해양오염론 입문-3주제

해양오염평가 방법론

1. 오염물질의 분석
2. 오염물질의 거동특성
3. 오염물질의 독성
4. 오염물질의 위해성평가

We Study!
Chemicals and Chemical Stress

Toxicology

- Toxicokinetics
- Physiology
- Biochemistry

- Biology
- Taxonomy
- Molecular Toxicology

Chemistry

Ecotoxicology

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

- Population Ecology
- Community Ecology

Chemodynamics

Issues
Earth, our Environment and Ecosystem

STATE OF THE PLANET
A special series

TRAGEDY OF THE COMMONS?
A special issue

Original article by
PDr. Garrett Hardin (1968)

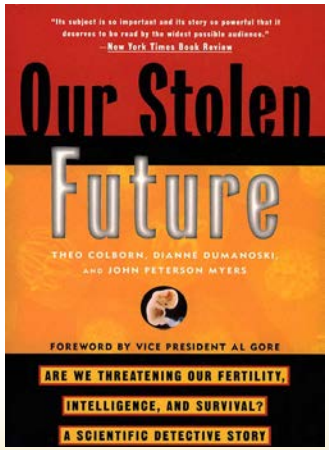
State of the Planet, But tragedy of the commons?

- 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

Hazardous Chemicals of Concern

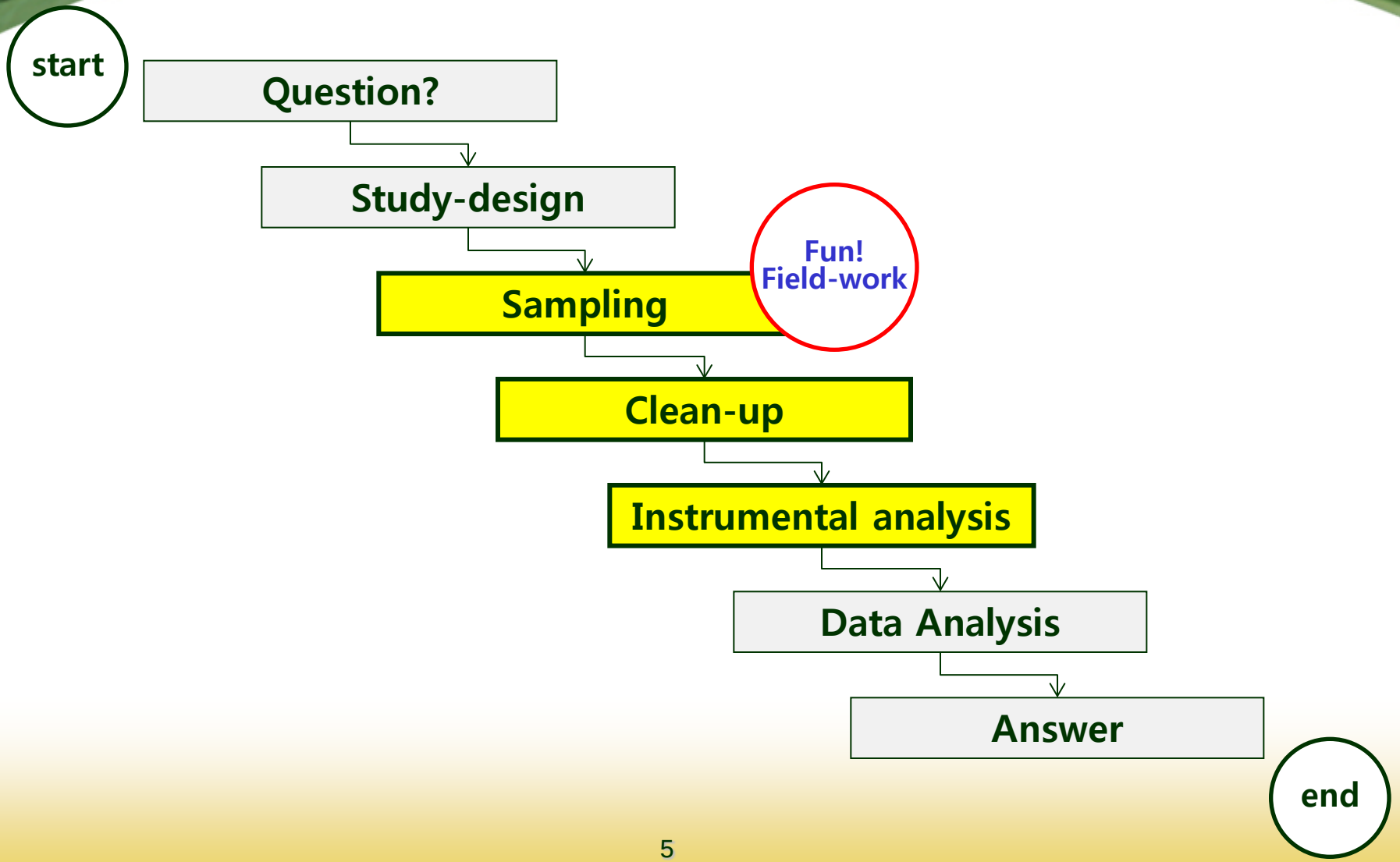
History & Issues

- **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)



Environmental Analytical Chemistry

analytical process (qualitative & quantitative)



Samples

sediment core samples

Box Core에서 2 cm 깊이로 퇴적물을 자르고 있는 모습

Gravity Core를 이용해서 퇴적물을 Sampling한 모습

Samples

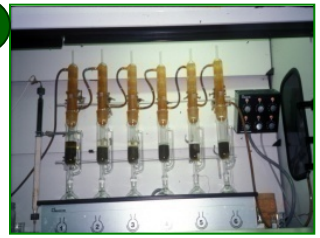
biological samples for community analysis

Sample Processing

chemical analysis = extraction + clean-up + injection

Extraction → **Clean-up** → **Injection**

1


2


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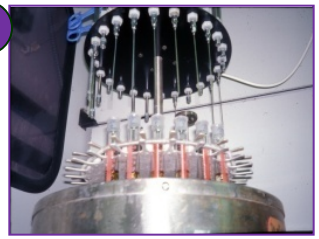

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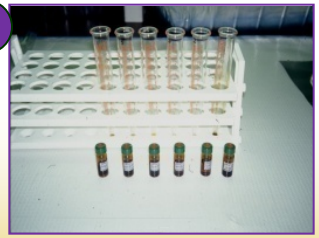

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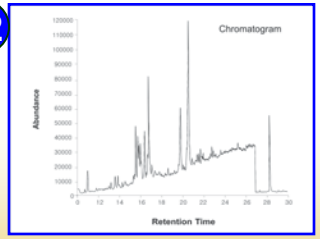


Extraction

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

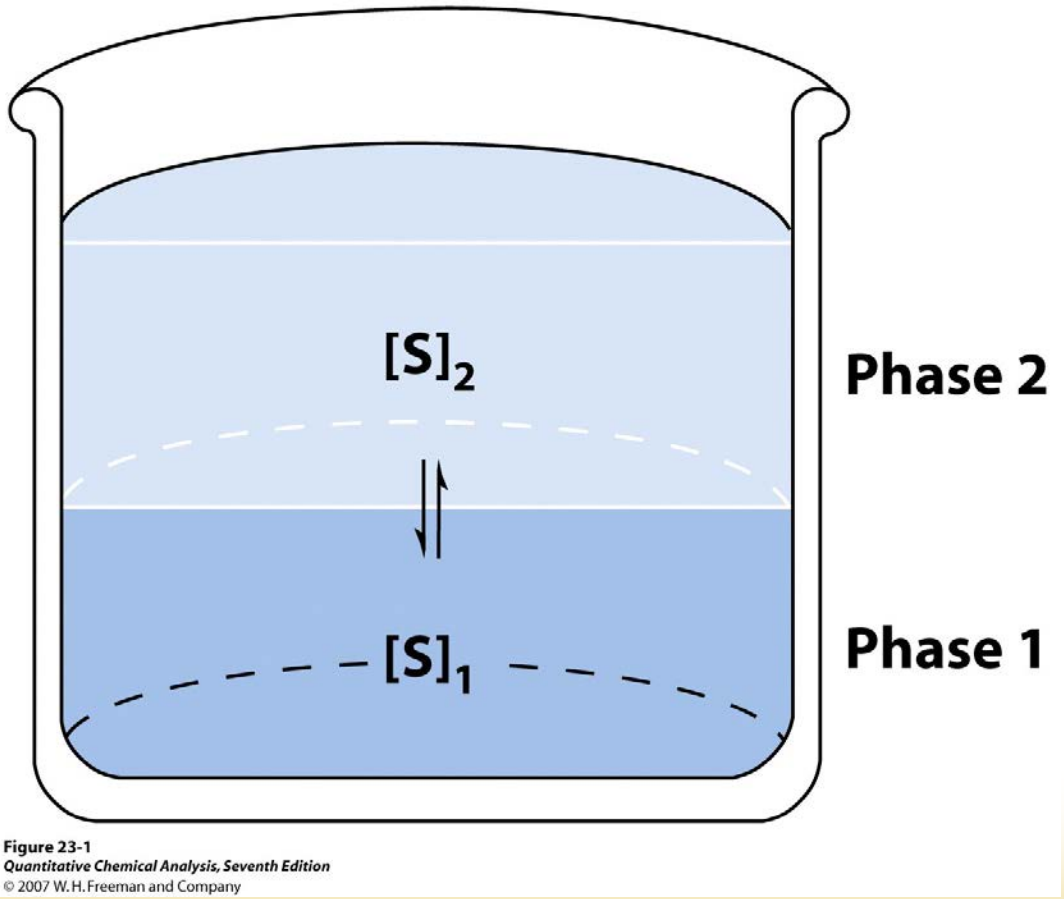
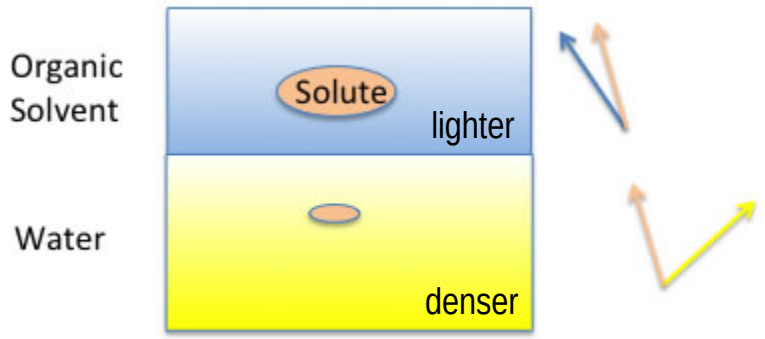


