Effects of degraded air-quality on precipitation and recharge quality

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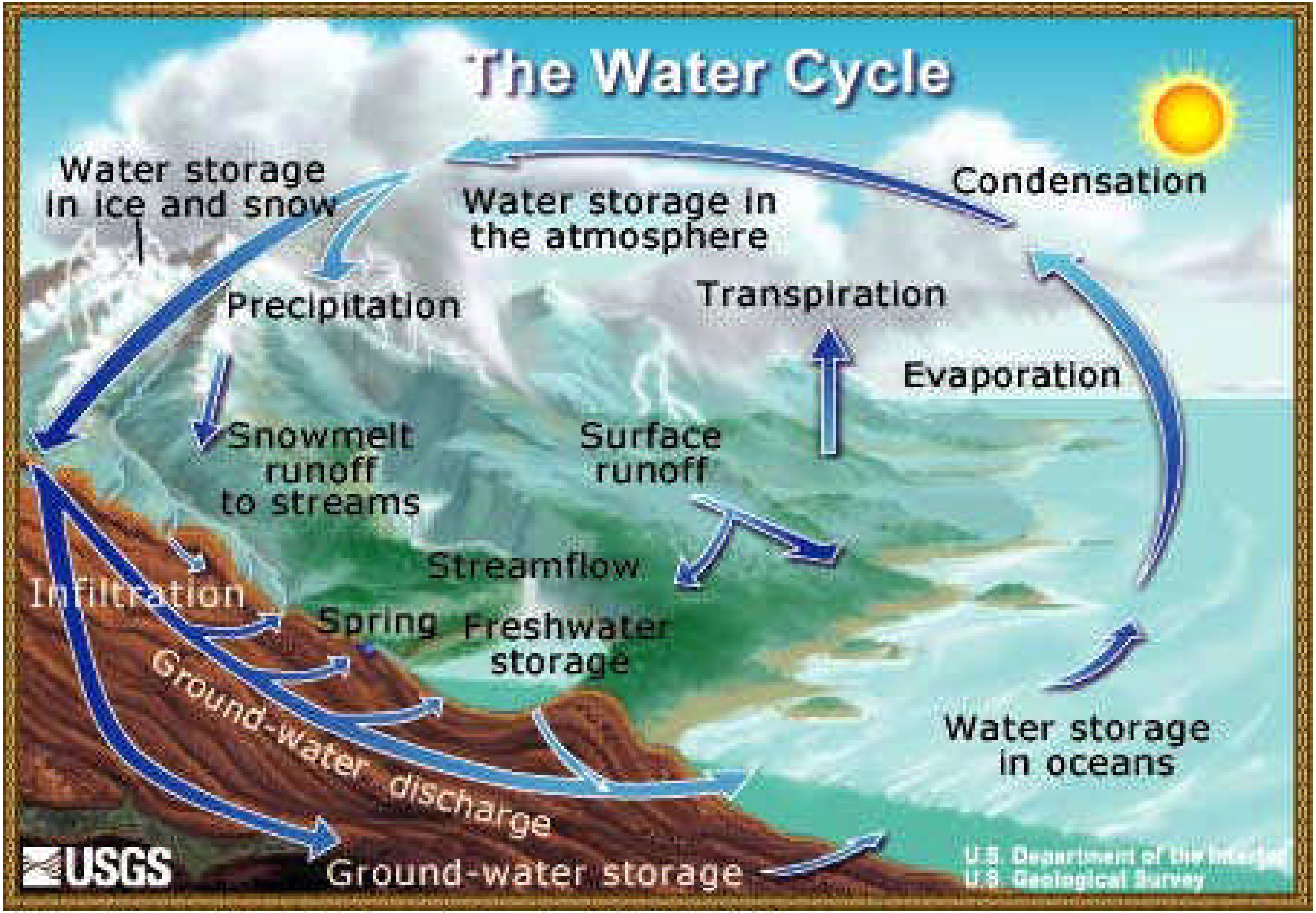
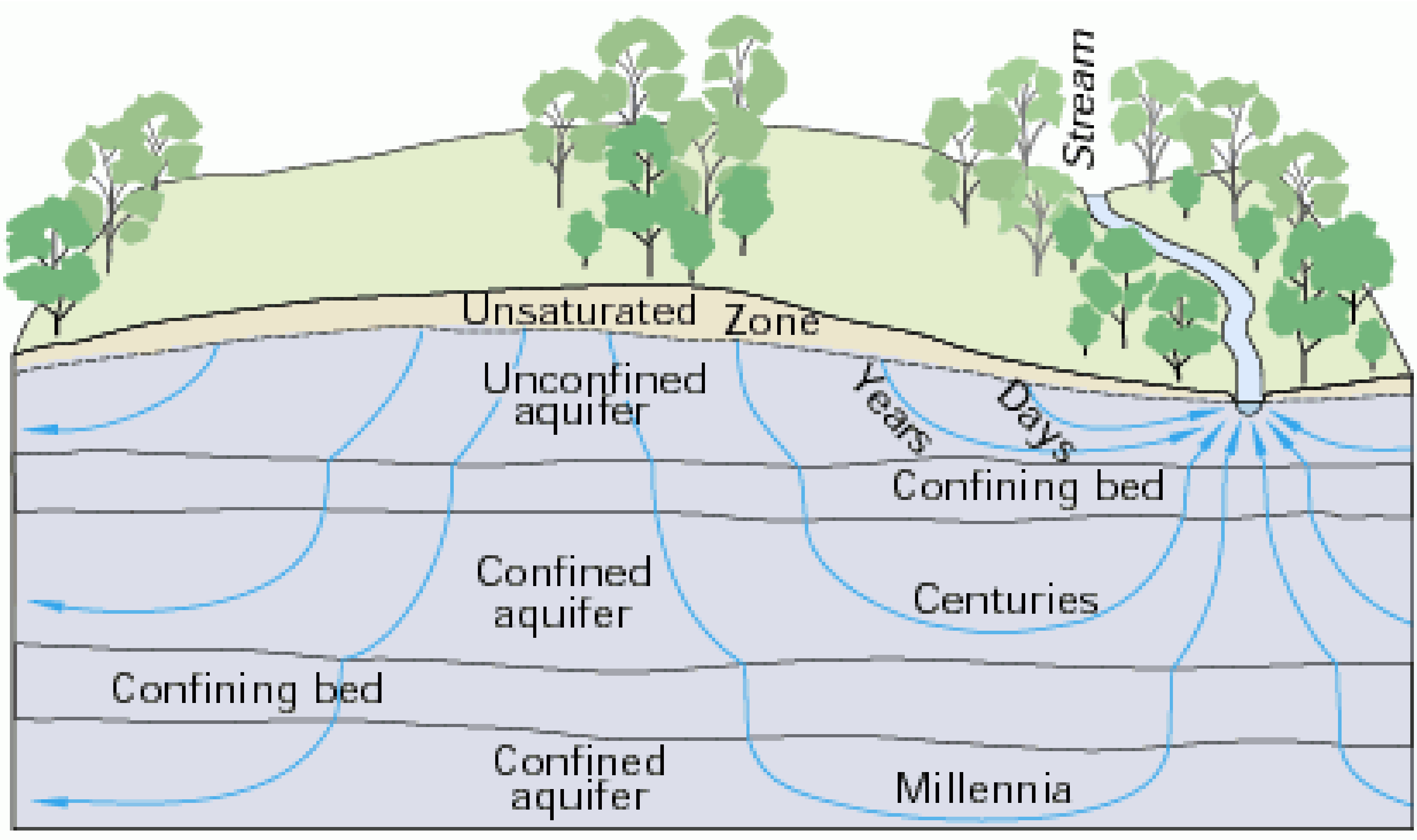


