United States
Environmental Protection
Agency

Fate and Transport



RISK ASSESSMENT TRAINING AND EXPERIENCE
Exposure Assessment Course Series – EXA 404

Office of Research and Development
National Center for Environmental Assessment

What You Can Expect to Learn from this Course

- Basic fate and transport concepts and terminology
- Influences on fate and transport
  - Source-related
  - Chemical
  - Environmental
- Means of physical transport
- Types of chemical transformations

United States Environmental Protection Agency

KEY CONCEPTS AND DEFINITIONS

Contaminant Fate and Transport

Release

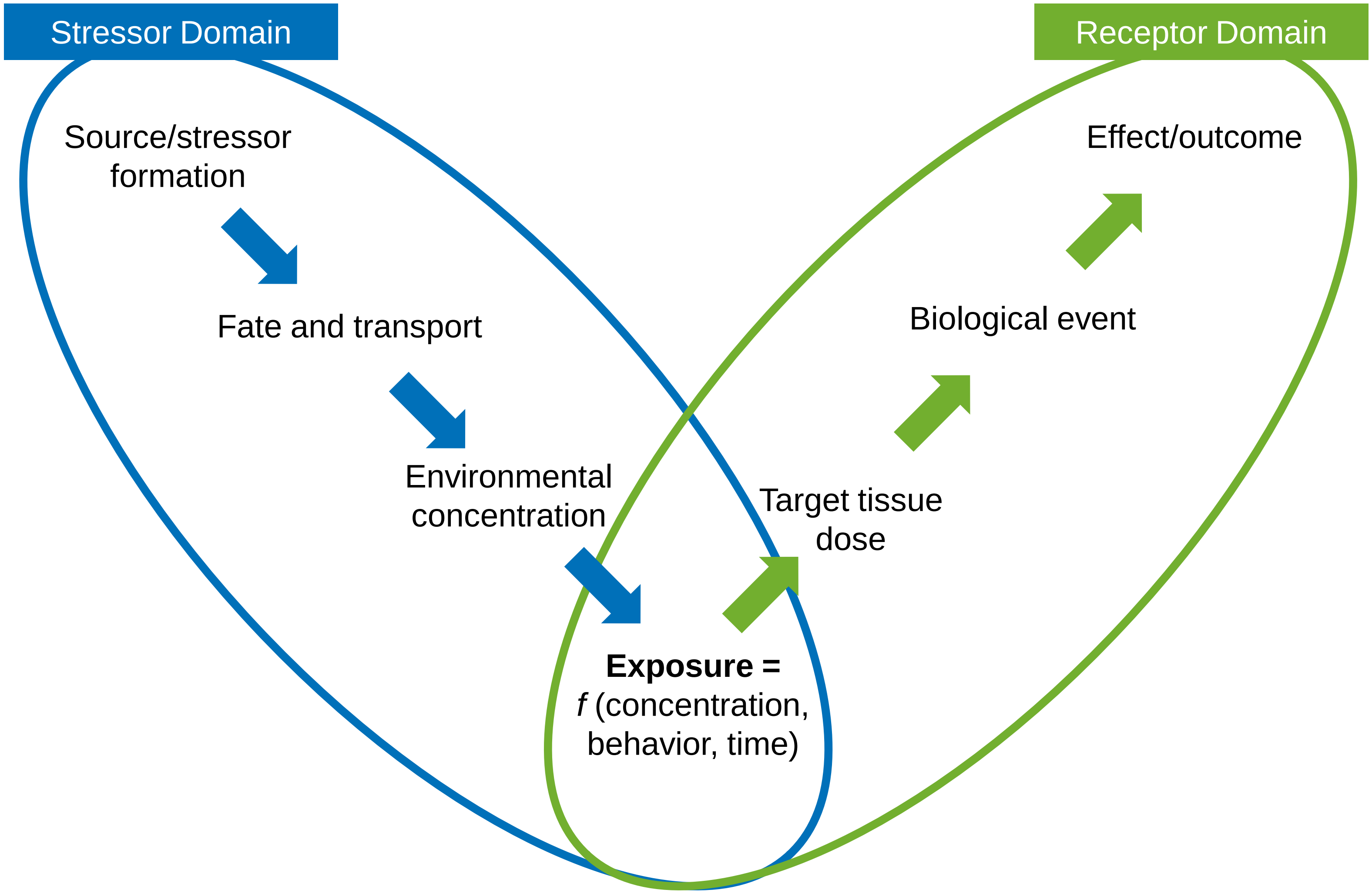
Contact

Contaminant Pathways

Sources

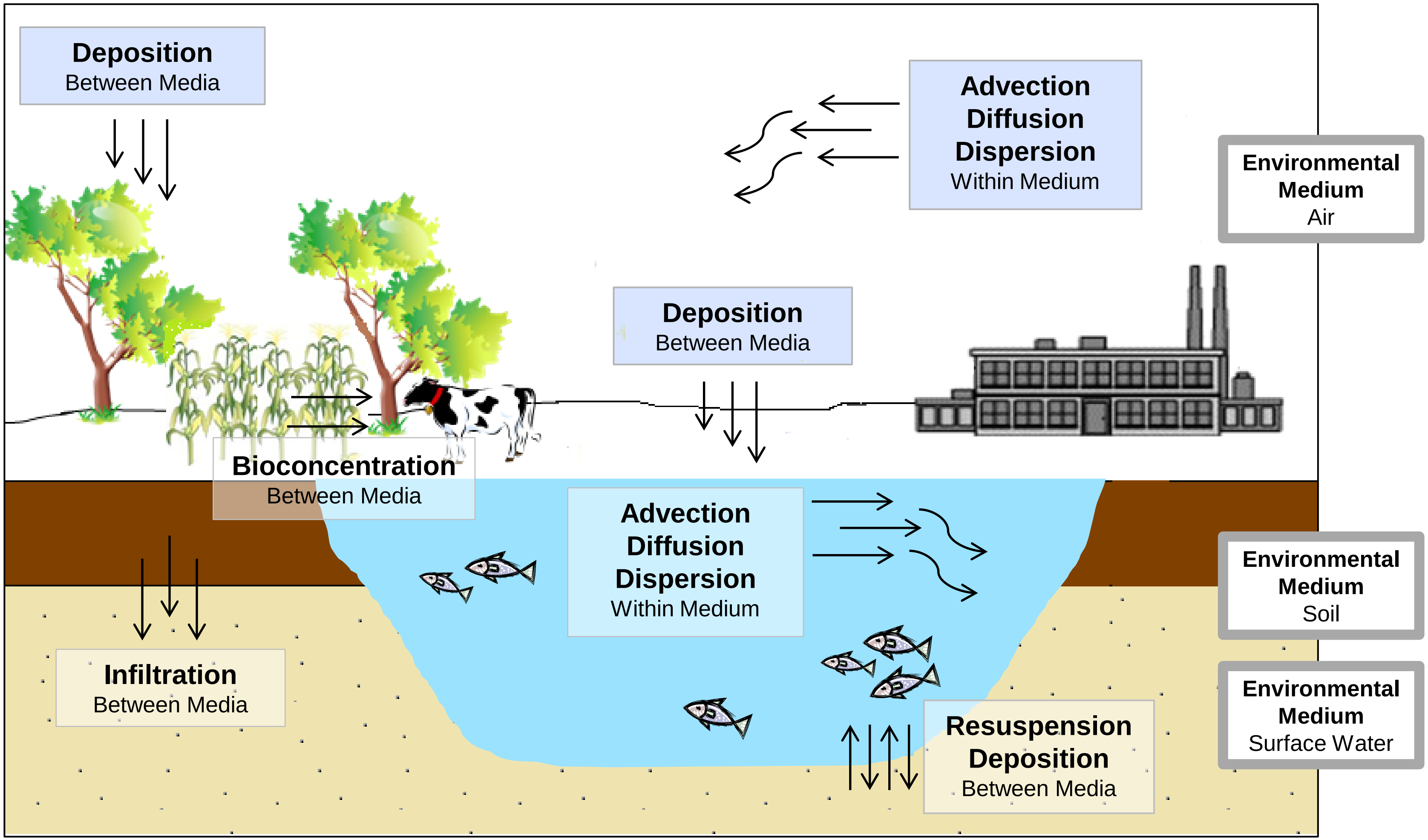
Receptors

Source-to-Effect Continuum

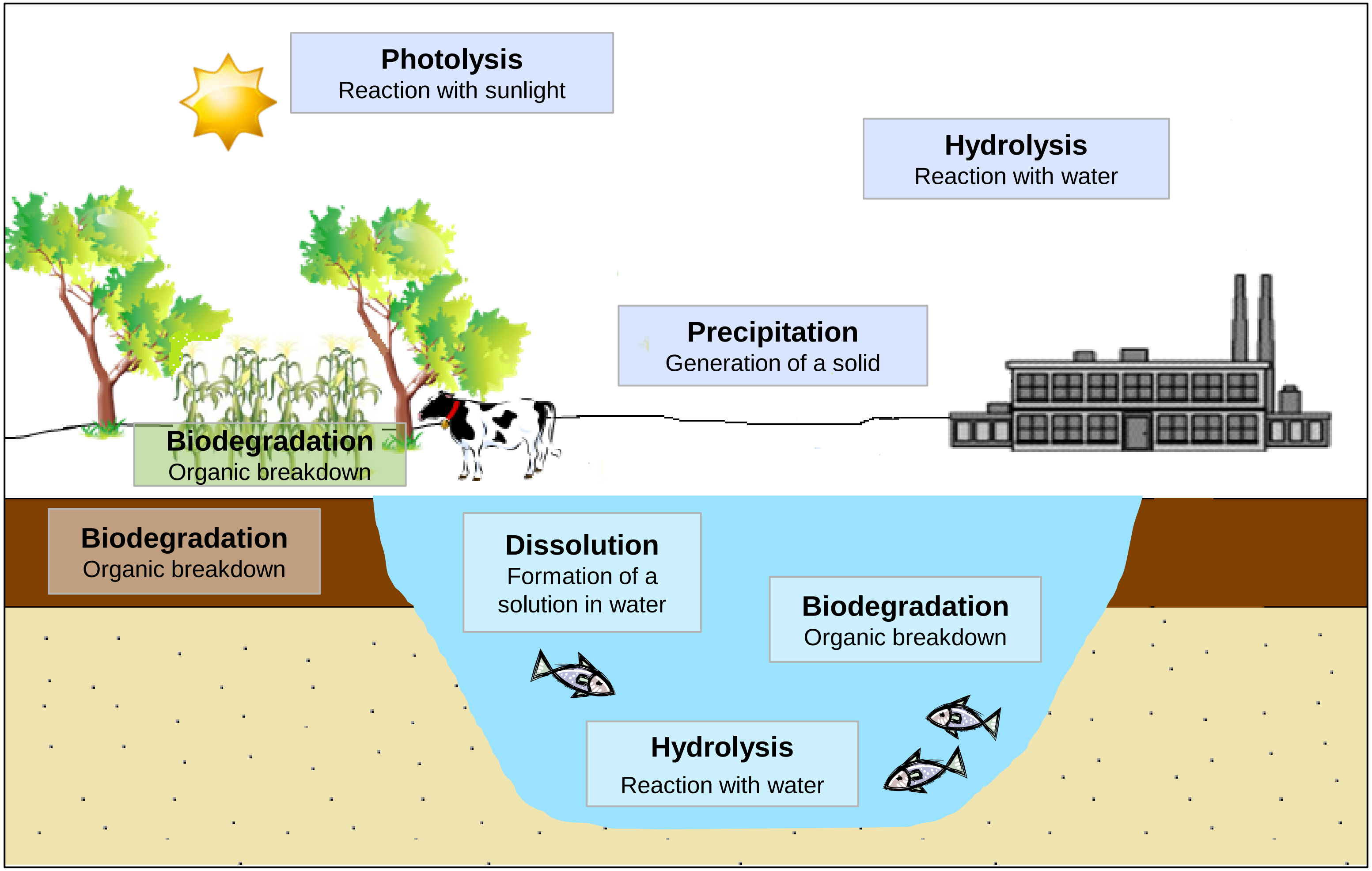


Transport:

