환경해양학 2013년 2학기

오염 생물학
PART 1. 유해물질 환경화학

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순서

오염 생물학-1.유해물질 환경화학

1. 환경분석화학의 과정
2. 기기분석의 기초
3. POPs
4. 분배특성

We Study!
Chemicals and Chemical Stress

Toxicology
- •Toxicokinetics
- •Physiology
- •Biochemistry

- •Biology
- •Taxonomy
- •Molecular Toxicology

DANGER
HAZARDOUS CHEMICALS

Chemistry
- •Chemistry
- •Environmental Chemistry
- •Analytical Chemistry
- •Organic Chemistry
- •Physical Chemistry
- •Chemodynamics

Ecotoxicology
- •Population Ecology
- •Community Ecology

Chemodynamics

Issues
Earth, our Environment and Ecosystem

Original article by
PDr. Garrett Hardin (1968)

State of the Planet, But tragedy of the commons?

- •In the issues running from 14 November 2003 to 5 December 2003
- •*Science* offered a comprehensive look at the issues facing Planet Earth over the next 50 years, in a special four-week "State of the Planet" series.
- •Included in the series were eight Viewpoint pieces on topics ranging from population to energy to fisheries to global change

Issues
Chemicals of Concern

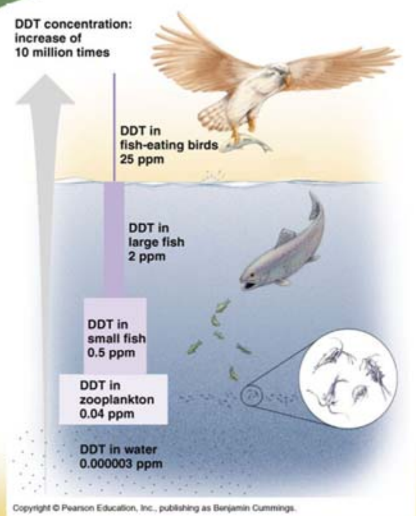
Toxic materials (primarily POPs etc.)
Oxygen-consuming wastes
Radioactive substances
Disease-causing agents
Thermal pollution
Suspended solids
Dissolved solids
Plant nutrients
Acids
Oil
…

Basic
Concentrations, How to Express?

- Air (gaseous): g/m^3, mg/m^3, $\mu g/m^3$
- Water (aqueous): mg/L, µg/L, ng/L
- Soil (solid): µg/g, ng/g, pg/g

What about unit conversion to 'ppm', 'ppb', or 'ppt'?
$$1\ ppm = 1\ (mg/m^3) / (\rho_a = M/V_n)$$
$$1\ ppm = 1\ (mg/L) / \rho_w$$

Basic
Concentrations, Examples



25 ppm

2 ppm = 2000 ppb

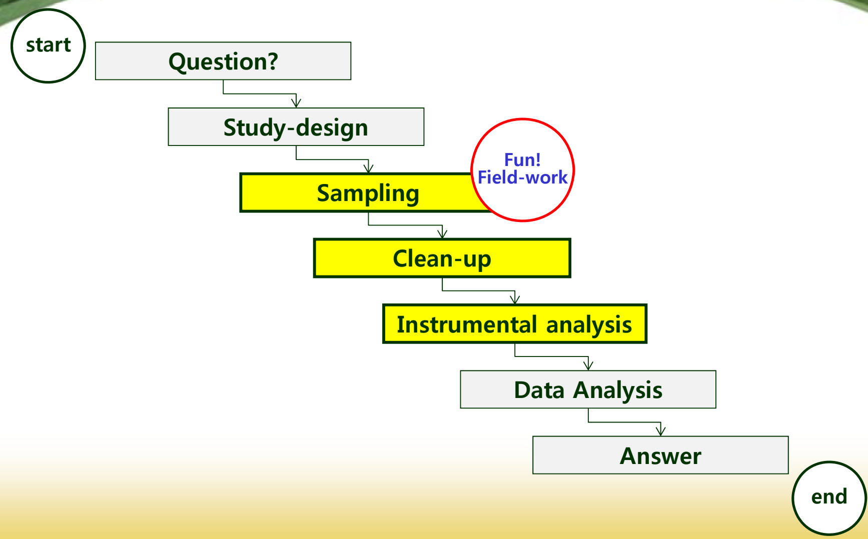
0.5 ppm = 500 ppb

0.04 ppm = 40 ppb

0.000003 ppm = 0.003 ppb = 3 ppt

Environmental Analytical Chemistry

analytical process (qualitative & quantitative)



