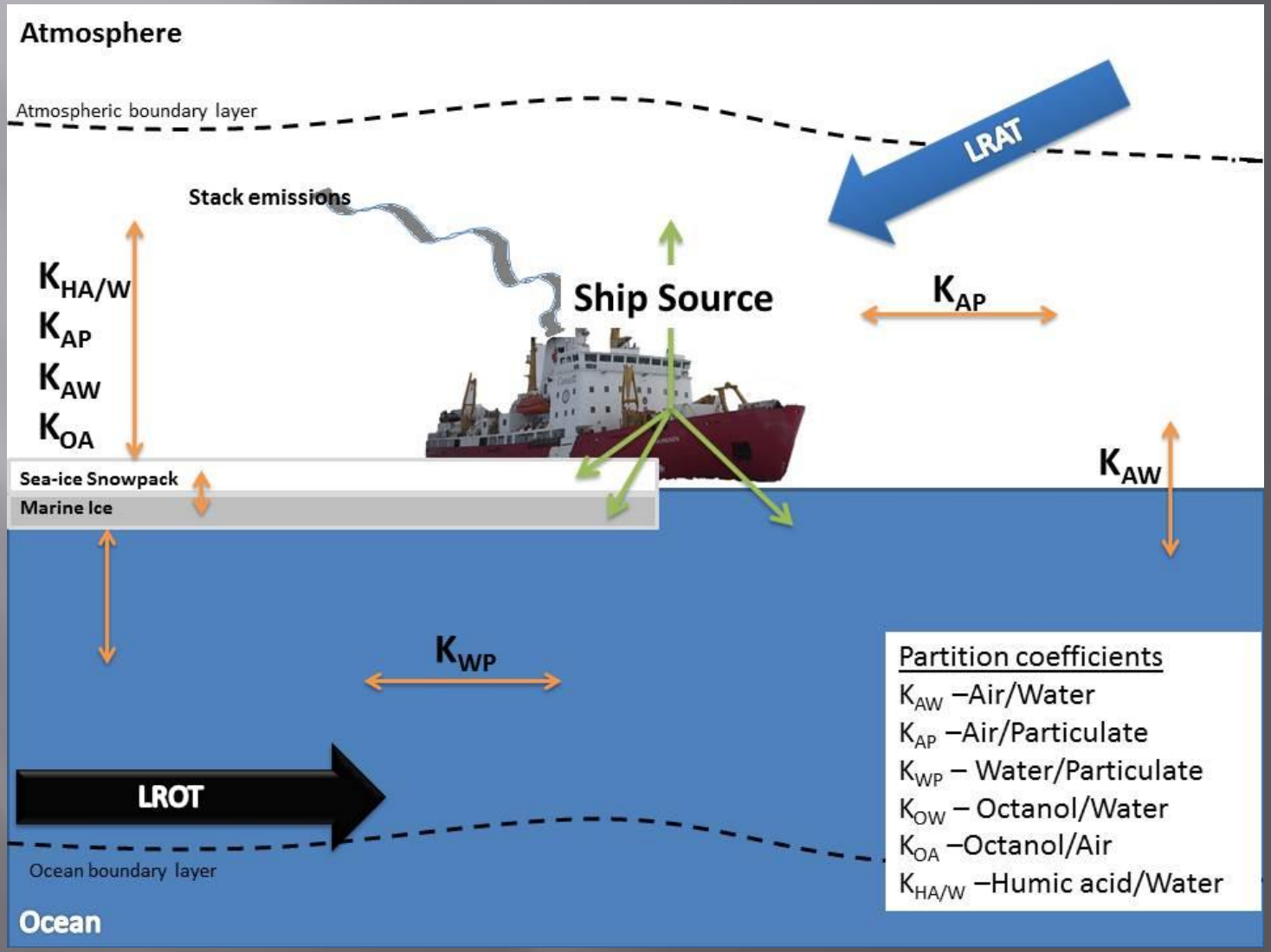

Solar radiation
Degradation
$K_{deg}$
Advection
Diffusion
ATMOSPHERE
Dry deposition
$K_P$
Rain
$K_{AW}$
Snow
$K_{AS}$
$K_{AW}$ exchange
$K_{AW}$ exchange
DRAINAGE BASIN
Seasonal melt cycle
$K_{AS}$
Deposition exchange
$K_P$
$K_{OW}$
$K_{AW}$
LAKE
TERRESTRIAL FOOD WEB
$K_{AW}$
AQUATIC FOOD WEB
$K_{OW}$
$K_{OA}$ burial
Volatility (VP) method of escape
Anadromous fish
Emission
OCEAN
MARINE FOOD WEB
$K_{OW}$
$K_{WP}$ burial
$K_{AS}$ – air/snow
$K_P$ – particle/air
$K_{OA}$ – octanol/air
$K_{OW}$ – octanol/water
VP – vapor pressure
$K_{deg}$ – degradation coefficient
$K_{AW}$ – the air/water partition coefficient
$K_{WP}$ – the water-particulate partitioning coefficient


Summer
revolitilization
Wet input
Dry input
Move to deep water
Sediment input
Sea bed
Early Winter
Wet input
Dry input
snow
ice
ice water exchange
Sediment input
Sea bed
Late Winter
Melt pond
snow
ice
ice water exchange
Melt pond
snow
ice
Sea
Sea-ice and snow melt
Bioaccumulation
Polar bear
Seal
Fish
Krill
Plankton
Seawater
Wet input
Dry input
snow
circulation
soil
Winter accumulation
Wet input
Dry input
snow
circulation
Melt
soil
Late winter
Revolitilization
snow
Melt to environment
To ground
soil
Spring melt