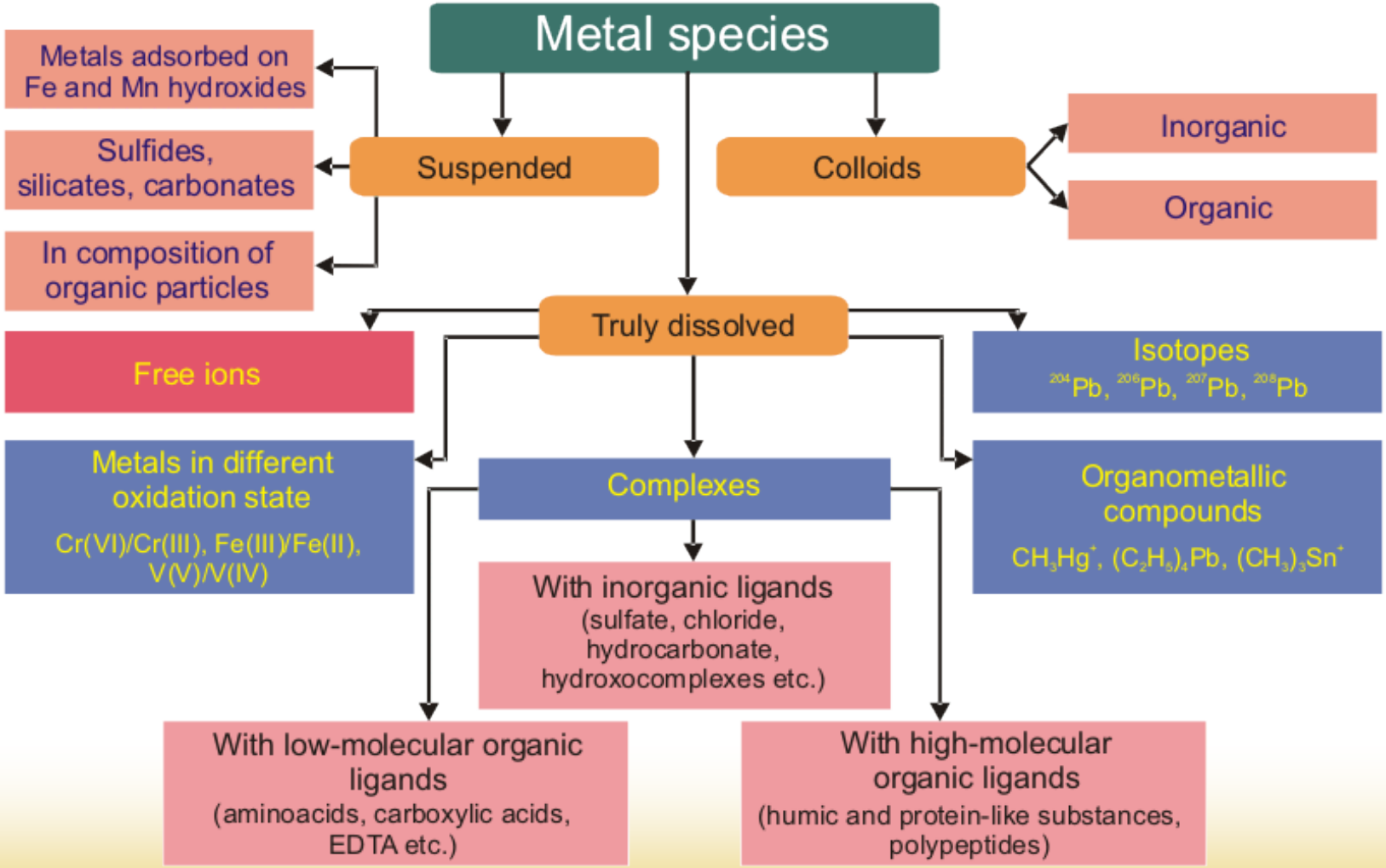
Figure 23-1
Quantitative Chemical Analysis, Seventh Edition

octanol=fatty alcohol=
surrogate of fat/lipid



Metal species

e.g., various type of metals



Clean-up=Fractionation=Pretreatment

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

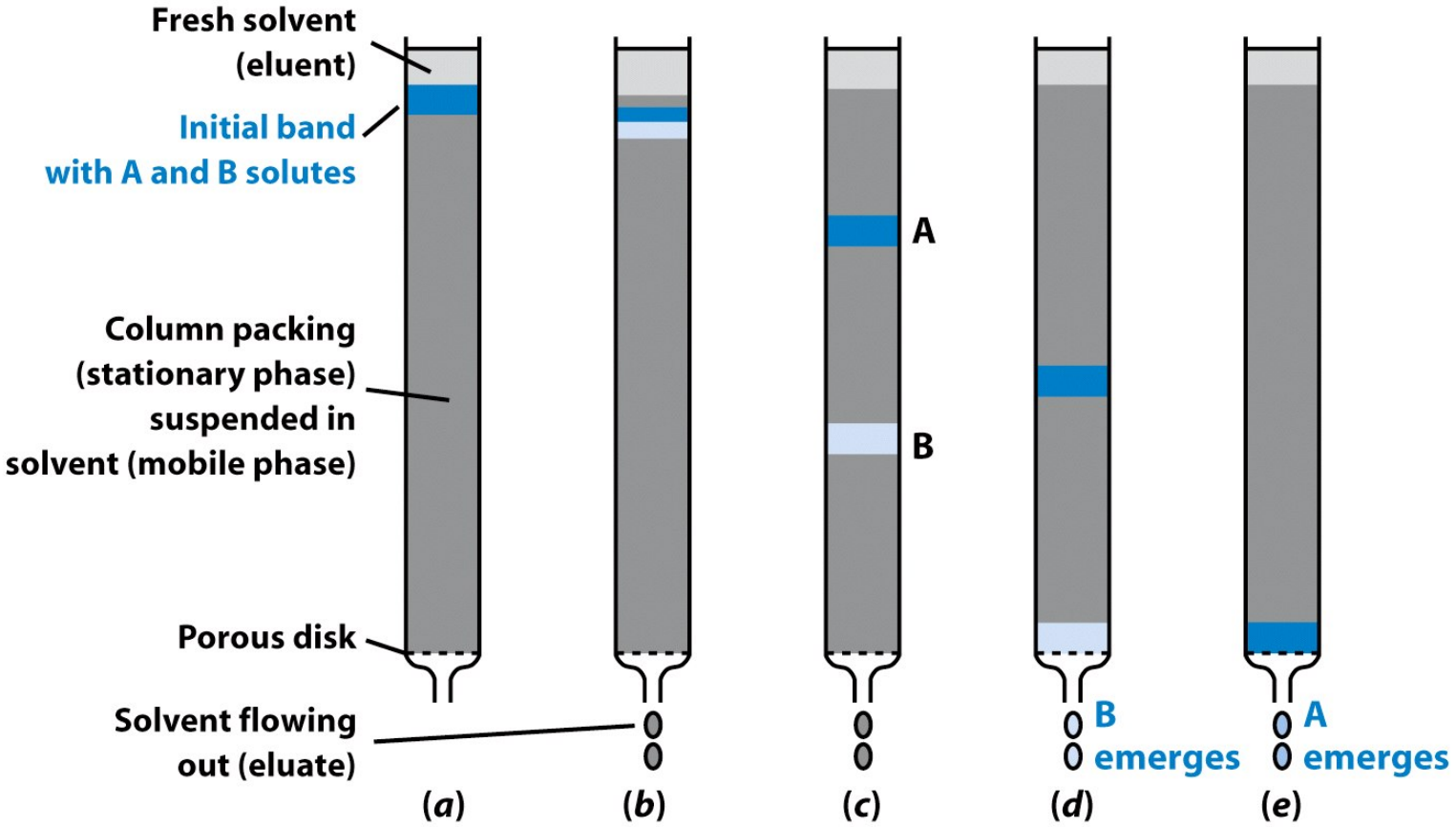


Figure 23-5
Quantitative Chemical Analysis, Seventh Edition

Gas-chromatography

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

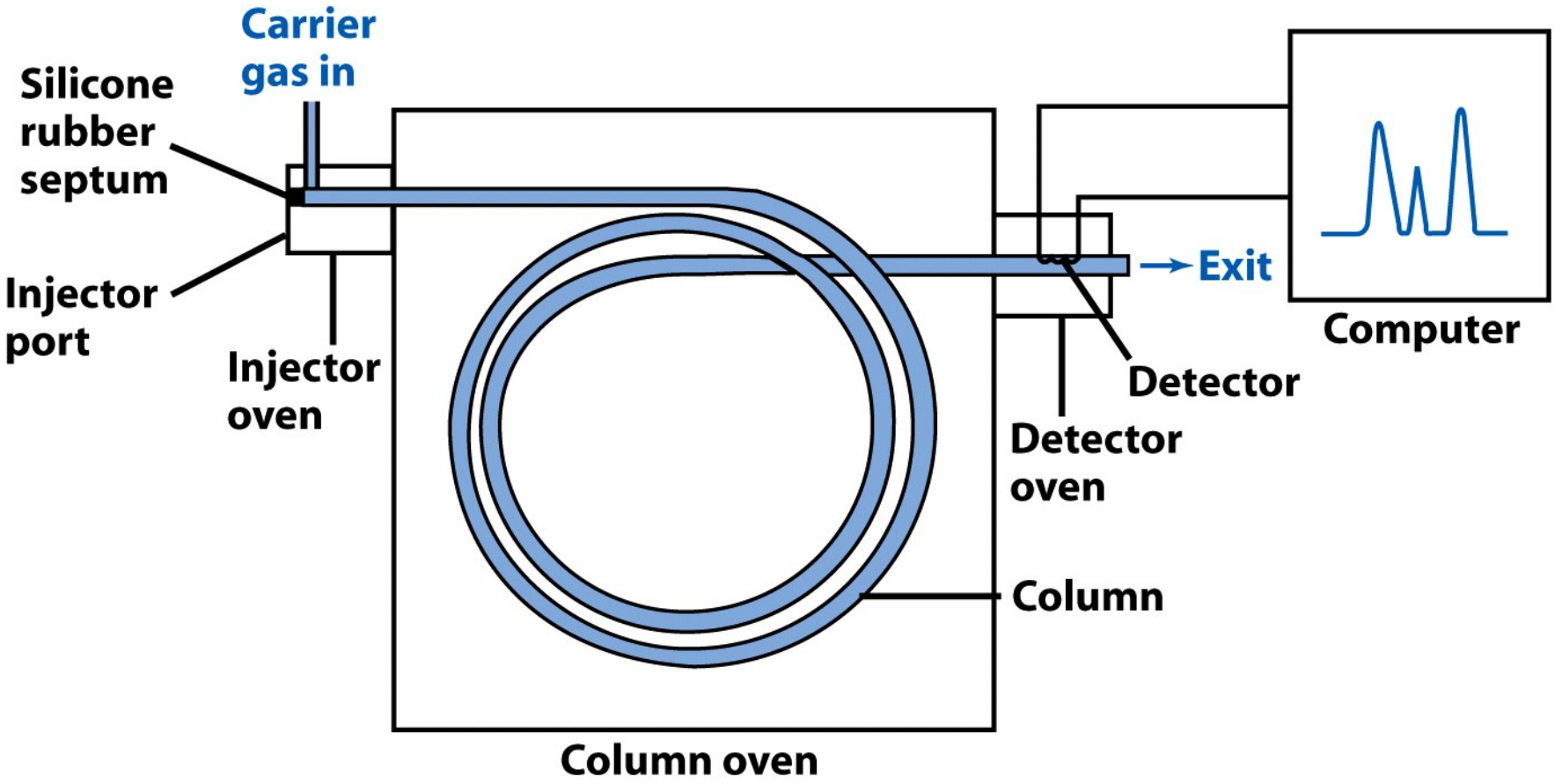
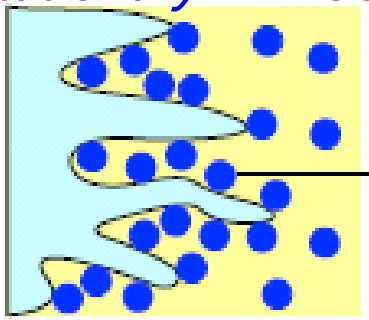


Figure 24-1
Quantitative Chemical Analysis, Seventh Edition

Chromatography Selection

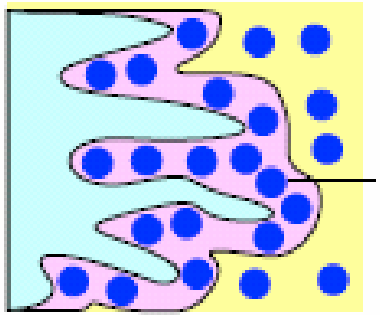
stationary *mobile*

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



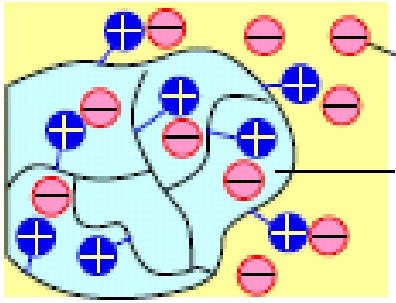
Adsorption Chromatography

Solute equilibrates between the stationary liquid and the mobile gas phase



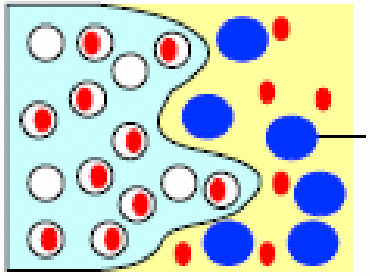
Partition Chromatography

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



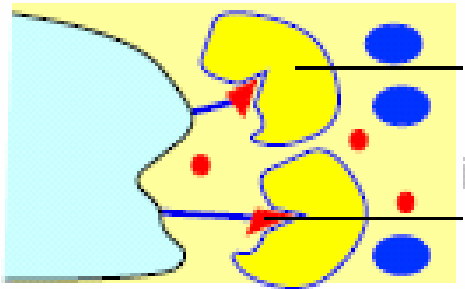
Ion-Exchange Chromatography

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



Molecular Exclusion Chromatography
Gel Permeation Chromatography
Gel-Filtration Chromatography