Movement Within and Between Environmental Media

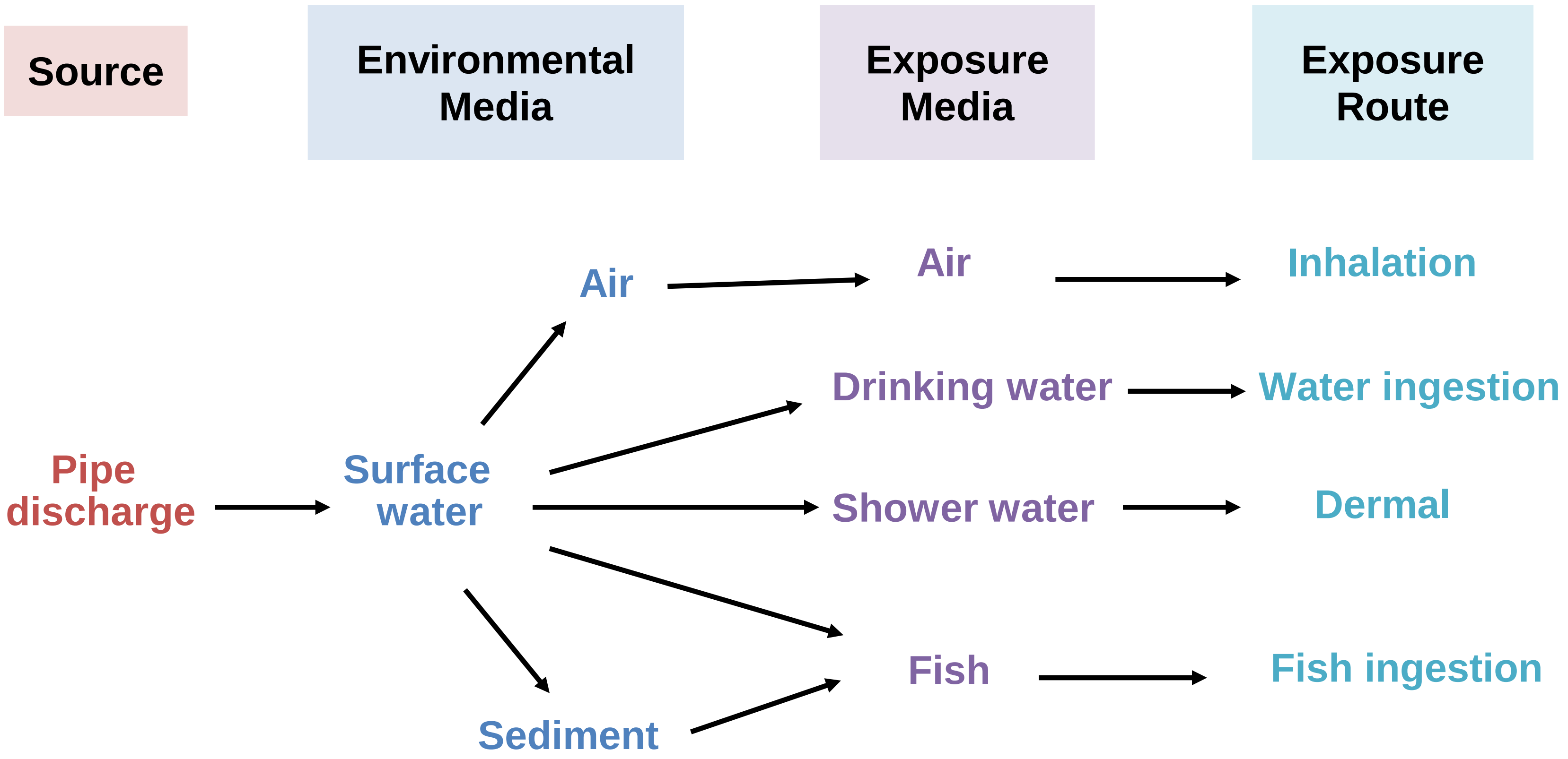


Transformation: Chemical Changes within a Medium



United States Environmental Protection Agency

Environmental and Exposure Media



United States Environmental Protection Agency