Samples

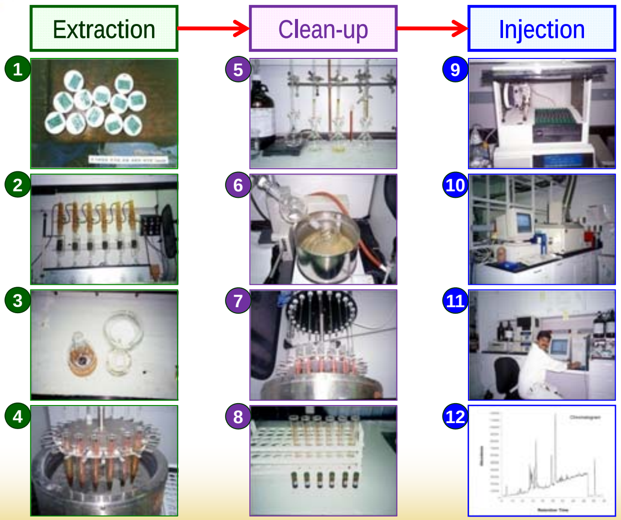
sediment core samples

Samples

biological samples for community analysis

Sample Processing

chemical analysis = extraction + clean-up + injection



Extraction

solvent extraction =
•partitioning of a solute between two liquid phases = like dissolves like

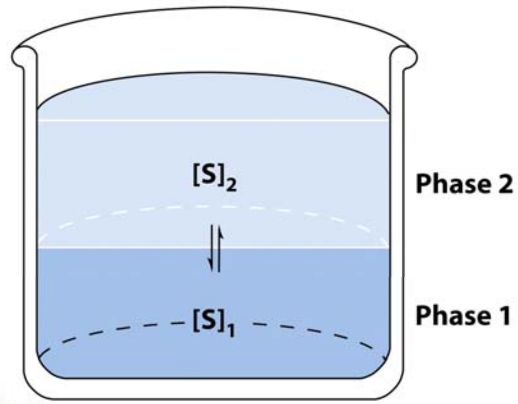
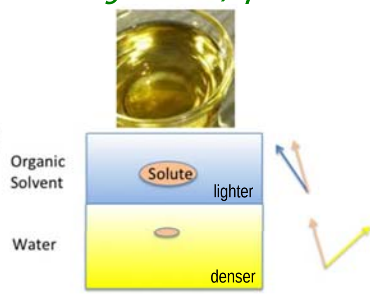


Figure 23-1
Quantitative Chemical Analysis, Seventh Edition

octanol=fatty alcohol= surrogate of fat/lipid



Clean-up=Fractionation=Pretreatment

chromatographic separation
mobile phase (이동상) vs. stationary phase (정지상)

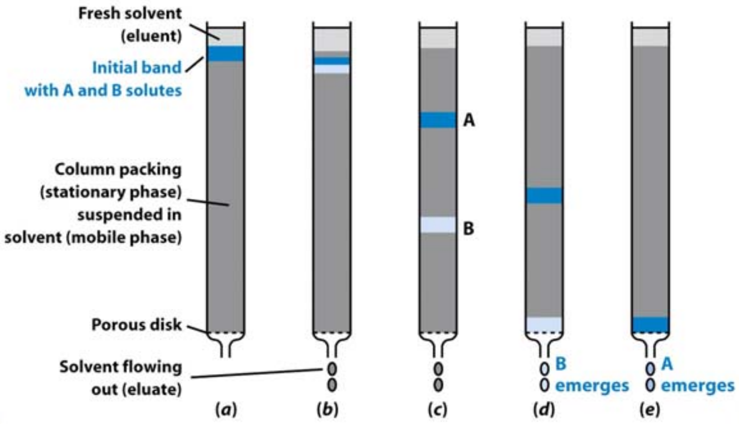


Figure 23-5
Quantitative Chemical Analysis, Seventh Edition

Gas-chromatography

analyte is transported through column
by a gaseous mobile phase (viz. carrier gas)