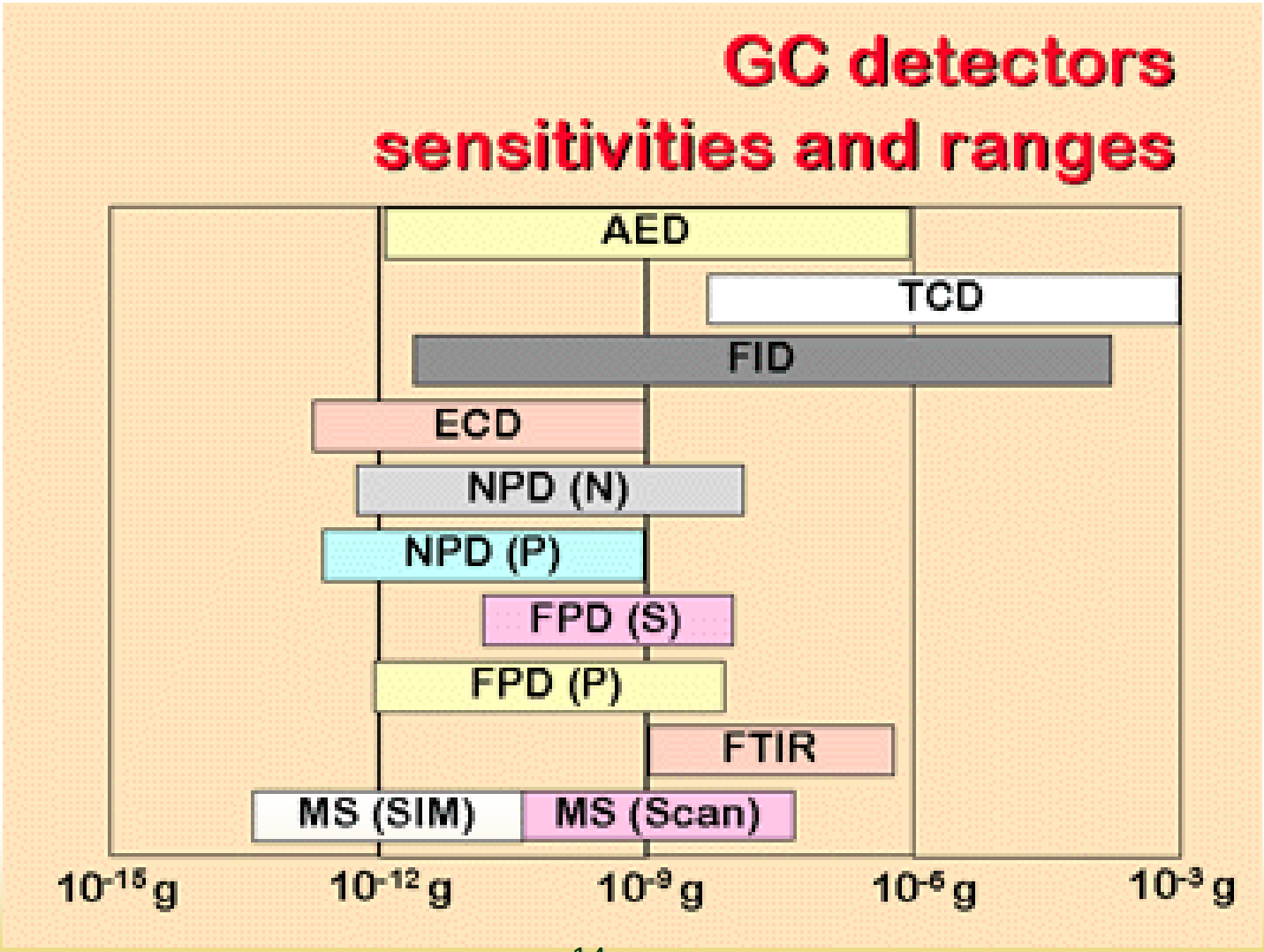
One kind of molecule in complex mixture becomes attached to molecule that is covalently bound to stationary phase
All other molecules simply wash through



Affinity Chromatography

Detector Sensitivity

calibration working range & limit of detection



Result…

Which one is the best?

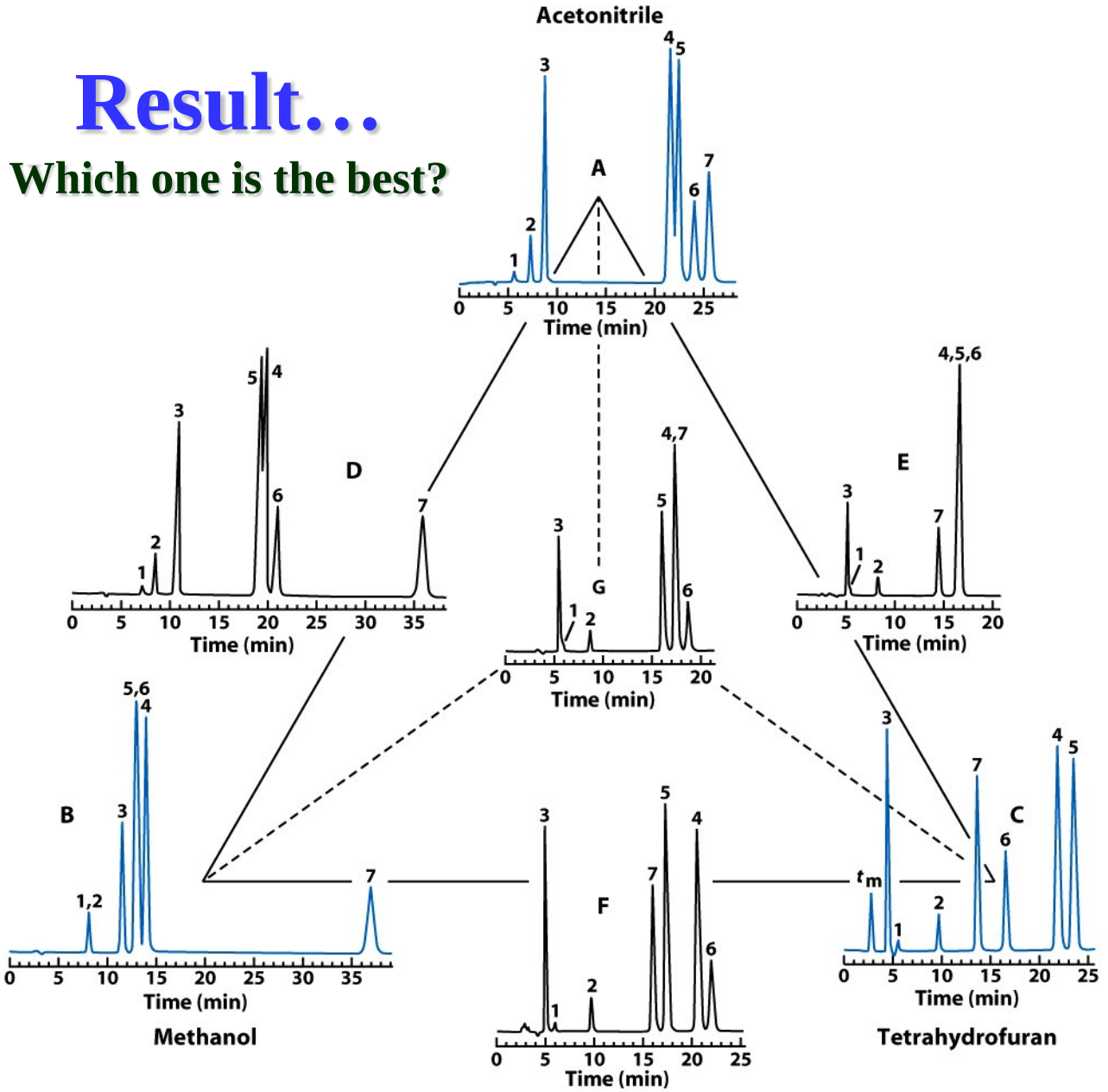
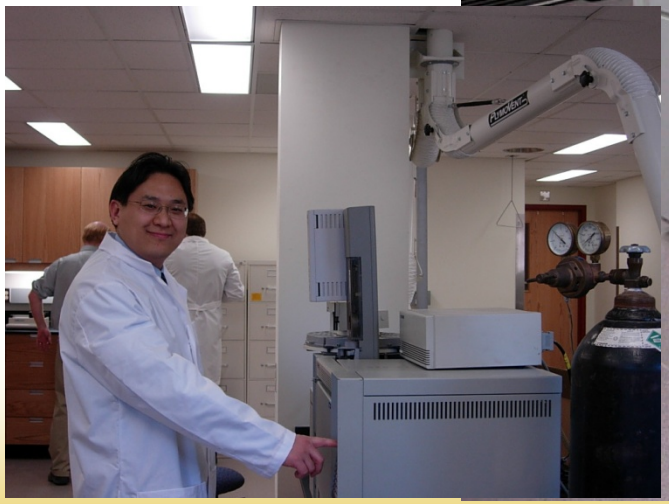