Illustration by John M. Evans, Colorado District, USGS



USGS website

Percolation

- Volatilization
  - Henry's Law — Low H
- Adsorption
  - Kd — Low Kd
- Absorption
  - f_{OM} — Low f_{OM}
  - K_{OW} — Low K_{OW}
- Biodegradation — Recalcitrant

$$H = \frac{p_l^0}{C_w^s}$$

$$K_d = \frac{C_{soil}}{C_{water}}$$

$$\log K_{om} \cong 0.82 \log K_{ow} + 0.14$$

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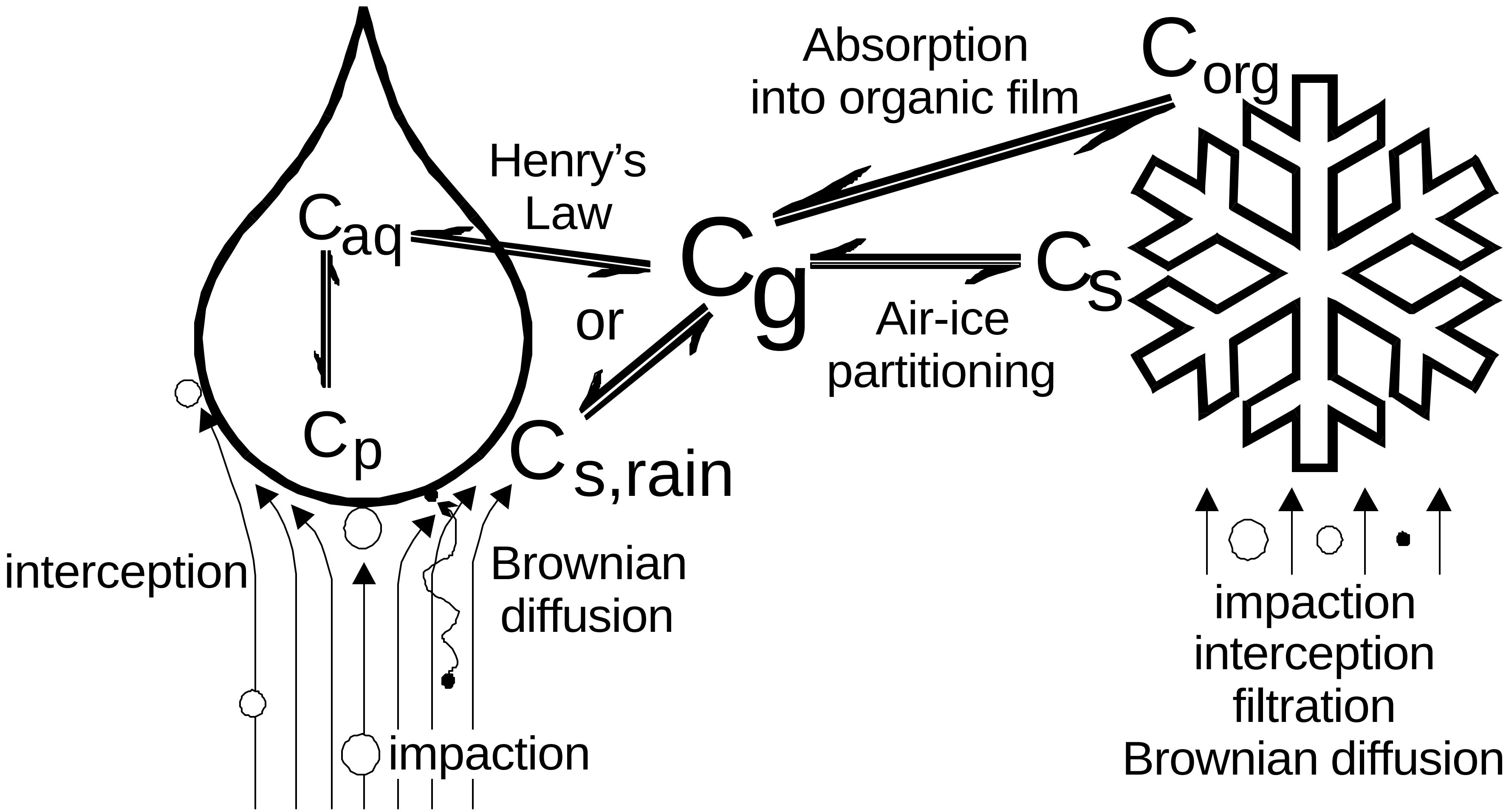
Precipitation/Deposition

- Precipitation
  - Solubility
  - Particulate
  - Surface adsorption
- Dry Deposition
  - Particle size distribution
  - Gas-Particle Partioning

Wet Deposition



Simcik, 2001 In: Persistent Organic Pollutants: Environmental Behavior and Pathways of Human Exposure

Washout of Air Pollutants

$$W_T = \frac{C_{\text{Precip}}}{C_{Air}} \qquad \frac{\left(\text{mass of SOC in rain}/\text{volume of rain}\right)}{\left(\text{mass of SOC in air}/\text{volume of air}\right)} \frac{\left(ng/m^3\right)}{\left(ng/m^3\right)}$$

$$W_T = W_P f + W_G (1 - f)$$

$$W_P = \frac{C_{\text{Precip, particle}}}{C_{\text{Air, particle}}} \qquad W_G = \frac{C_{\text{Precip, gas}}}{C_{\text{Air,gas}}}$$

Gas Scavenging

Henry's Law Partitioning

- partitioning to bulk dissolved phase
- equilibrium is reached in 10m fall of raindrop
- equilibrium described by Henry's Law:

$$H = \frac{P}{C_w}$$

Dimensionless HLC: $H' = \frac{H}{RT}$

$$C_{R,d} = \frac{C_{A,g}}{H'}$$

Partitioning to surface

$$K_{ia} = \frac{C_{\text{water surface}}}{C_{\text{Air, gas}}}$$

$$\frac{\left(\text{mass of SOC on surface} / \text{surface area of water}\right)}{\left(\text{mass of SOC in air} / \text{volume of air}\right)}$$

$$K_{ia} = \frac{m^3}{m^2}$$

K_{ia} is inversely proportional to p_L^0 just as K from gas-particle partitioning

Gas Scavenging

Henry's Law Partitioning

$$W_{G,\text{bulk}} = \frac{(1-f)}{H'}$$

Partitioning to surface

$$W_{G,\text{surface}} = K_{ia}\frac{6000}{d}(1-f)$$

$$W_G = \left[\frac{1}{H'} + K_{ia}\frac{6000}{d}\right](1-f)$$

Partitioning to surface becomes important only for compounds with high K_{ia} values and low enough *F*

Particle Scavenging

- Particle washout ratio not so easily calculated from theory
- Dependent on both particle size and raindrop size, but more so particle size
- Generally $10^4 - 10^6$, but often operationally defined