INFLUENCES ON FATE AND TRANSPORT

Chemical Source: The Beginning of the Continuum

How is the contaminant released?

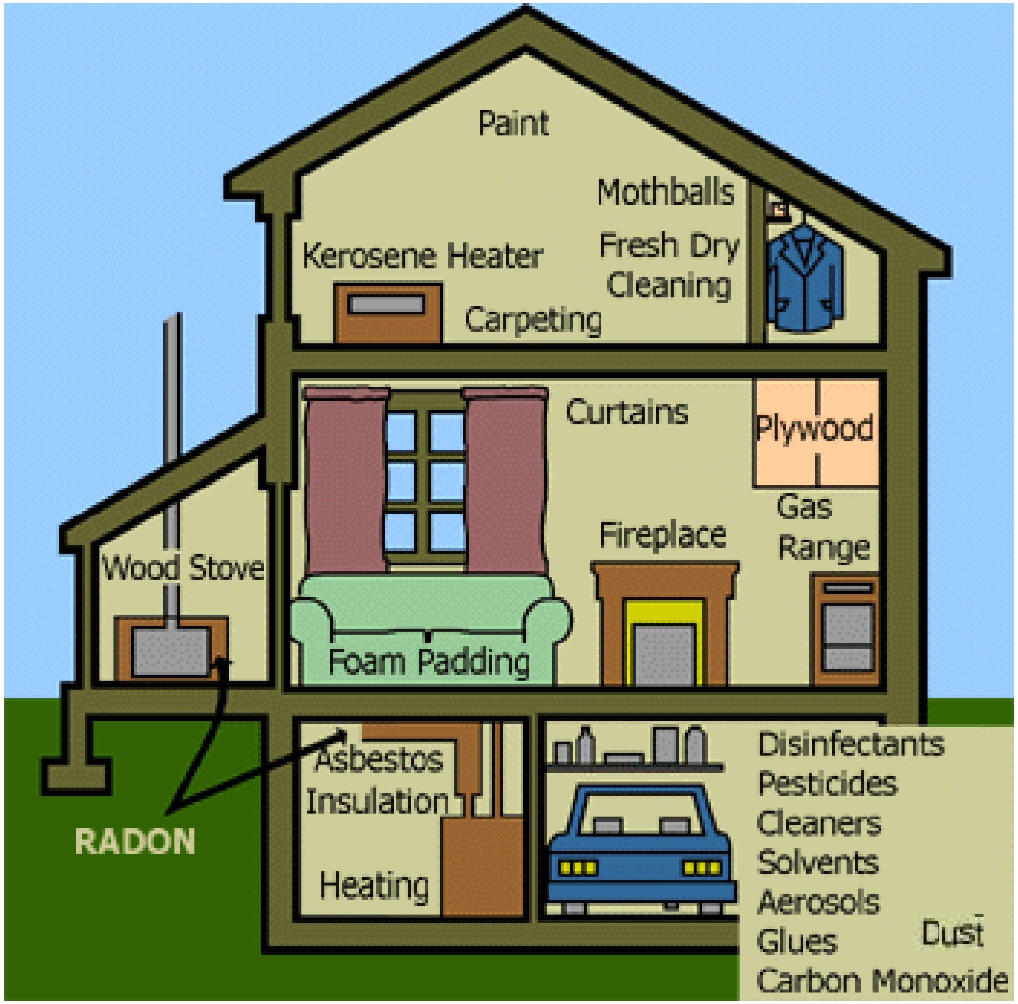
- Duration of release
- Quantity released
- Characteristics of source
- Area of contamination