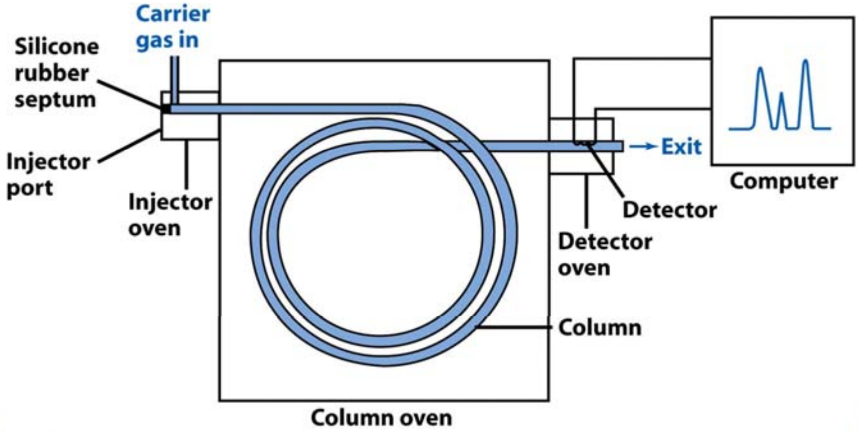


Figure 24-1
Quantitative Chemical Analysis, Seventh Edition

Column Selection

packed column vs. open tubular column

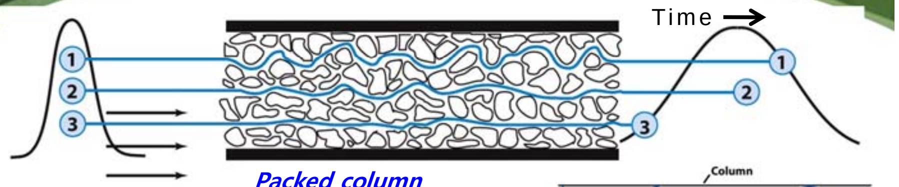
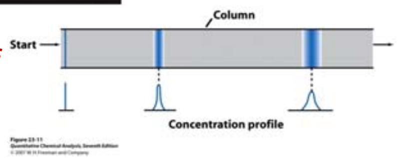
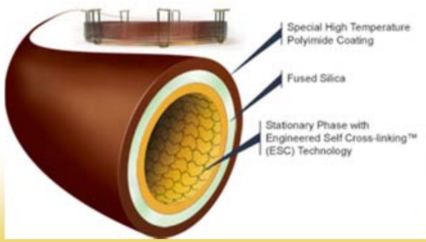


Figure 23-19
Quantitative Chemical Analysis, Seventh Edition

Packed column
1. multiple flow paths
2. band spreading



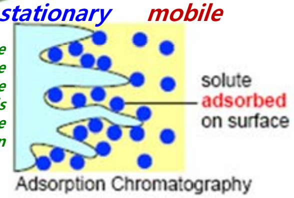


Compared with packed column,
Open tubular column can provide
1. Higher resolution
2. Shorter analysis time
3. Increased sensitivity
4. Lower sample capacity

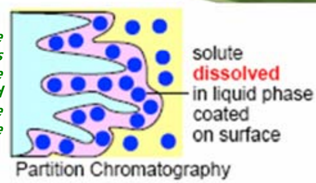
Chromatography Selection

stationary ***mobile***

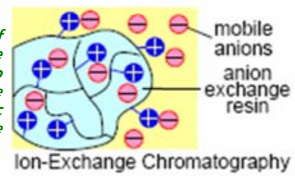
The more strongly a solute is adsorbed, the slower it travels through the column



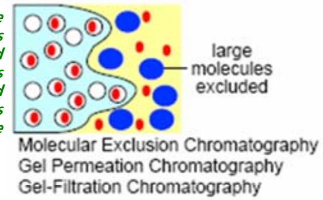
Solute equilibrates between the stationary liquid and the mobile gas phase



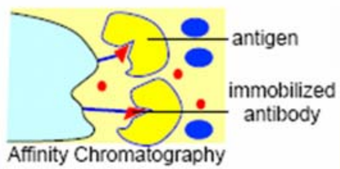
Solute ions of opposite charge are attracted to stationary phase by electrostatic force