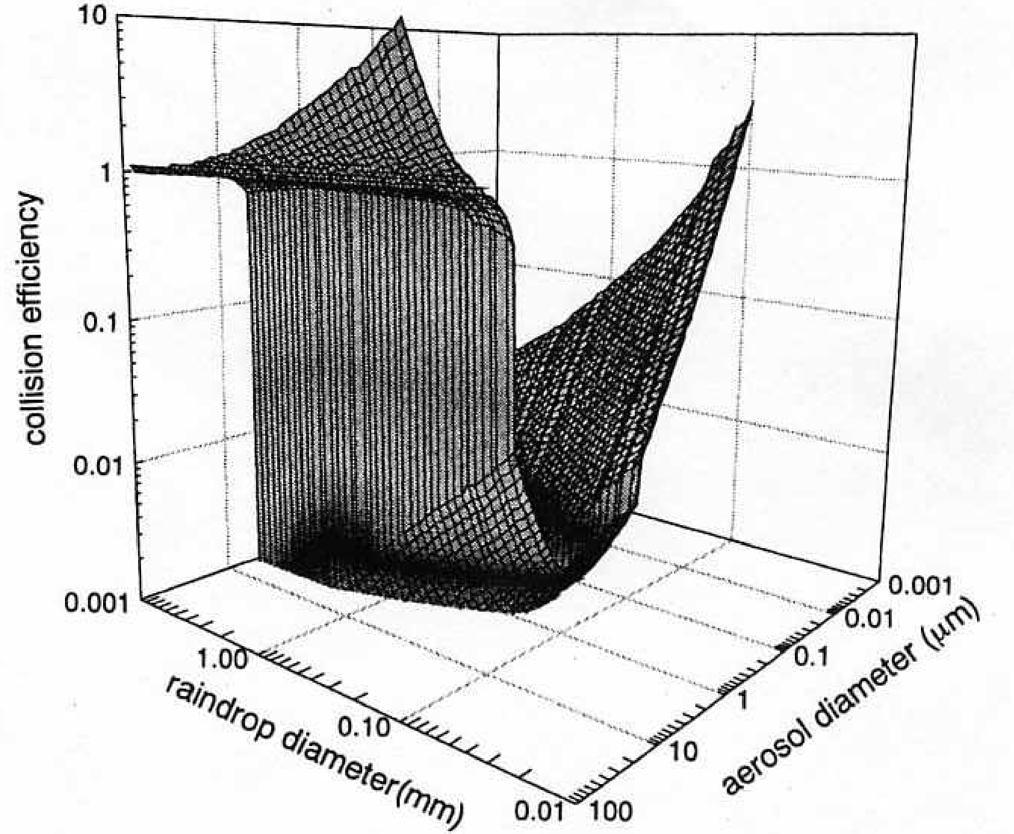
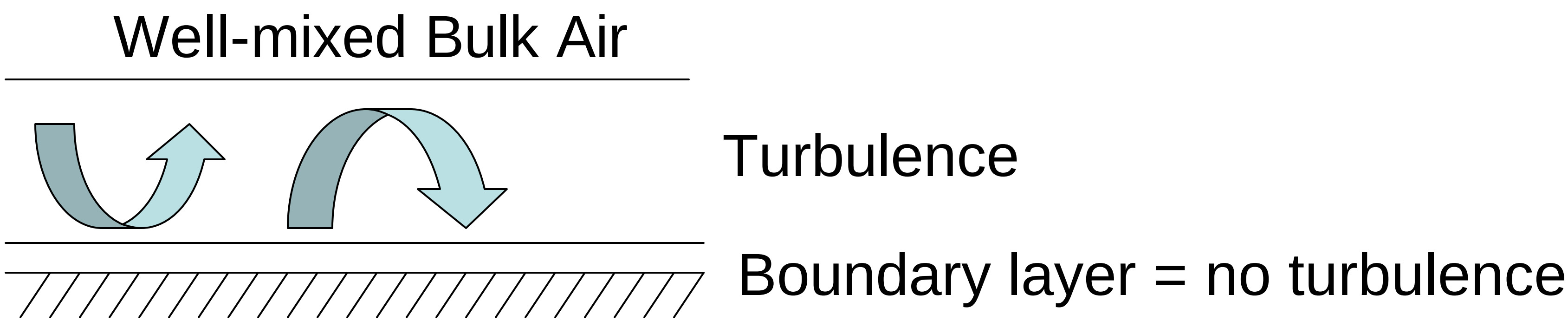


Fig. 1. Collision efficiency as a function of aerosol and raindrop diameter.