Where is the contaminant discharged?

- Soil or sediment
- Surface water
- Ground water
- Biota
- Air

Point Sources and Non-Point Sources

Indoor Sources of Contaminants



Source: U.S. EPA. 2004. Air Toxics Risk Assessment Reference Library. Volume 1. Technical Resource Manual. EPA-453-K-04-001A.

Consumer Products as Sources of Contaminants

- Flame retardants (PBDEs)
- Plasticizers (phthalates, BPA)
- Surfactants (PFOA, PFOS)
- Chemicals in cleaning products, solvents, and paints
- Pesticide products
- Pharmaceuticals

EPA United States Environmental Protection Agency

Background Sources

- Existing levels of chemicals in the environment
- Chemicals derived from sources other than the “source of interest”

? Quantify, or not?

Organic vs. Inorganic Chemical Contaminants

	Organic (carbon-based)	Inorganic (not carbon-based)
Influences on transport	Partitioning, sorption	Soil structure, environmental chemistry
Influences on fate	Degradation and chemical transformation	Chemical transformation
Examples	Dioxins, PCBs, pesticides	Nitrates/nitrites, Cr, Fe, Pb

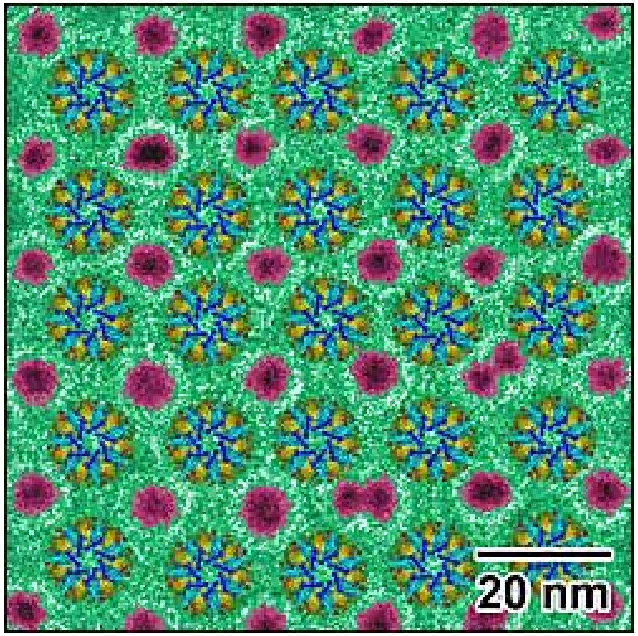
Vapor Pressure and Water Solubility

- **Vapor pressure**: How likely a compound will evaporate, or convert from a liquid phase to a gaseous phase
  - ↑ Vapor pressure: more likely to be found in gas phase
- **Water solubility**: Measure of the maximum amount of a chemical that will dissolve in pure water
  - ↑ Solubility: more likely to be mobile in environment
  - Less likely to sorb to other media or bioconcentrate
- Both vapor pressure and water solubility are temperature dependent

United States Environmental Protection Agency

Contaminants for which Physical Characteristics are Important

- Important characteristics
  - Size
  - Surface coating
  - Chemical composition
  - Among others...
- Examples
  - Particulate matter
  - Nanoparticles



Magenta circles are gold nanoparticles situated on an array of enzymes.
Source: Brookhaven National Laboratory.
http://www.bnl.gov/bnlweb/pubaf/pr/PR_display.asp?prID=07-73

→ **Size** is the defining characteristic for these contaminants

Environmental Characteristics

Soil and sediment properties
(particle size, porosity)

Climate and meteorology
(wind speed, rainfall amounts)

Impacts on chemical transport and transformation

Surface and ground water properties
(flow, temperature, pH)