Figure 25-26
Quantitative Chemical Analysis, Seventh Edition

HRGC-MSD

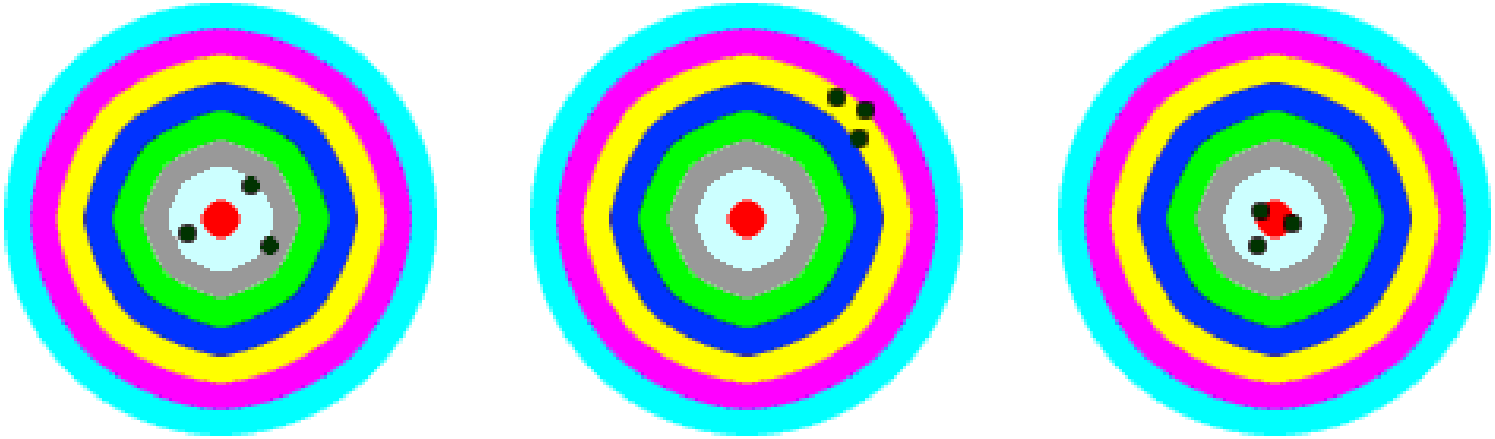
GC-MS



QA/QC

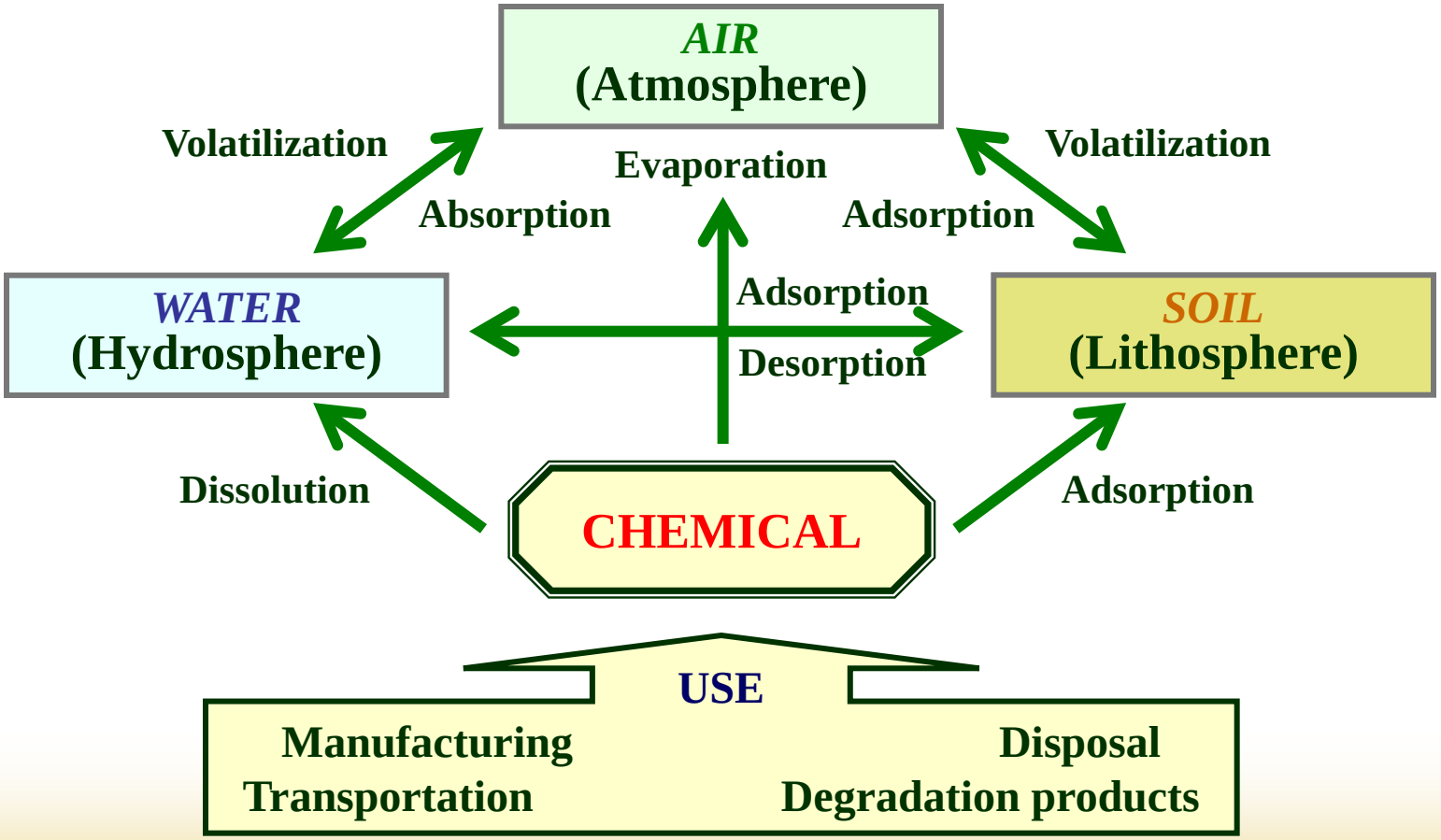
Accuracy vs. Precision

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

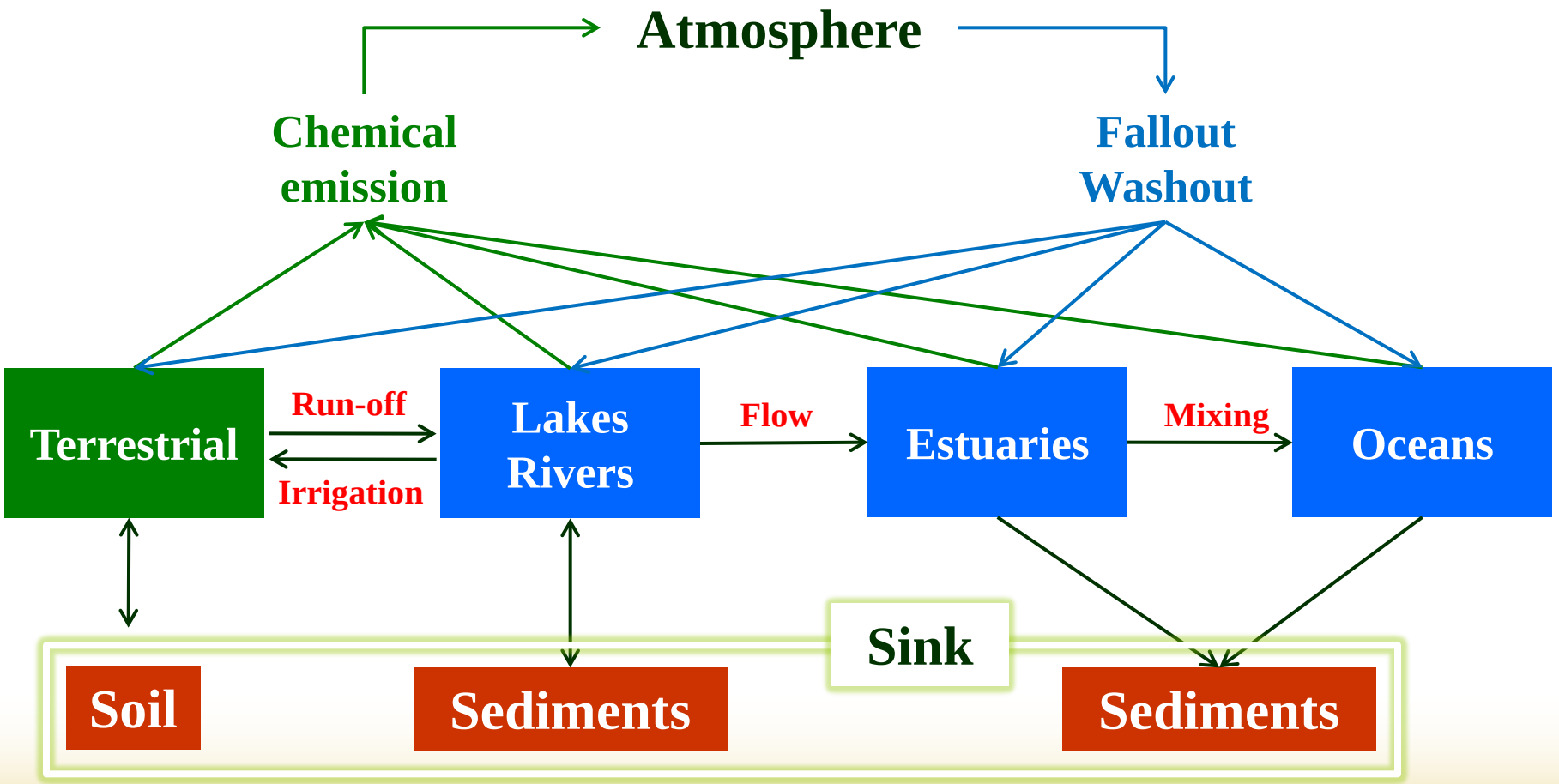


- ***Accuracy is telling the truth . . .***
- ***Precision is telling the same story over and over again.***

A Generalized Scheme of Movement of Chemicals



An Example of Chemical Distribution



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

PBTs
Priority Level-1

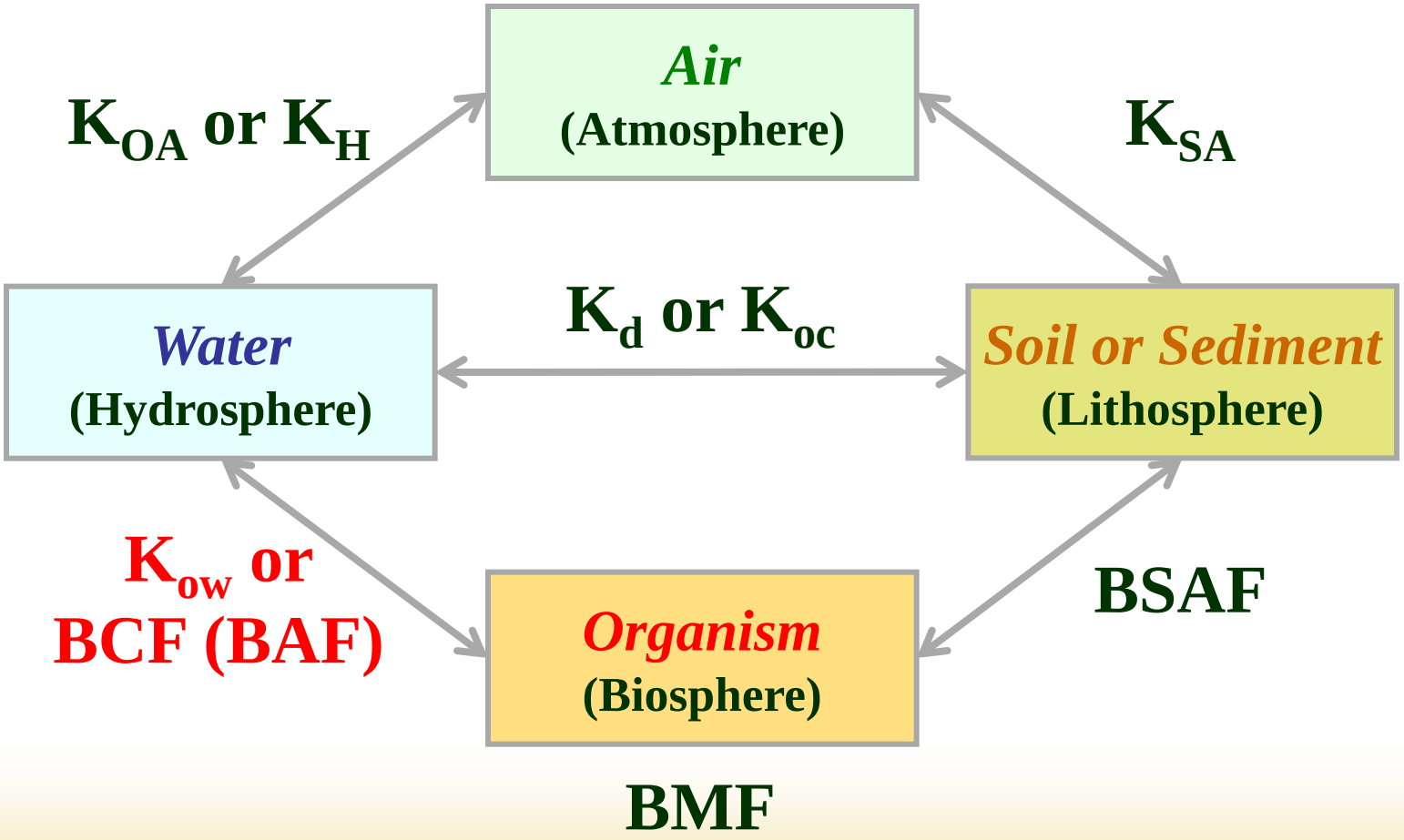
Table 15.2

EPAs Priority Level-1 PBTs

PBT Compound	Use
Aldrin/Dieldrin	crop insecticide (corn, cotton)
Alkyl-lead	octane booster in leaded gasoline
Benzo(a)pryene	unintentionally produced during combustion
Toxaphene	insecticide (livestock and crops)
Chlordane	crop insecticide (vegetables, citrus, cotton, potatoes)
DDT	crop insecticide (cotton)
Dioxins/Furans	unintentionally produced during combustion
Hexachlorobenzene	fungicide for seed treatment
Mercury and mercury compounds	incineration of medical and municipal waste
Mirex	insecticide (termites, fire ants)
Octachlorostyrene	produced from carbon electrodes used in electrolytic process for producing chlorine
PCBs	industrial chemical (heat exchange fluid for electrical transformers, paint and plastic additive)