Dry Deposition

- Particle phase pollutants depositing on terrestrial aquatic surfaces
- Gravitational settling
- Molecular diffusion



Transfer Depends on:

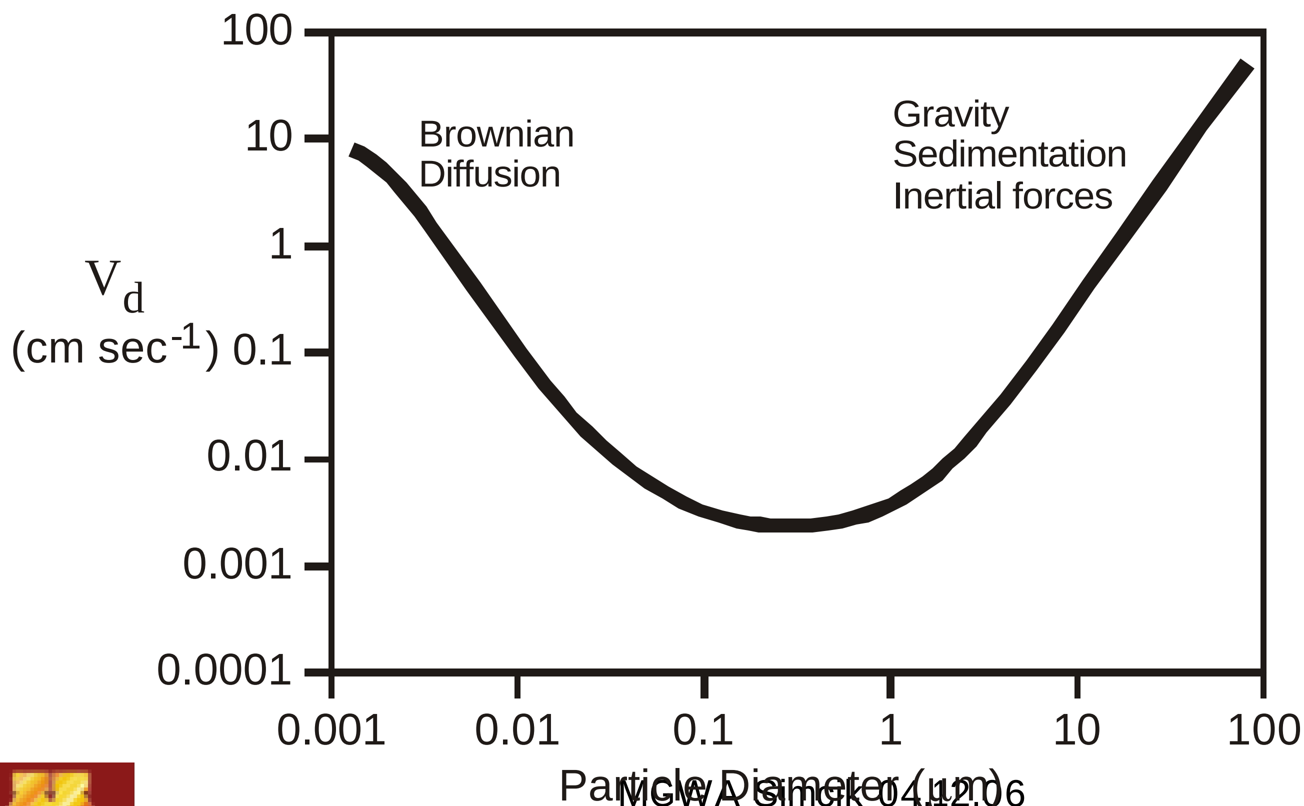
- Meterology
  - T, atmospheric stability, relative humidity, wind speed, pollutant concentration
- Particles
  - Size, electrostatic effects, density, shape
- Surface
  - Type (terr vs. aquatic), canopy structure, pH effects, roughness