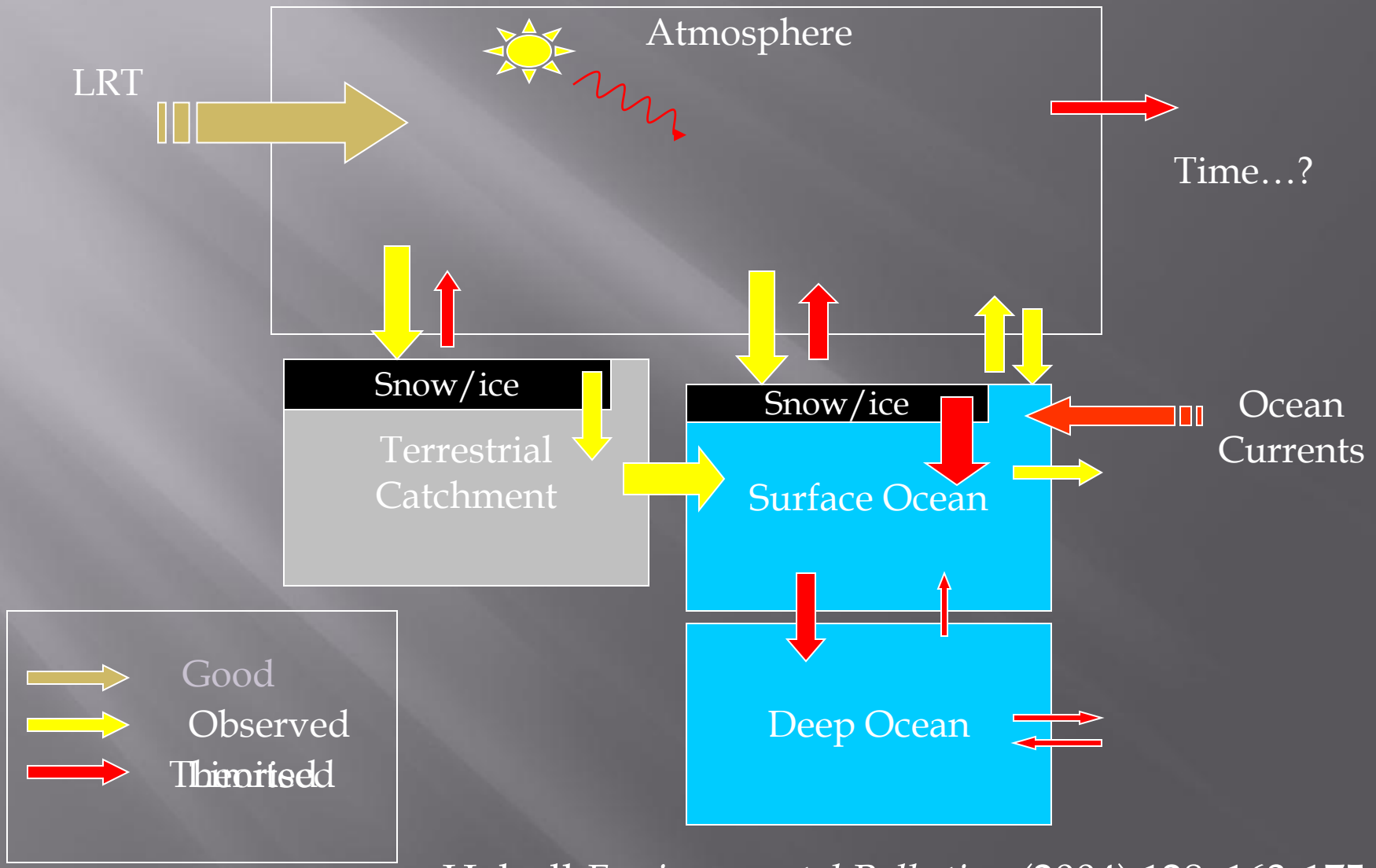
# The Polar Marine System



# Oceanic Exchange

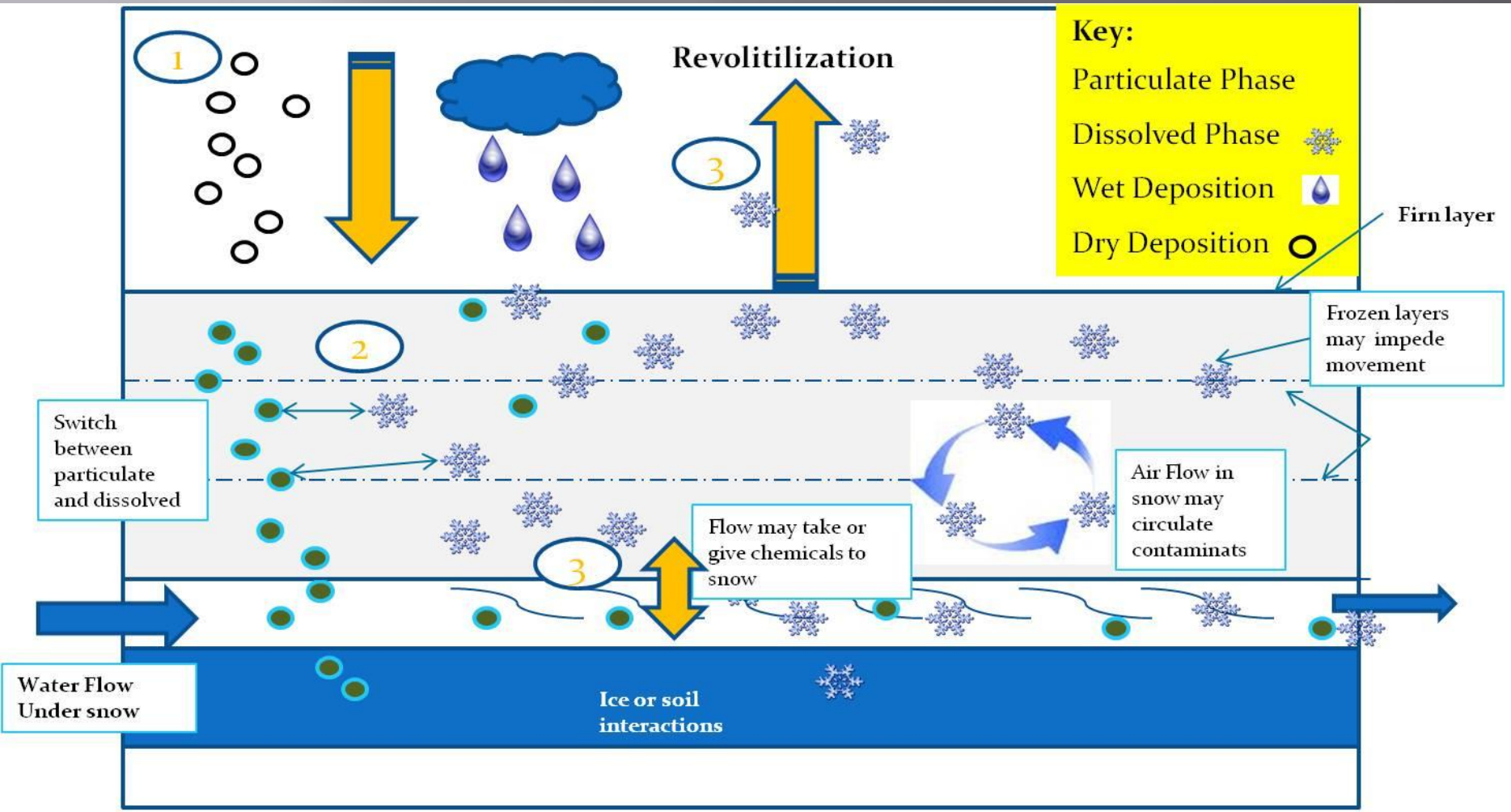


# PBDE Arctic Distribution




Halsall *Environmental Pollution* (2004) 128: 163-175

# Chemicals in a Snowpack




1: Chemicals maybe delivered to snow either by wet or dry deposition

2: Within snow they may move in 3 dimensions driven by air, or hydraulic movement, Ice layers may impede vertical flow

3: Chemicals revolitize to air, move into water or enter base layer be that ice or soil

# Clausius-Clapeyron Equation

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

- **Pressure**
- $\Delta H_{vap}$
- R is universal gas constant
- Temperature

# What is R?

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

$$PV = nRT$$

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