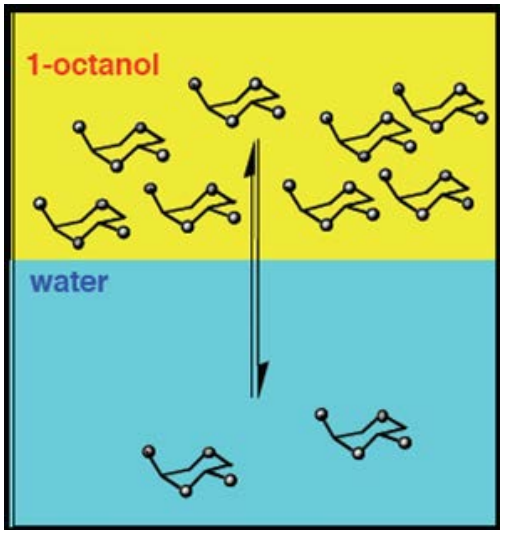
www.epa.gov/pbt

Multimedia Fate
Distribution Coefficients



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)**

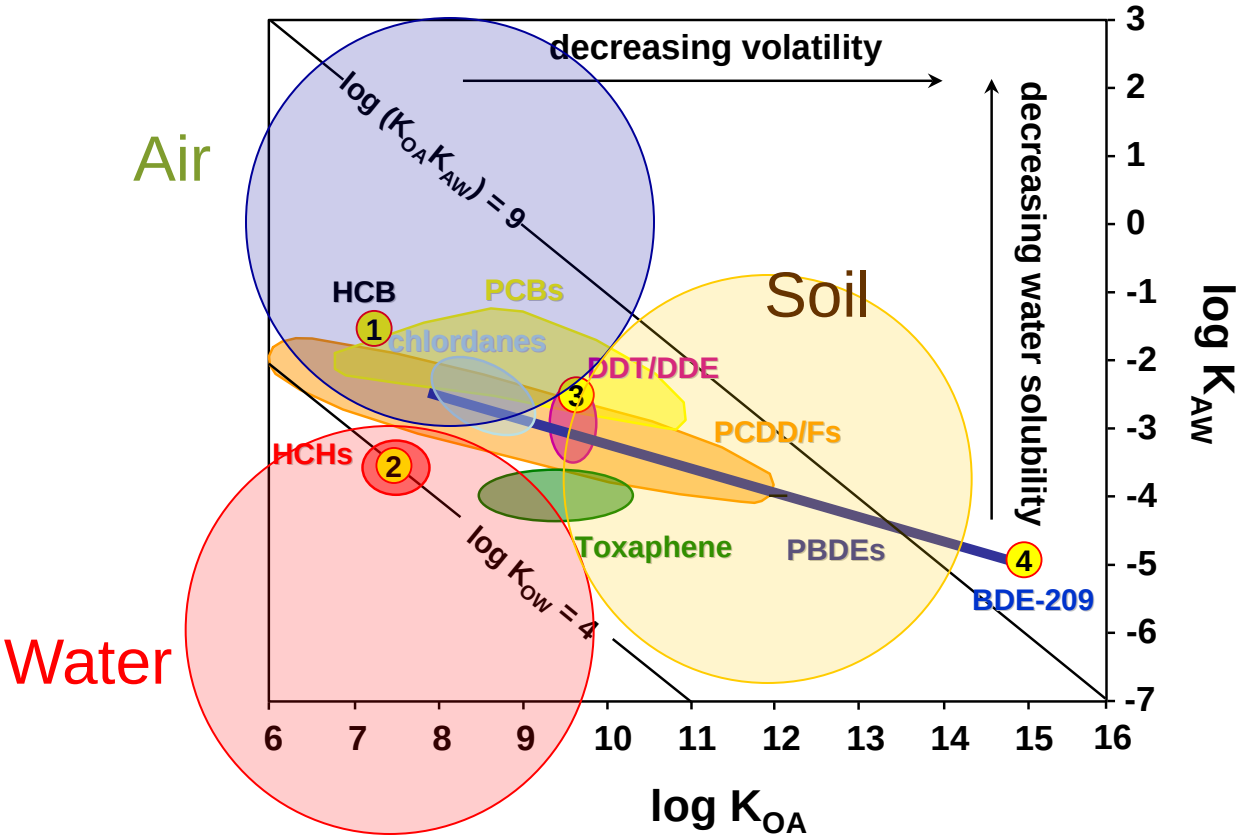
- **BCF = $C_{organism}/C_{water}$ (dimensionless)**
- **A linear relationship between BCF and K_{ow} (e.g. log BCF = 0.79 x log K_{ow} - 0.40)**
- **BCF is species-specific but comparable bw. species (e.g. log BCF_{fish} = 1.001 x log $BCF_{daphnia}$ + 043**
- **BCFs range from 1 to 1000,000**
- **BCF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



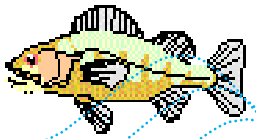
Chemical space map defined by their partitioning properties of log K_{AW}, log K_{OA}, and log K_{OW} at 25°C.

Risk of PCBs

Utility of Distribution Coefficients

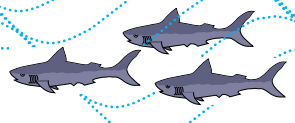
Mink
<0.75-14 ng/kg bw/d
(caltd)

Osprey
3.9-74 ng/kgbw/d
(caltd)



Predatory fish
10-19 ng/kg muscle *(caltd)*
50-95 ng/kg whole body *(measd)*

Water
0.5 pg/L
(caltd)



Small fish
>5-16 ng/kg muscle
(caltd)

Sediment
1.95-2.14 mg/g OC
(measd)

Maximum Allowable Chemical Concentration in Sediment

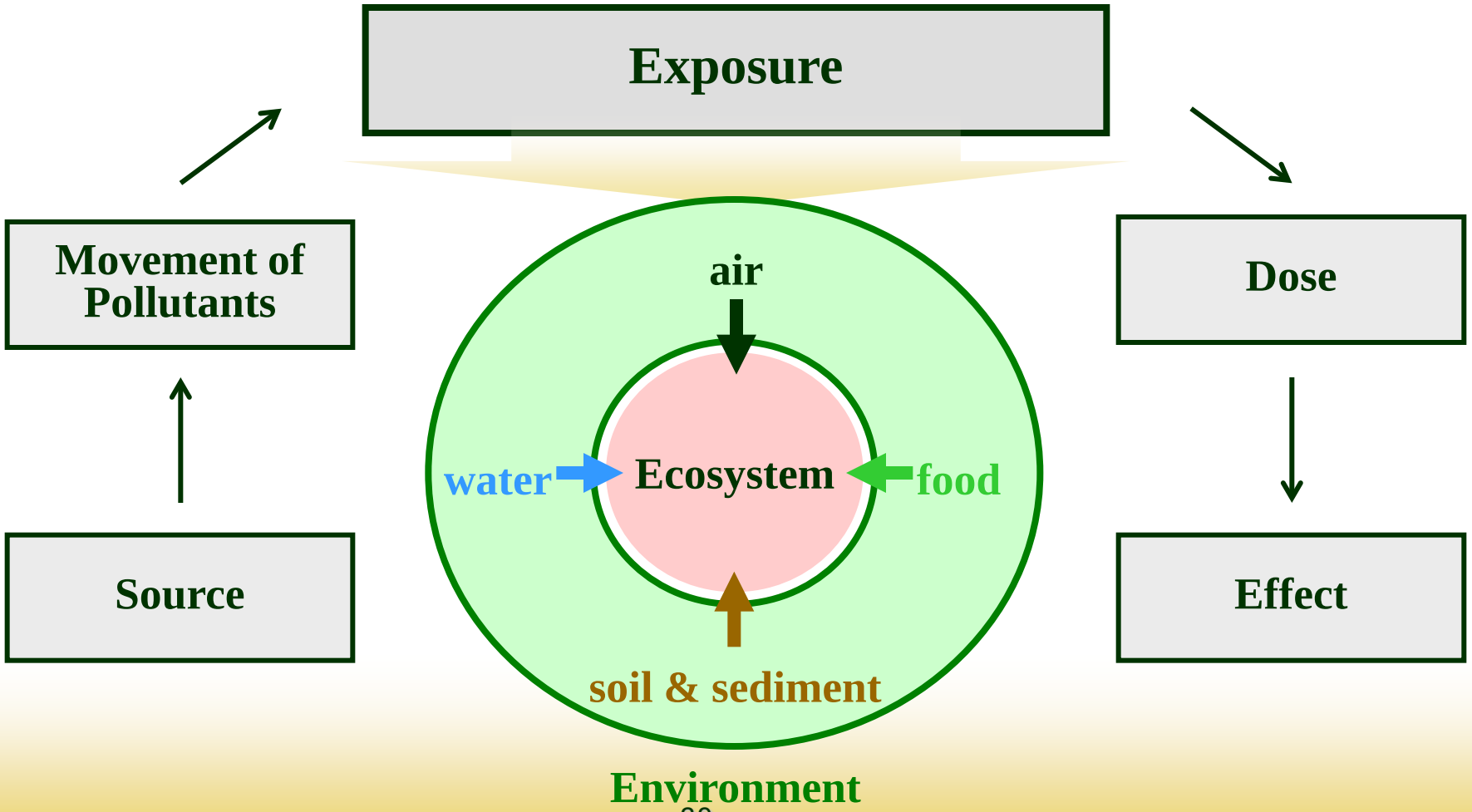
- **SQG = Sediment Quality Guideline**

  - ✓ **SQG = $[Chemical\text{-}Diet]_{lipid}$ / BSAF**
  - ✓ **BSAF = $[Chemical\text{-}Diet]_{lipid}$ / $[Chemical\text{-}Sediment]_{oc}$**
  - ✓ **$[CAD]_{lipid}$ = $[Chemical]_{Diet}$ / lipid content**
  - ✓ **Sediment oc = $[Chemical]_{sed}$ / sediment OC**
  - ✓ **OC = Organic carbon (mg/kg)**

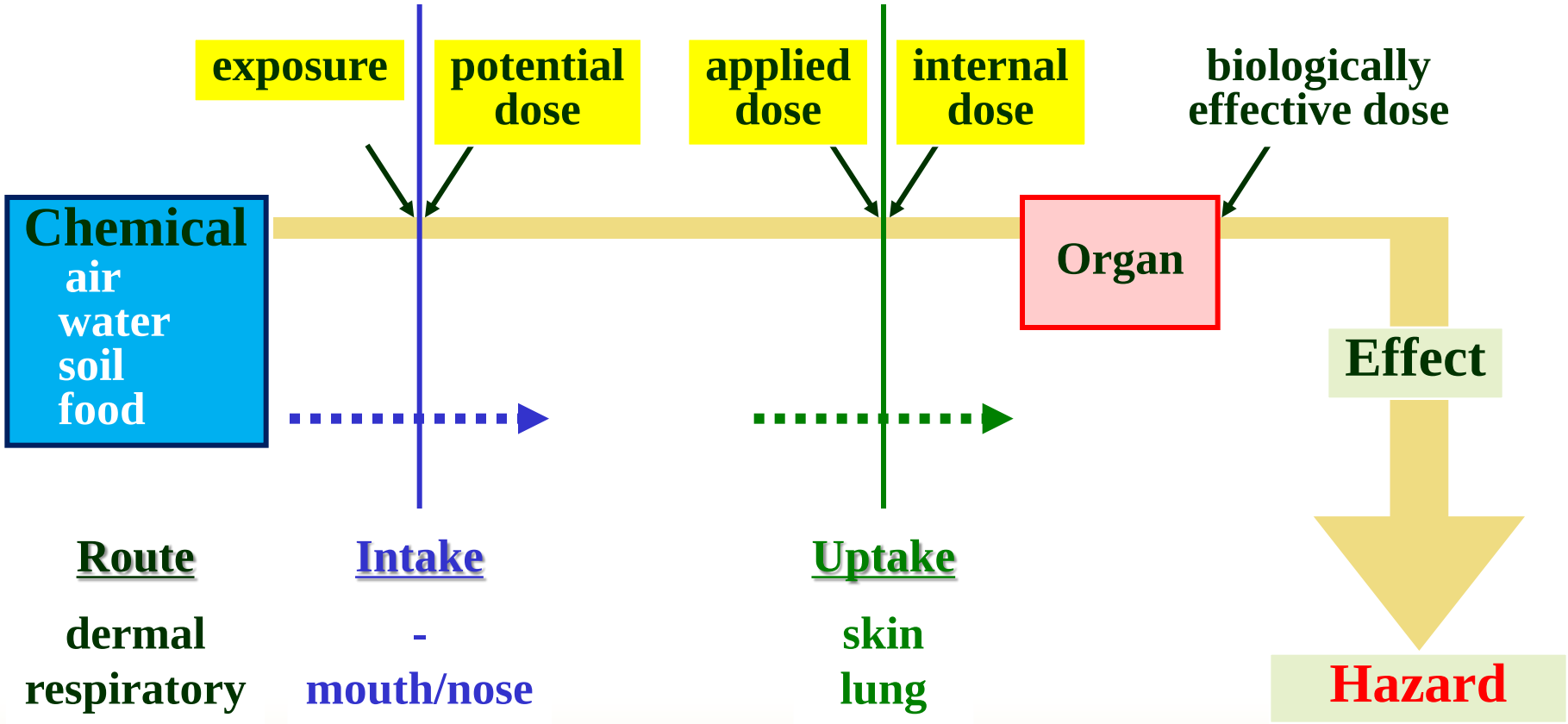
    - ➢ **SQG = 0.014 ng TEQ/g OC**
    - ➢ **BSAF (Sediment to Fish) = 0.32**
    - ➢ **Lipid Content of Diet = 15%**