Removal Rate = Flux, F

$F = Vd\ Ca,p$

Vd – Deposition velocity

Ca,p – Air particle concentration of pollutant



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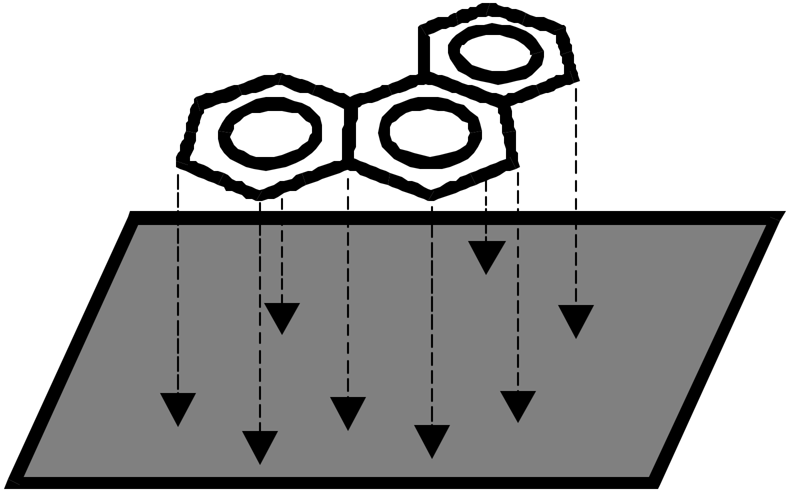
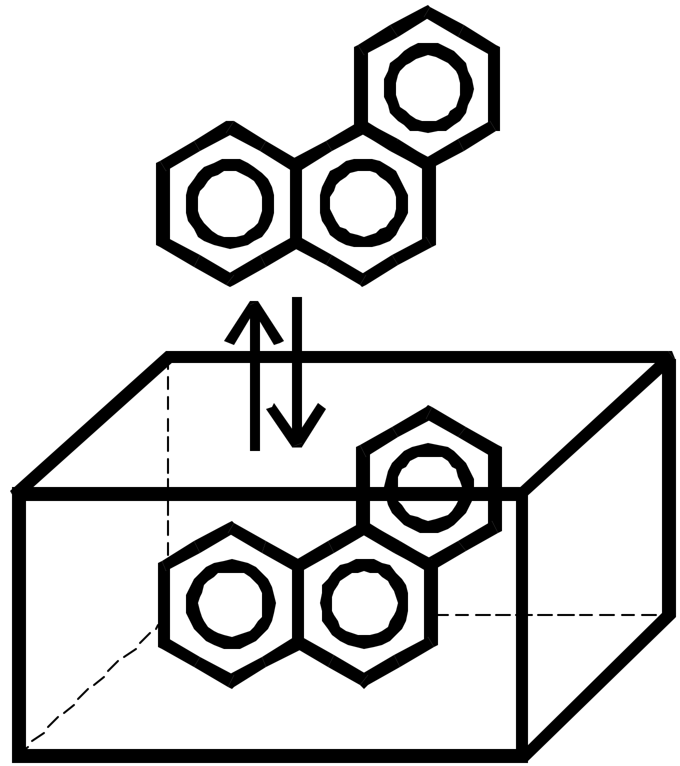
Physi-chemical
Adsorption

Absorption
into Liquid-like Matrix





Surfaces:
Mineral
Elemental Carbon
Ice

Liquid-like Matrices: Organic Carbon   Water

What determines whether a HAP will be a gas, particle or both?

Vapor Pressure = partial pressure of a compound above the pure substance at STP

$p^0 < 10^{-7}$ Pa	→	particles	Metals and some large organics
$10^{-7} < p^0 < 10$Pa	→	both	SOCs
$p^0 > 10$ Pa	→	gas	Hg^0, radon, VOCs

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Precipitation/Deposition

- Precipitation
  - Solubility — High Solubility/Low H
  - Particulate — Particulate
  - Surface adsorption — air-water afinity
- Dry Deposition
  - Particle size distribution — larger/smaller
  - Gas-Particle Partioning — low volatility

Atmospheric transport

- Gas-Particle
  - Gases transport farther
  - Particles greater potential for deposition
- Reactions
  - Reactive compounds won’t make it very far
  - Reaction products may
  - Gas-particle partitioning

Physical Chemical Properties

- Low H
- Low Kd
- Low Kow
- Recalcitrant
- Low vapor pressure
- Non-Reactive
- High aqueous solubility

Large sources are necessary to be significant

Candidate Chemicals

- BTEX
- Ammonia
- Metals
- Pesticides
- Perfluorochemicals

BTEX

- High H
- Low solubility
- Moderate Kd
- High vapor pressure

Ammonia

- Gas/particle
  - Relative humidity
- Large sources
- Present in precipitation
- Biodegradation?
- Adsorption?

Metals (Se, Al, Zn etc.)

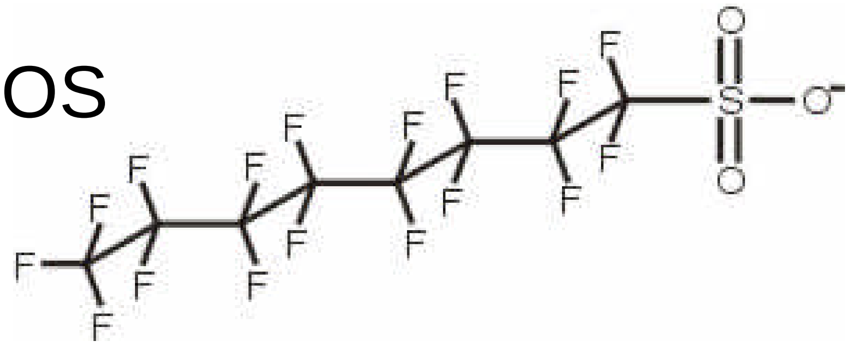
- Low H
- Low vapor pressure
- Low Kow
- Kd?
- Solubility?

Pesticides

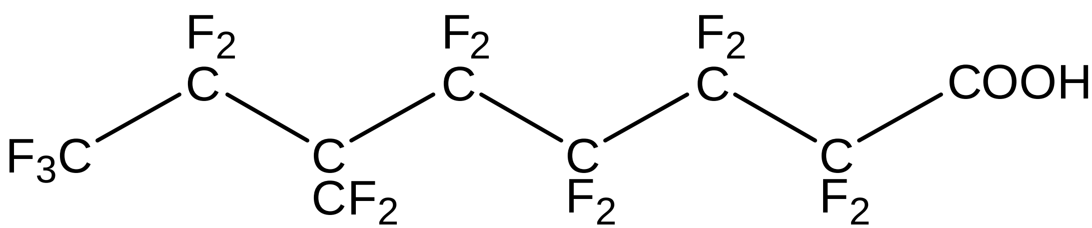
- Long-range transport
- Low H
- High solubility
- Moderate Kow
- Kd?
- Reactive?