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

$$PV = NRT = mR_{specific}T$$

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

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

# Henry's Law Constant

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

- Henrys law constant (H)
- Concentration in the gas phase (Cg)
- Universal gas constant (R)
- Temperature in Kevin (T)
- Concentration in water (Cw)

# Air Water Partitioning

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

- Air Water partitioning coefficient ($K_{aw}$)
- Henry's Law Constant (H)
- Universal Gas Constant (R)
- Temperature (T)

# So what does it mean?

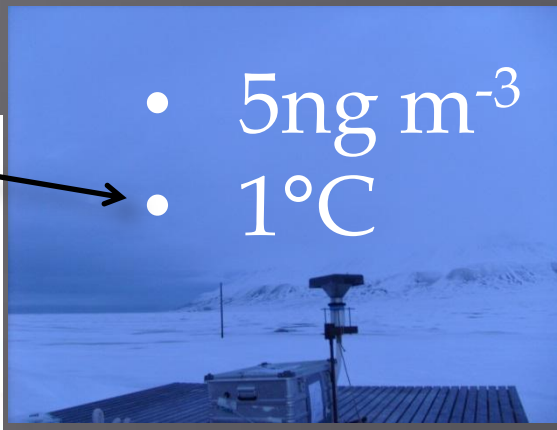
- $$\ln\left(\frac{P_1}{P_2}\right) = \left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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