Environmental Exposure

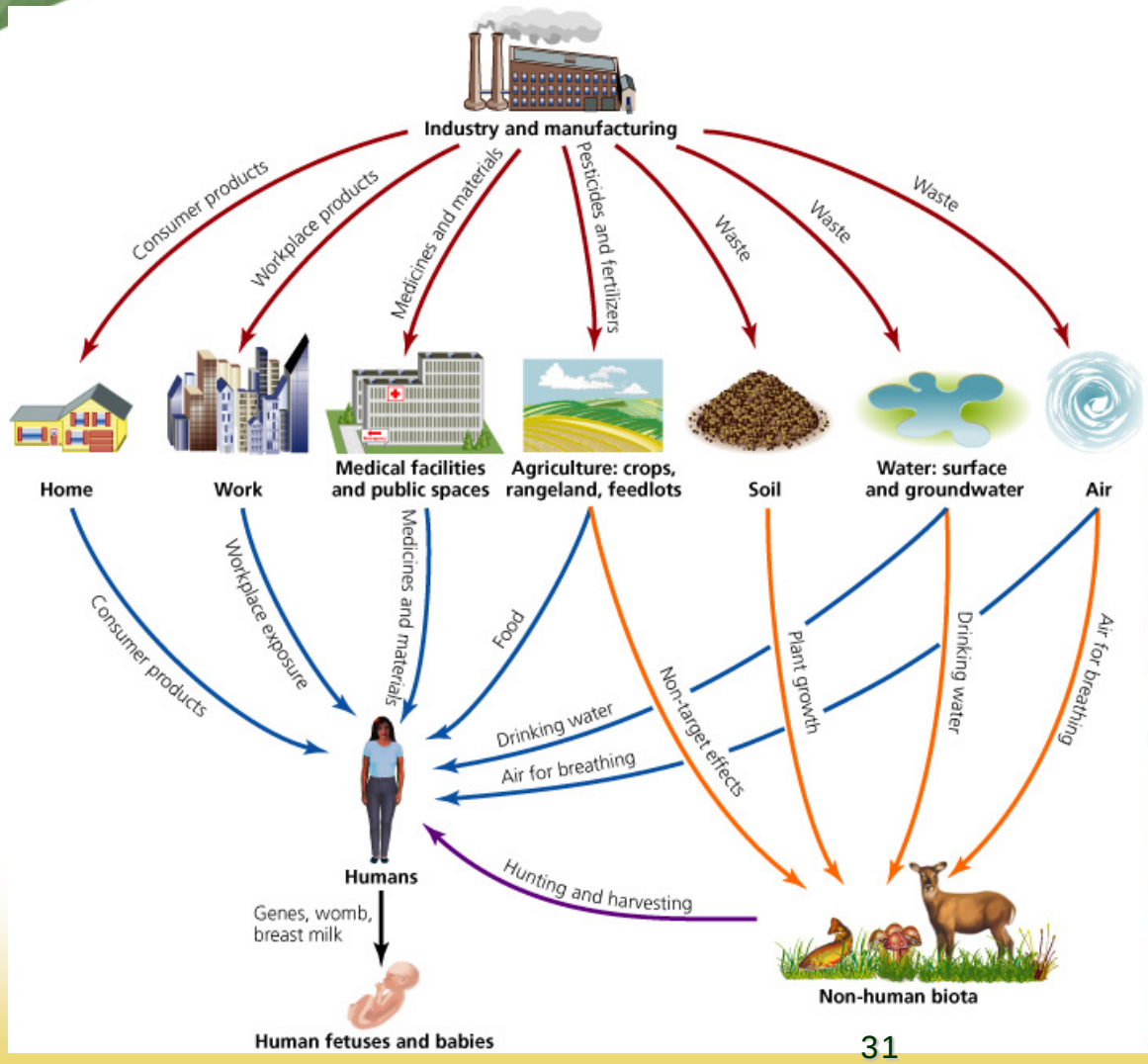
(conceptual)

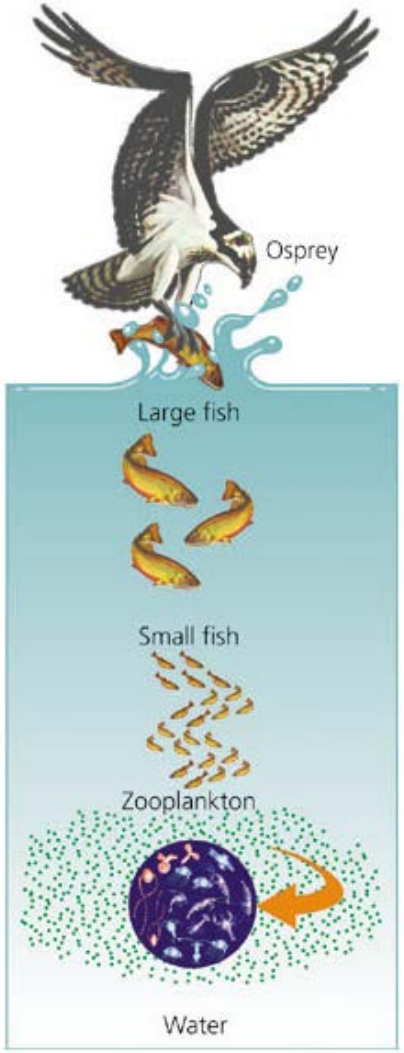


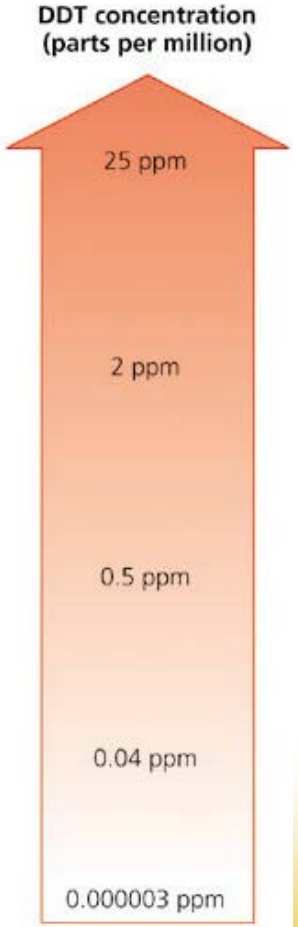
Toxicology: Routes of Exposure



Exposure of Toxicants







Toxicology: Important Terms!

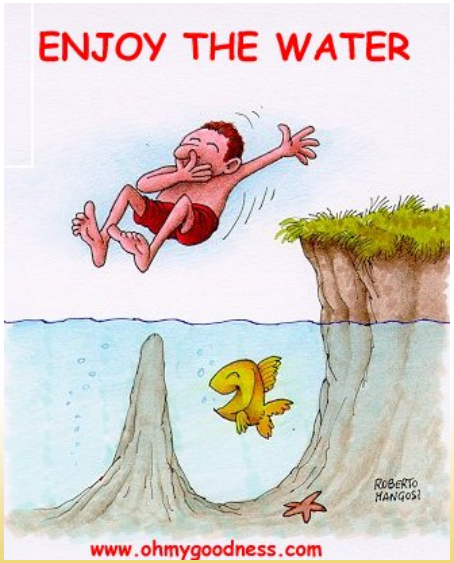
- **Toxicity:**
  The adverse effects that a chemical may produce

- **Dose:**
  The amount of a chemical that gains access to the body

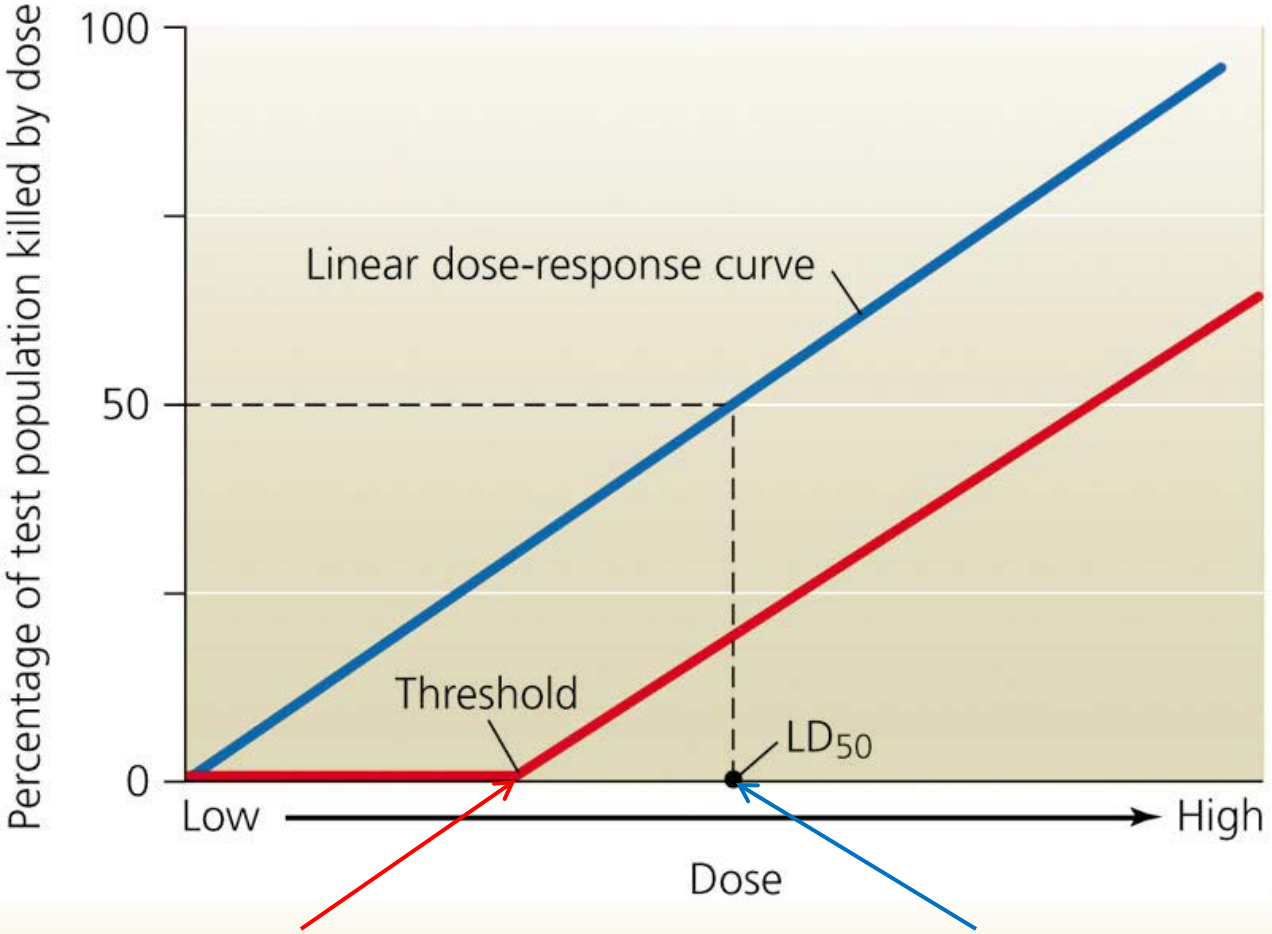
Toxicology: Important Terms!