Perfluorochemicals

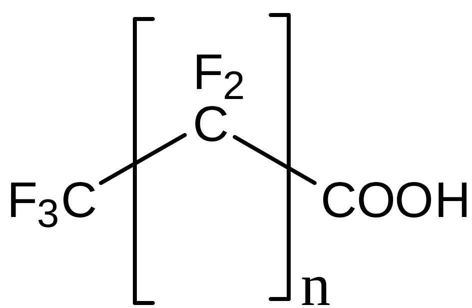
PFOS



PFOA



Other perfluorinated acids



n = 4-10

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Perfluorochemicals

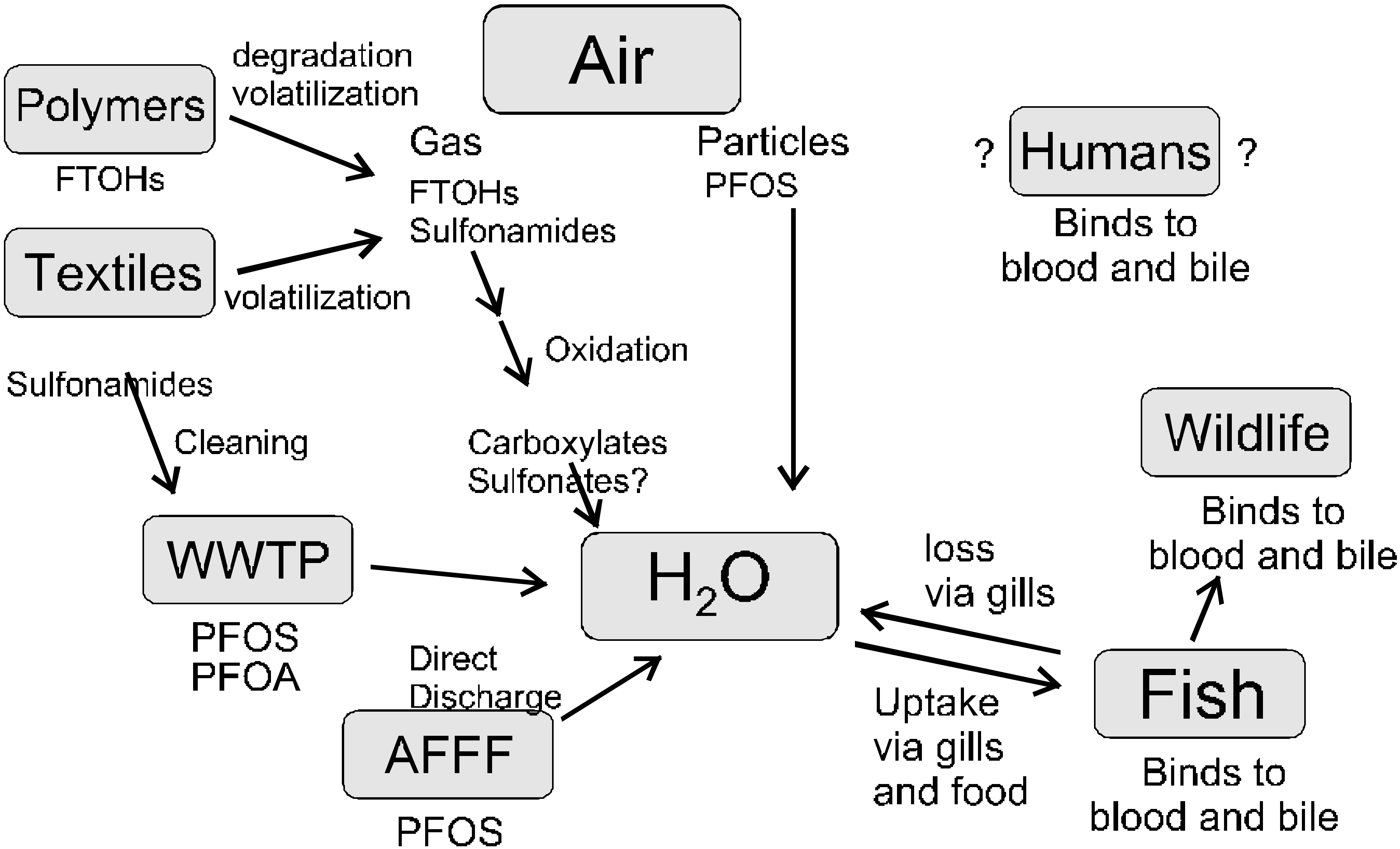
- Surface active molecules
- Stain protectant
- Non-stick surfaces
- AFFF – Aqueous Film Forming Foam
- Residual by-products