Small molecule penetrate pores of particles and large molecules are excluded i.e., separates molecules by size



One kind of molecule in complex mixture becomes attached to molecule that is covalently bound to stationary phase
All other molecules simply wash through



Detectors

various detectors
to be selected considering chemical properties

- •Thermal Conductivity Detector (TCD)
- •Flame Ionization Detector (FID)
- •Electron Capture Detector (ECD)
- •Nitrogen-Phosphorus Detector (NPD)
- •Flame Photometric Detector (FPD)
- •Photoionization Detector (PD)
- •Sulfur Chemiluminescence Detector (SCD)
- •Mass Spectrometric Detector (MSD)

…

HRGC-MSD

GC-MS

QA/QC

Analytical Procedure

- •Blanks – laboratory and field blanks
- •Duplicate samples – Sample splits
  – Procedural splits
- •Spiked Samples – Percent recovery
  – Extraction efficiency
  – Chromatography markers
- •Blind Samples
- •Storage/Fortified Samples
- •Round Robin studies
- •Certified Reference Materials
- •Two analysts conduct same analysis

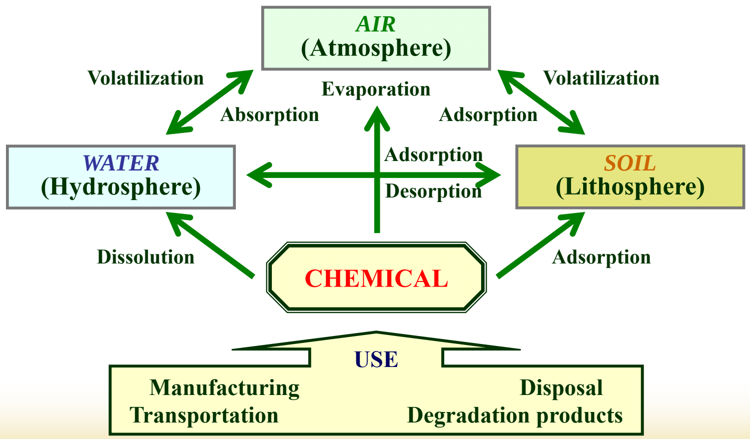
QA/QC

Accuracy vs. Precision

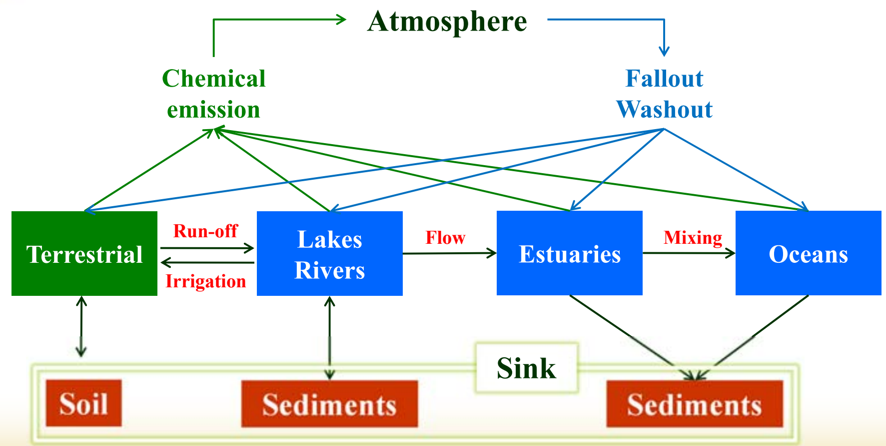
Accuracy ***Precision*** ***Accuracy with Precision***

•Accuracy is telling the truth . . .
•Precision is telling the same story over and over again.