- **Exposure:**
  Contact providing opportunity of obtaining a poisonous dose

- **Hazard:**
  A likelihood that the toxicity will be expressed
  viz. hazardous chemicals = potential toxic chemicals



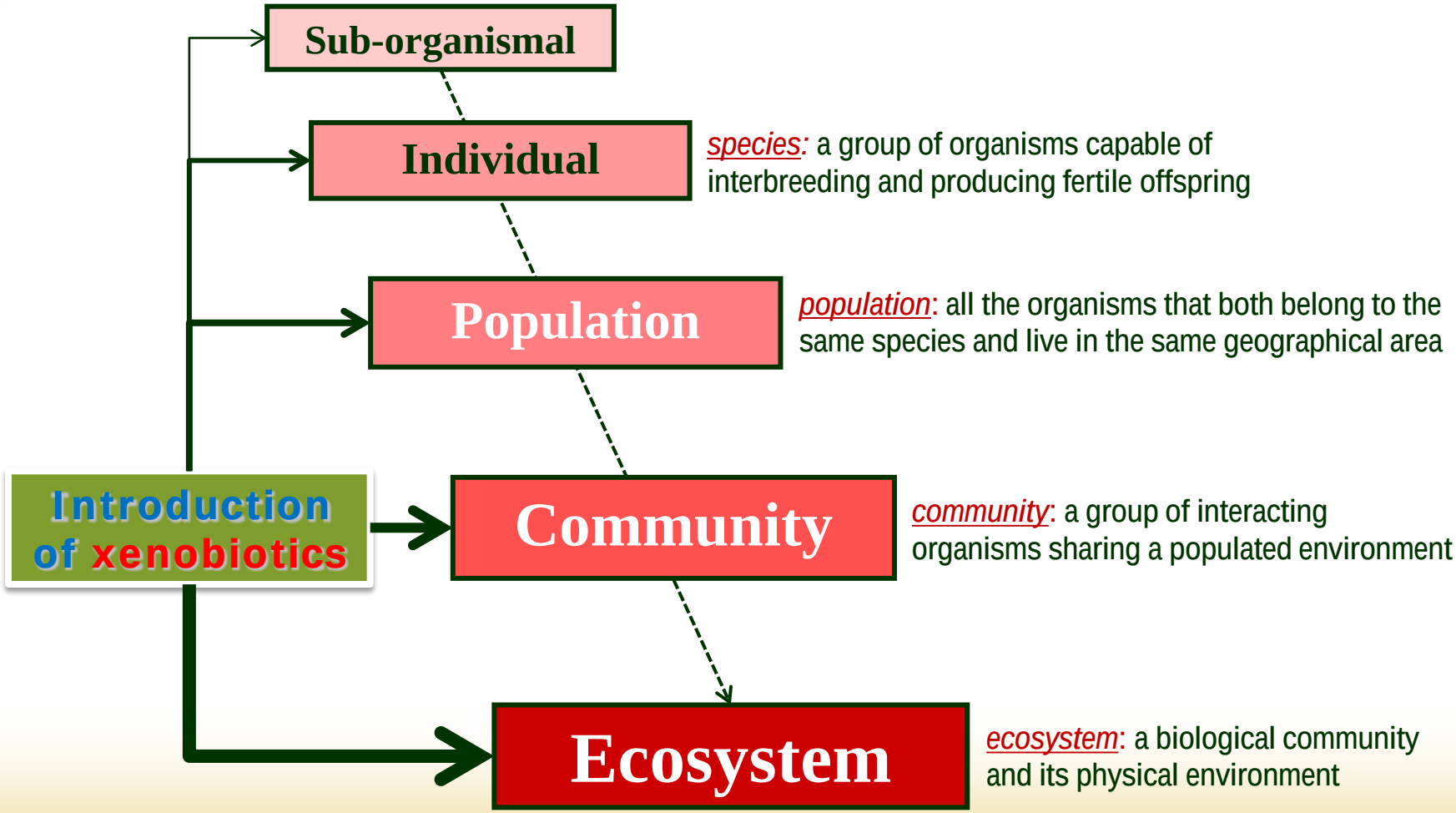
Dose-Response Curve



Threshold
(dose at which response begins)

LD_{50}
(dose lethal to 50% of test animals)

Xenobiotic Interaction with Ecosystem



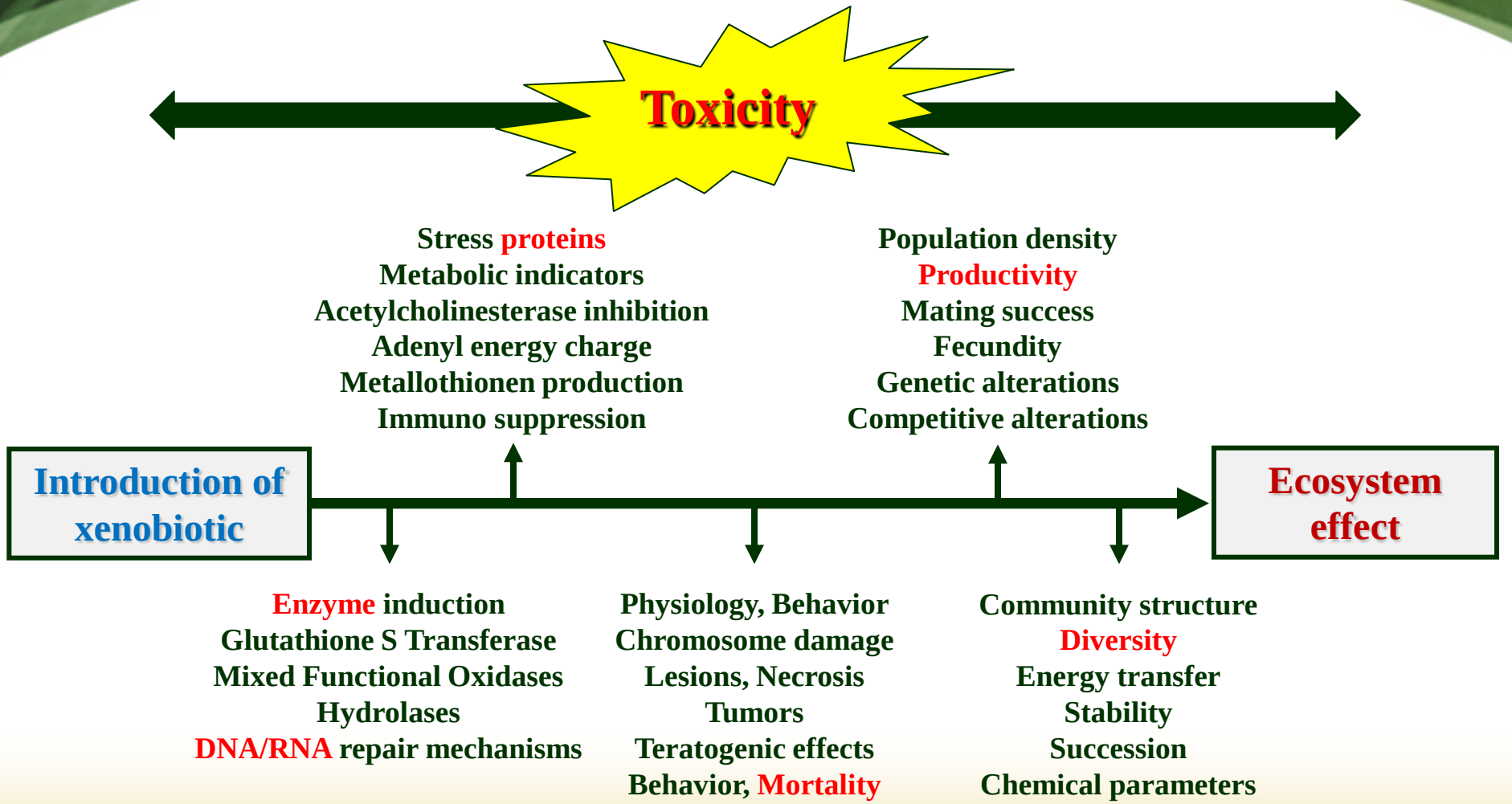
species: a group of organisms capable of interbreeding and producing fertile offspring

population: all the organisms that both belong to the same species and live in the same geographical area

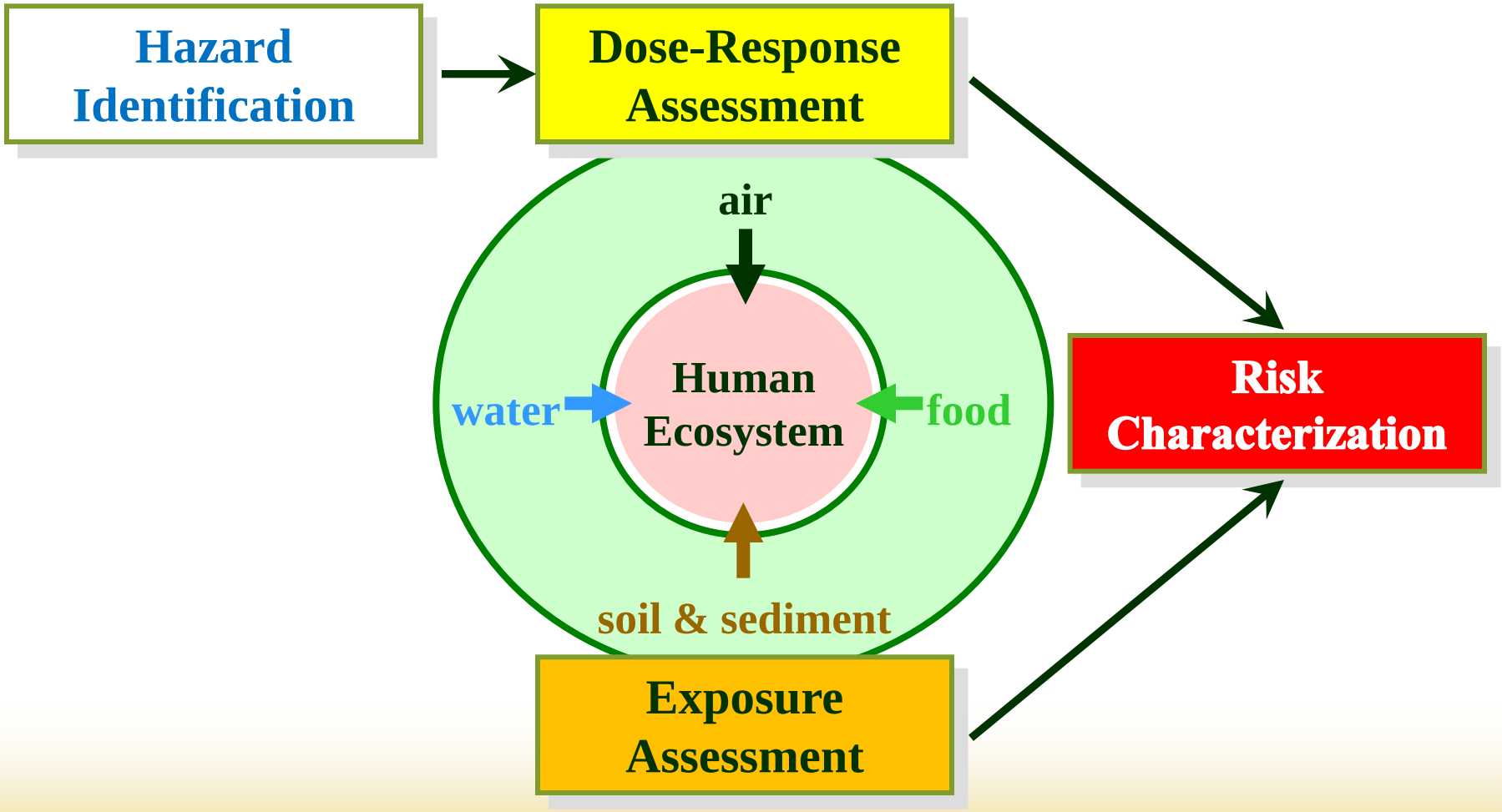
community: a group of interacting organisms sharing a populated environment