Other properties of ecosystem
(species, topography)

United States Environmental Protection Agency

PHYSICAL TRANSPORT AND PARTITIONING

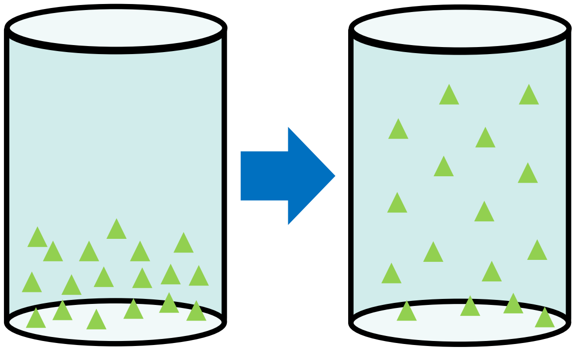
Advective Transport

- Transport of chemicals as a result of movement of an environmental medium
  - "Piggy-backing" on or in moving air, water, or soil
- Important parameters:
  - How much?
    - Amount of chemical in the moving phase
  - How fast?
    - Rate of movement of phase

Diffusive and Dispersive Transport

Diffusion

- Movement of a substance that results from a concentration gradient
  - Molecules diffuse over time to areas of lower concentration until equilibrium

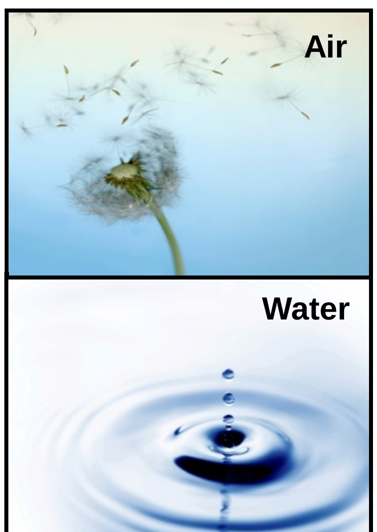


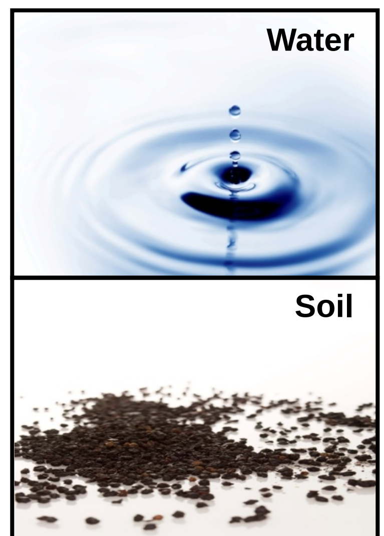
Dispersion

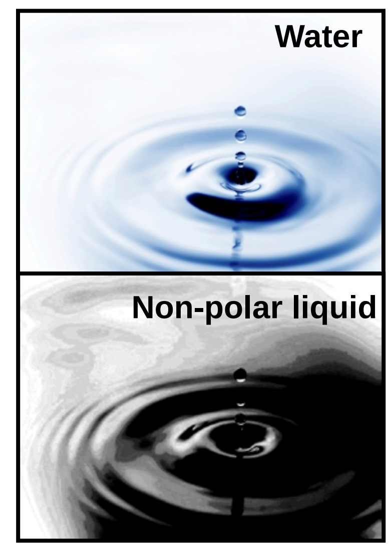
- Spreading out of chemicals within an environmental medium
  - Can occur simultaneously with advective transport

Partitioning between Environmental Media

- Movement of chemical ***between*** environmental phases
  - Primary environmental phases are air, soil, water
    - Also non-polar liquids, such as oils and solvents
  - Determined by characteristics of the chemical, environmental (physical/chemical) characteristics, other properties