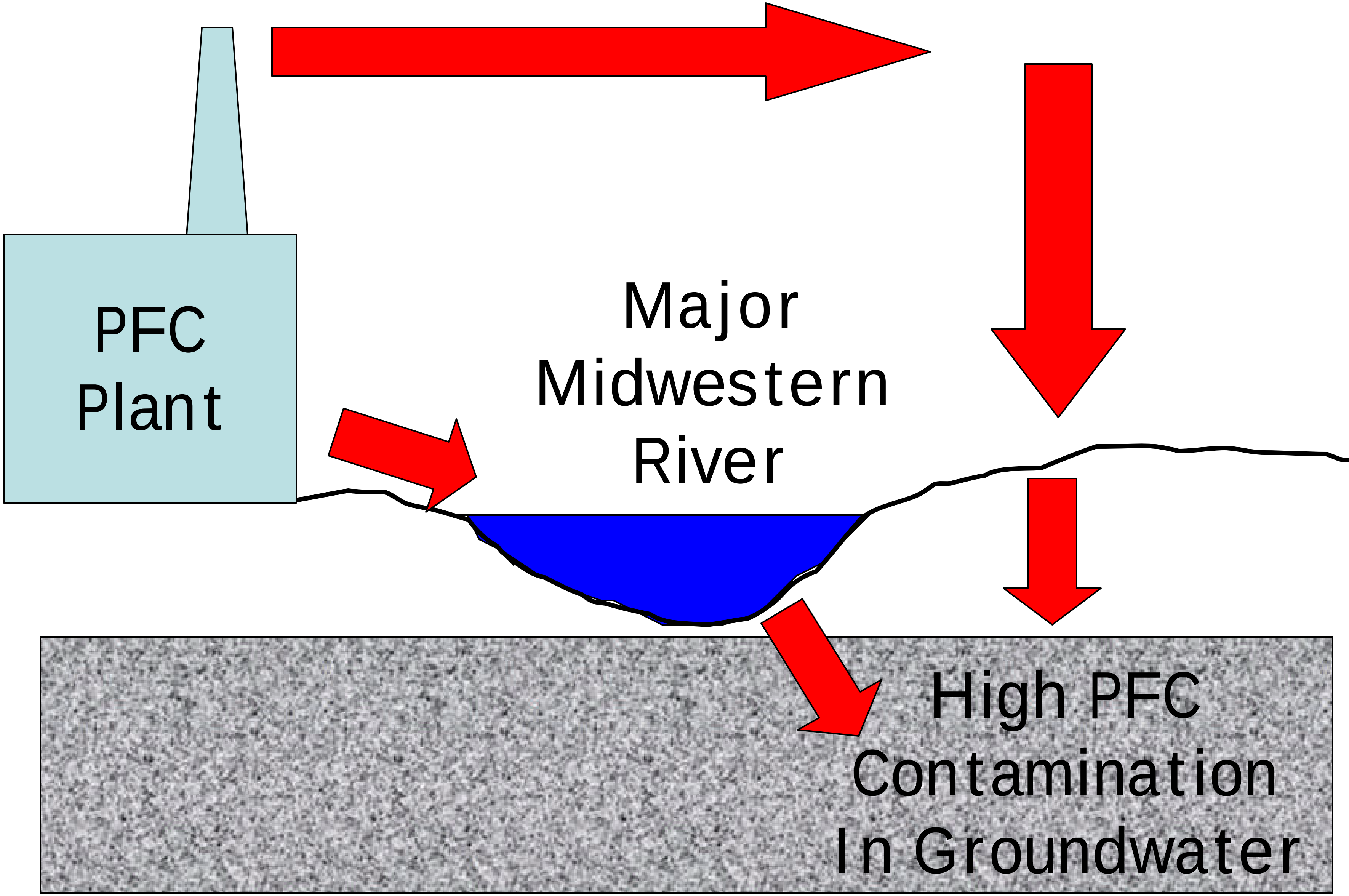
Physical/Chemical Properties

- Extremely low H
- Low Kd
- Kow?
- Extremely recalcitrant & non-reactive
- Low vapor pressure
- Relatively high aqueous solubility (mg/L)

Transport

- Global distribution
  - Biota
  - Water
- Atmospheric transport
  - Precursors
- Direct discharge
  - WWTP
  - Landfill leaching


Air
Polymers
FTOHs
degradation
volatilization
Gas
FTOHs
Sulfonamides
Textiles
volatilization
Particles
PFOS
? Humans ?
Binds to
blood and bile
Oxidation
Sulfonamides
Cleaning
Carboxylates
Sulfonates?
Wildlife
Binds to
blood and bile
WWTP
PFOS
PFOA
H2O
loss
via gills
Uptake
via gills
and food
Direct
Discharge
AFFF
PFOS
Fish
Binds to
blood and bile


PFC
Plant
Major
Midwestern
River
High PFC
Contamination
In Groundwater