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

# Concentration in the air

- 50ng $m^{-3}$
- 25°C



- 5ng $m^{-3}$
- 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

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

$C_w = 50 / 8.6 \times 10^{-3} = 5808\ pg\ m^{-3} = 5.8\ pg\ L^{-1}$

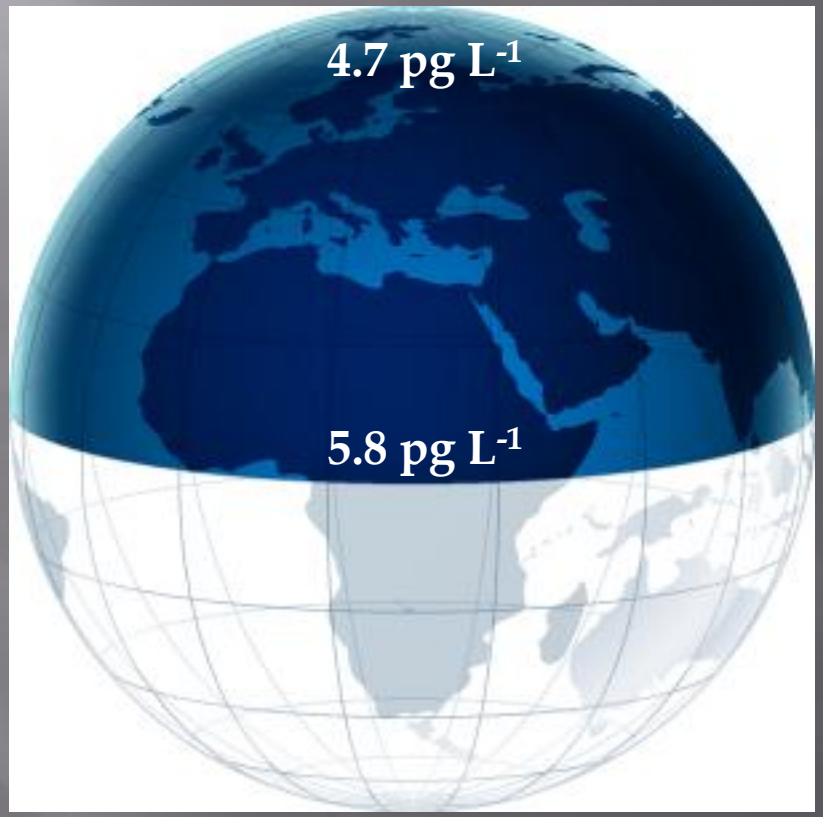
# For Arctic

- 