A Generalized Scheme of Movement of Chemicals

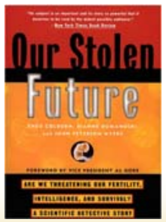


An Example of Chemical Distribution

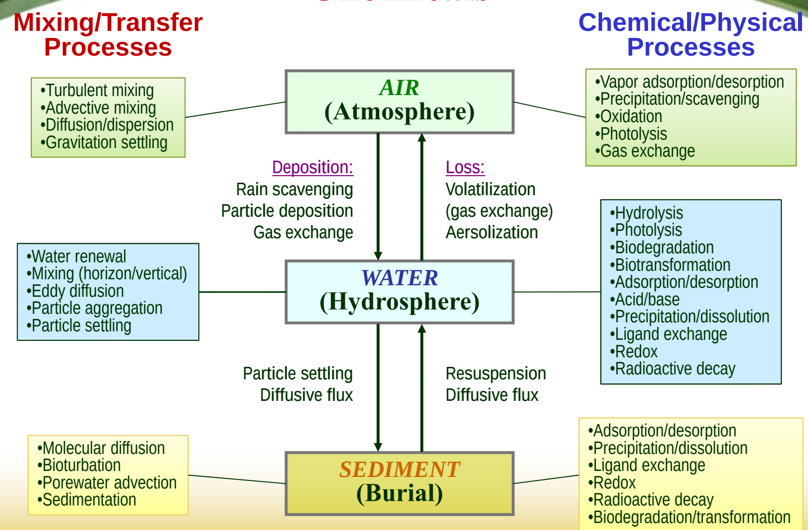


Hazardous Chemicals of Concern History & Issues

- 1930's: **DDT** (during WW-II)
- 1950's: **Hg** (Minamata disease)
- 1960's: **PCBs and Cd** (Itai-itai disease)
  - 1962: *Silent spring* (by Rachel Carson, DDT issue)
- 1980's: **Industrial wastes (Metals)** (Onsan disease)
- 1990's: **Dioxins and EDCs**
  - 1996: *Our stolen future* (by Theo Colborn et al.)
- 2000's: **PBDEs** (Brominated Flame Retardants)
  - **PFCs** (PFOS & PFOA)
  - **Nanoparticles** (P_{10}, $P_{2.5}$)
  - **Pharmaceuticals** (antibiotics etc.)
  - **PCP** (Personal Care Product)



Fluxes of Chemicals



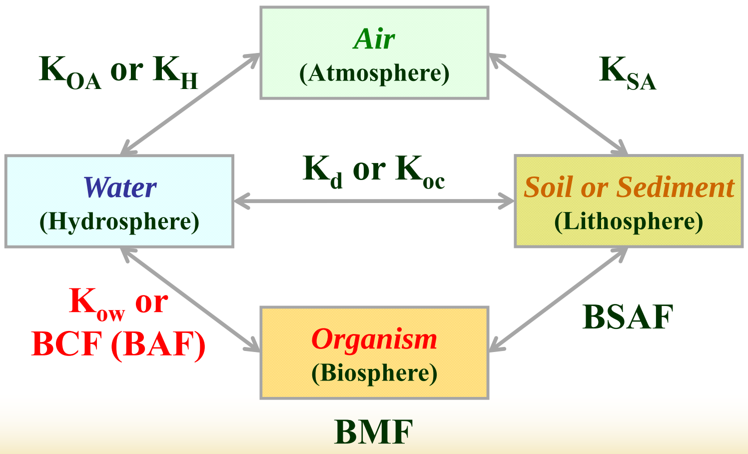
POPs
Terms

	Full name	Description
• PBT	Persistent	(chemical property)
	Bioaccumulative	(biochemical process)
	Toxic	(biological effect)
• TOMP	Toxic	(biological effect)
	Organic	(chemical property)
	Micro	(environmental level)
	Pollutant	(environmental aspect)
• EDC	Endocrine	
	Disrupting	
	Chemical	

POPs
Definition & Characteristics

- highly stable and semi-volatile
- move long distance; long-range transport
- persist in the environment; persistence
- pose a risk of causing adverse effects; toxicity
- bioaccumulate through the food web; bioaccumulation
- used as pesticides or in industry
- or generated unintentionally as byproduct

Multimedia Fate
Distribution Coefficients

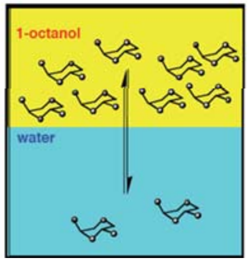


POPs
Fate Characteristics

- Aspect of 'Partitioning'
  - Organism vs. Water — K_{ow}
  - Soil vs. Water — K_d or K_{oc}
  - Air vs. Water — K_H
  - Air vs. Soil — K_{SA}
- Aspect of 'Bioaccumulation'
  - Organism vs. Water — BCF
  - Organism vs. Water — BAF
  - Organism vs. Organism — BMF
  - Organism vs. Sediment — BSAF