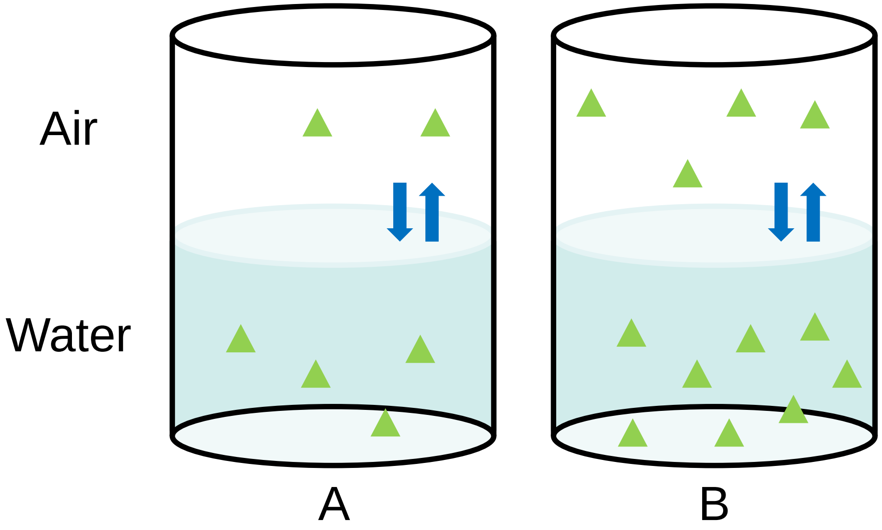


Equilibrium: A State of No (Observable) Change

- Equilibrium system: No spontaneous, unaided changes
  - No changes in concentration on either side of an interface
  - Dynamic equilibrium: No **net** change with time
    - Particular type of steady state
- Equilibrium constant: K
  - Equal to ratio of concentrations when at equilibrium

Air-Water Partitioning: Henry's Law

Henry's Law constant: H, or K_H = $\frac{\text{Partial pressure in air}}{\text{Concentration in water}}$



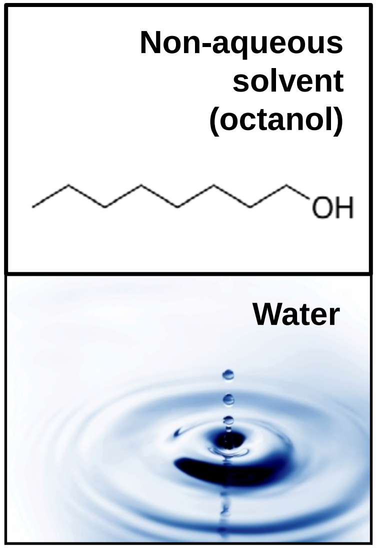
- **Higher H** → Chemical will partition more readily from water to air
- Log K_H often used due to wide range of K_H values

Sample values (atm·L·mol^{-1})

Chemical	log K_H	K_H
Phenol	-3.39	4.1E-04
DDT	-2.02	9.5E-03
2,3,7,8-TCDD	-1.3	5.0E-02
Naphthalene	-0.37	4.3E-01
Hexachlorobenzene	0.18	1.5E+00
Benzene	0.74	5.5E+00
Perchloroethylene	1.44	2.8E+01
Methane	2.82	6.6E+02

EPA United States Environmental Protection Agency

Octanol-Water Partitioning: K_{OW}



$$K_{OW} = \frac{\text{Concentration in octanol}}{\text{Concentration in water}}$$

Higher K_{OW} → Chemical more readily bioaccumulates

Lower K_{OW} → Chemical partitions preferentially to water

- Representative of behavior of organic chemical in environmental media, fat
- Typical units are (mol/L of octanol) over (mol/L of water) *("unitless")*
- Log K_{ow} often used due to wide range of K_{ow} values

Sample values (mol/L)/(mol/L)

Chemical	log K_{OW}	K_{OW}
Methane	1.09	1.2E+01
Phenol	1.45	2.8E+01
Benzene	2.13	1.3E+02
Perchloroethylene	2.88	7.6E+02
Naphthalene	3.36	2.3E+03
Hexachlorobenzene	5.50	3.2E+05
DDT	6.36	2.3E+06
2,3,7,8-TCDD	6.64	4.4E+06

Soil-Water Partitioning: K_d

$$K_d = C_s/C_w = \frac{\text{Concentration in soil}}{\text{Concentration in water}}$$

- Concentration “in” soil = chemical sorbed to soil particles
- Highly dependent on properties of soil
- K_d can vary as total amount of chemical mass changes
- Typical units are (mg/kg)(mg/L), or L/kg
- Behavior of soil and sediment - analogous
  - K_d can be measured for sediment as well

EPA United States Environmental Protection Agency

Organic Carbon-Water Partitioning: K_{oc}

$$K_{oc} = \frac{\text{Concentration sorbed to organic carbon}}{\text{Concentration in water}}$$

- K_{oc} is chemical-specific
  - Largely independent of environmental conditions (except for amount of organic carbon in the soil)
  - Typical units: (mg/kg)(mg/L), or L/kg
  - Does not vary for a given type of soil, regardless of amount of chemical present
- Soil organic matter (e.g., humic/fulvic acids) composed of ~half organic carbon
  - f_{oc} is roughly equal to ½ × f_{om}
  - K_{oc} is roughly equal to 2 × K_{om}

Using K_{oc} (and K_{ow}) to Estimate Soil Partitioning

- Soil-water partitioning proportional to:
  - Fraction of organic carbon in soil
  - Partitioning between organic carbon and water (K_{oc})

$$K_d = f_{oc} \times K_{oc}$$

- Linear relationship between K_{ow} and K_{oc} for a given chemical
  - K_{ow} can be used to estimate K_{oc}