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

- ΔH for PCB18 is 59000 J $mol^{-1}$

# Concentration

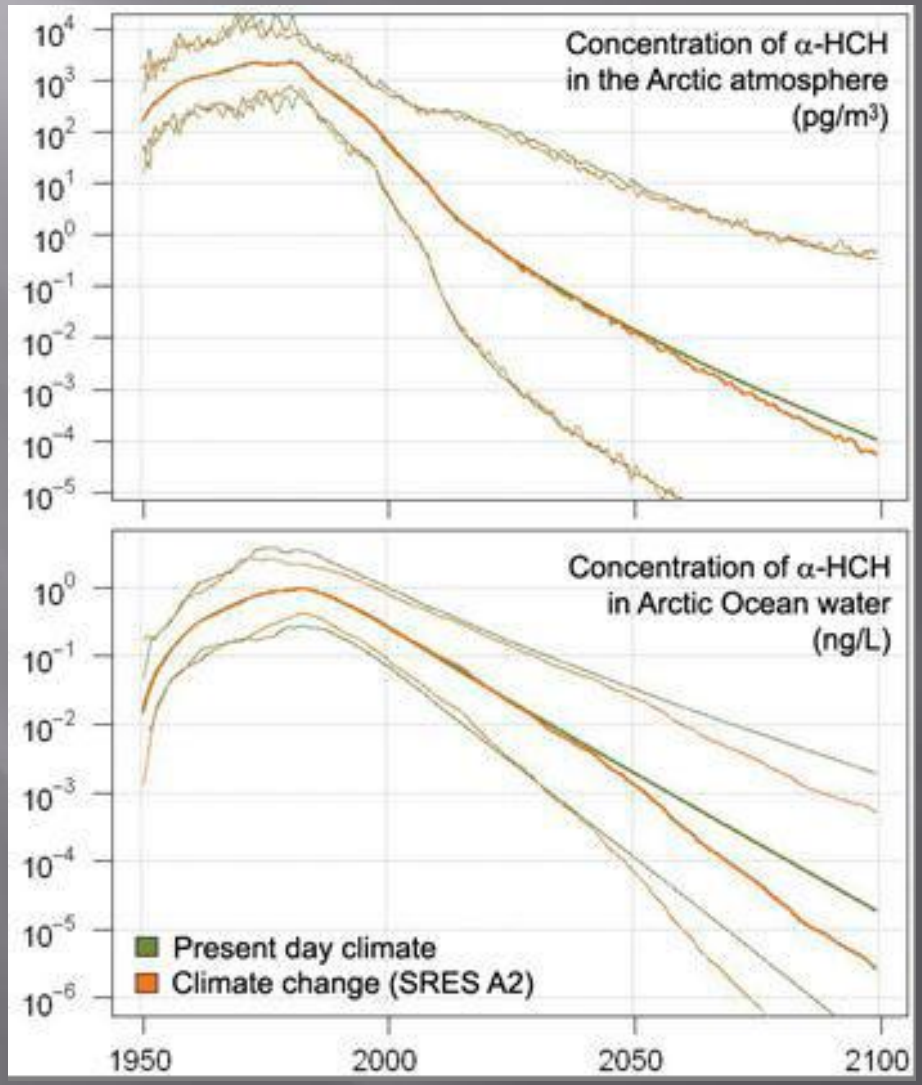


# Polar bear

- 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

Dietz 2008

# Not all doom and gloom




Arcrisk

# Conclusions

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

# Silent Spring –Rachel Carson 1962