K_{OW}
Octanol vs. Water

- Ratio of a chemical's concentration in octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system



- $K_{ow} = C_{octanol}/C_{water}$ (dimensionless)
- K_{ow} for POPs ranges between 10^{-3} and 10^{7}
- K_{ow} describes the lipophilicity of a chemical
- K_{ow} inversely proportional to water solubility

BCF
Organism vs. Water

- Bioconcentration Factor (BCF) is the concentration of a particular chemical in organism (tissue) per concentration of chemical in water (at steady-state, considering only media = viz. water)

- $BCF = C_{organism}/C_{water}$ (dimensionless)
- A linear relationship between BCF and K_{ow} (e.g. $\log BCF = 0.79 \times \log K_{ow} - 0.40$)
- BCF is species-specific but comparable bw. species (e.g. $\log BCF_{fish} = 1.001 \times \log BCF_{daphnia} + 043$
- BCFs range from 1 to 1000,000
- BCF ↑ = water solubility ↓ = lipophilicity ↑ = bioaccumulation ↑ = biodegradation ↓

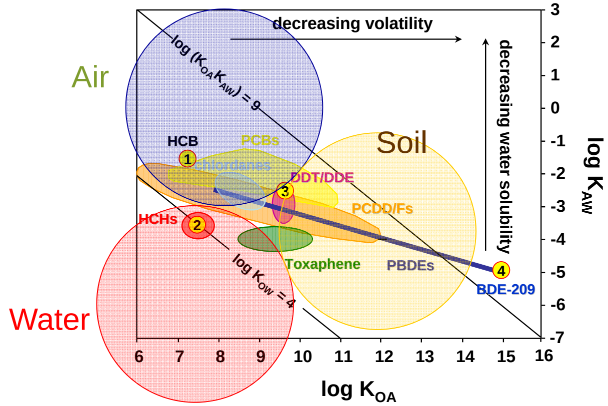
BAF, BMF, and BSAF
Organism vs. Environment

- Bioaccumulation Factor (BAF) is the concentration of a particular chemical in organism (tissue) per concentration of chemical in water (observed in the environment, considering all uptake pathways)

- $BAF = C_{organism}/C_{water}$ (dimensionless)
- $BMF = (C_{organism}/f_{lipid})/(C_{diet}/f_{lipid})$ (dimensionless)
- BCF ↑ = BAF ↑ = BMF ↑

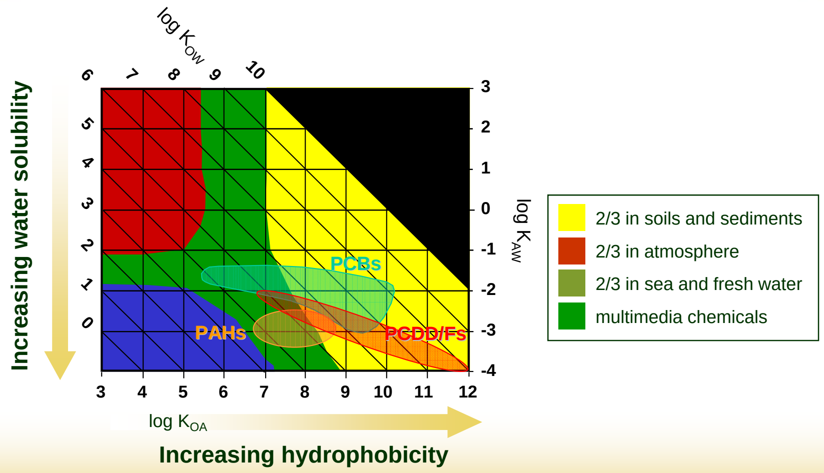
- Biota-Sediment Accumulation Factor (BSAF)
- $BSAF = (C_{organism}/f_{lipid})/(C_{sed}/f_{oc})$
- Useful to predict concentrations in organism from known concentrations in sediment

POPs
Chemical Space Map



Chemical space map defined by their partitioning properties of $\log K_{AW}$, $\log K_{OA}$, and $\log K_{OW}$ at 25°C.

POPs
Chemical Property



Risk of PCBs
Utility of Distribution Coefficients