Partitioning (and other Transfer) into Biota

- **Bioaccumulation**: Chemical uptake by biota from environmental media (e.g., water, soil, food) by direct exposure or ingestion of contaminated media
  - **Bioconcentration factor (BCF)** – typical units of L/kg
    - Water → fish by direct exposure only
  - **Bioaccumulation factor (BAF)** – typical units of L/kg
    - Water → fish by all pathways, including ingestion
    - Typical BAF range for organics in water = 1 to 10^5 (sometimes higher)
    - A biota-sediment accumulation factor (BSAF) is analogous to a BAF
- **Biotransfer factor (BTF)**: Empirical ratio relating the mass of the chemical to which the animal is exposed to the chemical in biota

Interactive Discussion:

How will this chemical behave in the environment?

Chemical Characteristics	Likely Environmental Behavior
Released by combustion	Present in air
Low water solubility	Sorbed to particles in air, soil, and sediment
High K_{oc}	High bioaccumulative potential

United States Environmental Protection Agency

CHEMICAL TRANSFORMATION

Transformation of Organic and Inorganic Compounds

Organic Compounds

- Chemical degradation
  - Photolysis
  - Hydrolysis
  - Oxidation
- Biodegradation

Inorganic Compounds

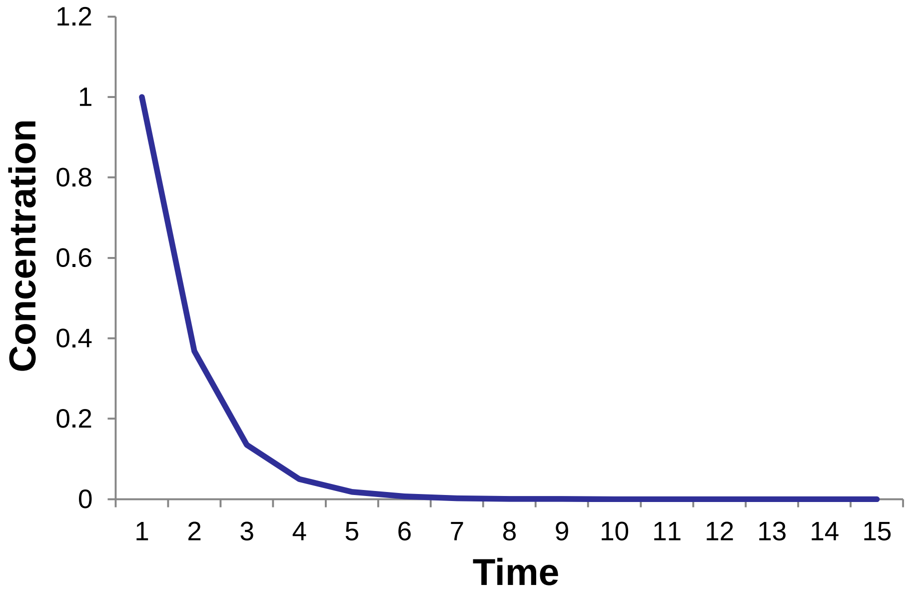
- Change in speciation
- Change in complexation or dissolution

First-order Decay

$$C_t = C_0 \exp(-kt)$$

Where:

- C_t = concentration at time t
- C_0 = concentration at time 0
- k = first-order decay rate constant (expressed in units of 1/t)
- t = time



- Half-life ($t_{1/2}$): Time required for original concentration to be reduced by half
- Rate constant (k) = $\ln(2)/t_{1/2}$

First-order Decay Exercise: Ozone

$C_t = C_0 \exp(-kt)$

$C_0 = 600$ ppb

$t_{1/2} = 10$ minutes

$k = 0.693$/half life

Ozone Solution

$C_t = C_0 \exp(-kt)$

$t = ?$

$C_t = 75$ ppb

$C_0 = 600$ ppb

$t_{1/2} = 10$ minutes

$k = 0.693/\text{half life}$
$= 0.693/10$
$= 0.0693$

United States Environmental Protection Agency

CONCLUSION

United States Environmental Protection Agency

Key Concepts

- Influences on fate and transport
  - Chemical, source, environmental characteristics
- Important fate processes
  - Intraphase: transport, diffusion, dispersion
  - Interphase: partitioning
- Transformations
  - Degradation, conversion, other processes for organic, inorganic chemicals
  - First-order decay

Applying Fate and Transport Concepts for Exposure Assessment

- Before modeling or monitoring as part of an exposure assessment:
  - Consider media linkages
  - Key questions:
    - How do the characteristics of the source and contaminant affect the transport and transformation in the environment?
    - How do the chemicals move within and between environmental media?
    - How do the chemicals change within the environmental media?
  - Flowcharts or exposure pathway analysis can be helpful