ecosystem: a biological community and its physical environment

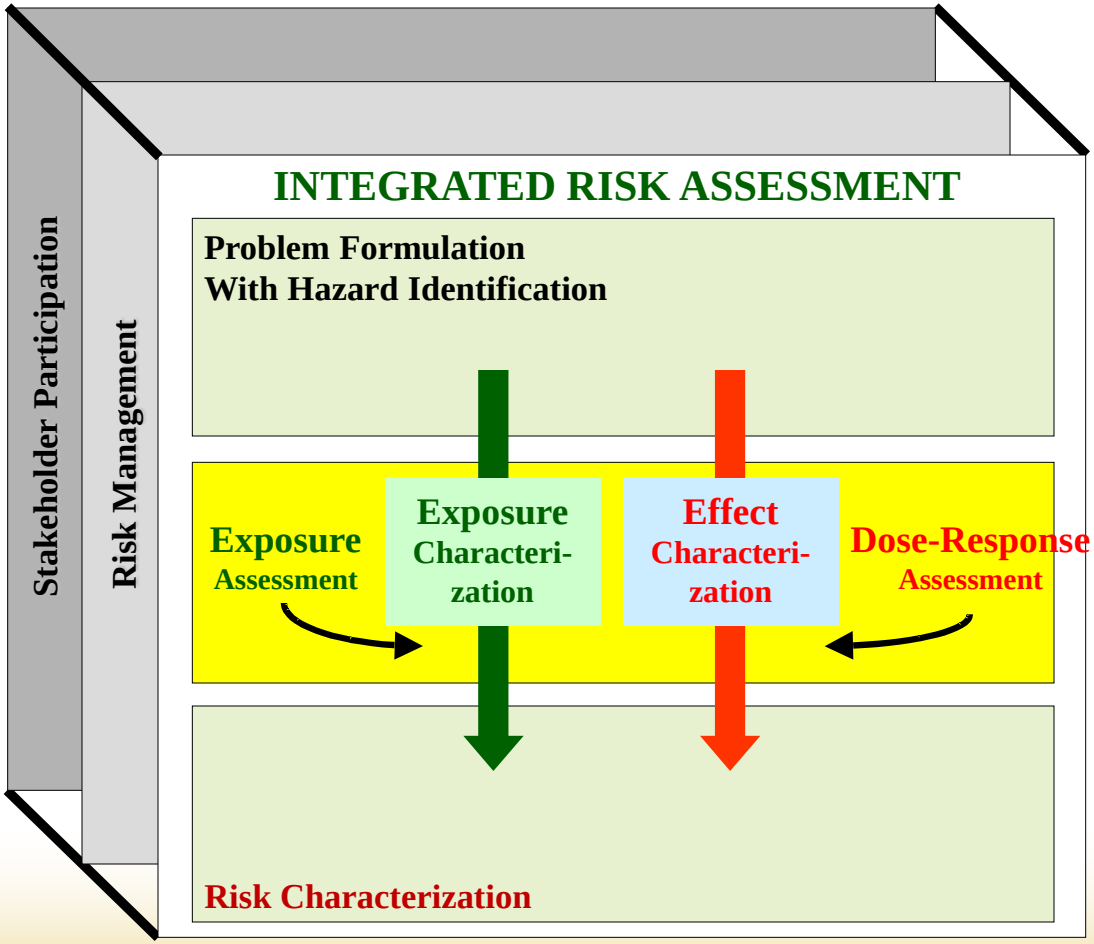
Xenobiotic *vs.* Toxicity



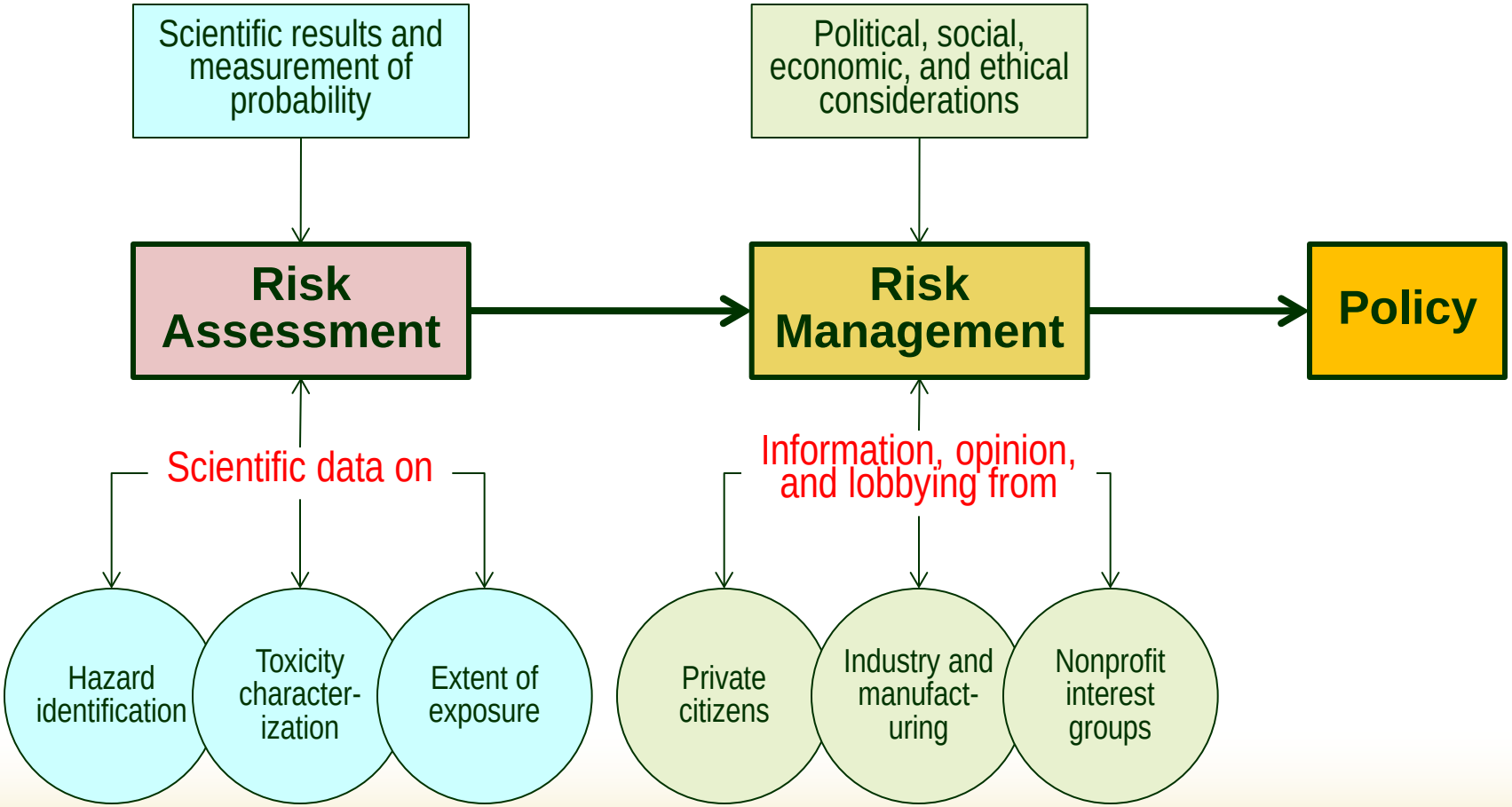
Four Steps in Risk Assessment



Integrated Risk Assessment (IRA)

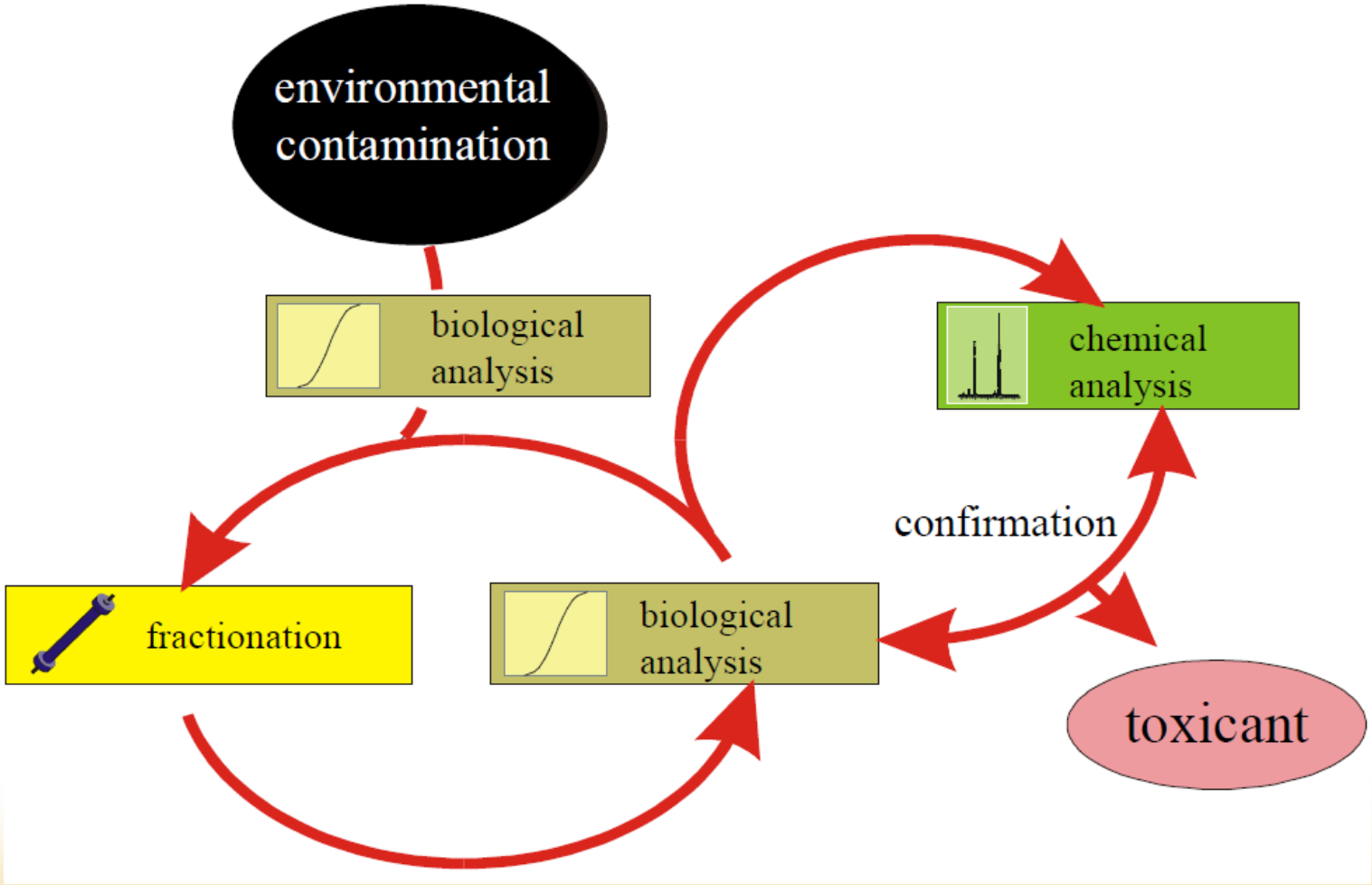


Risk Assessment & Risk Management



Effect-Directed Analysis

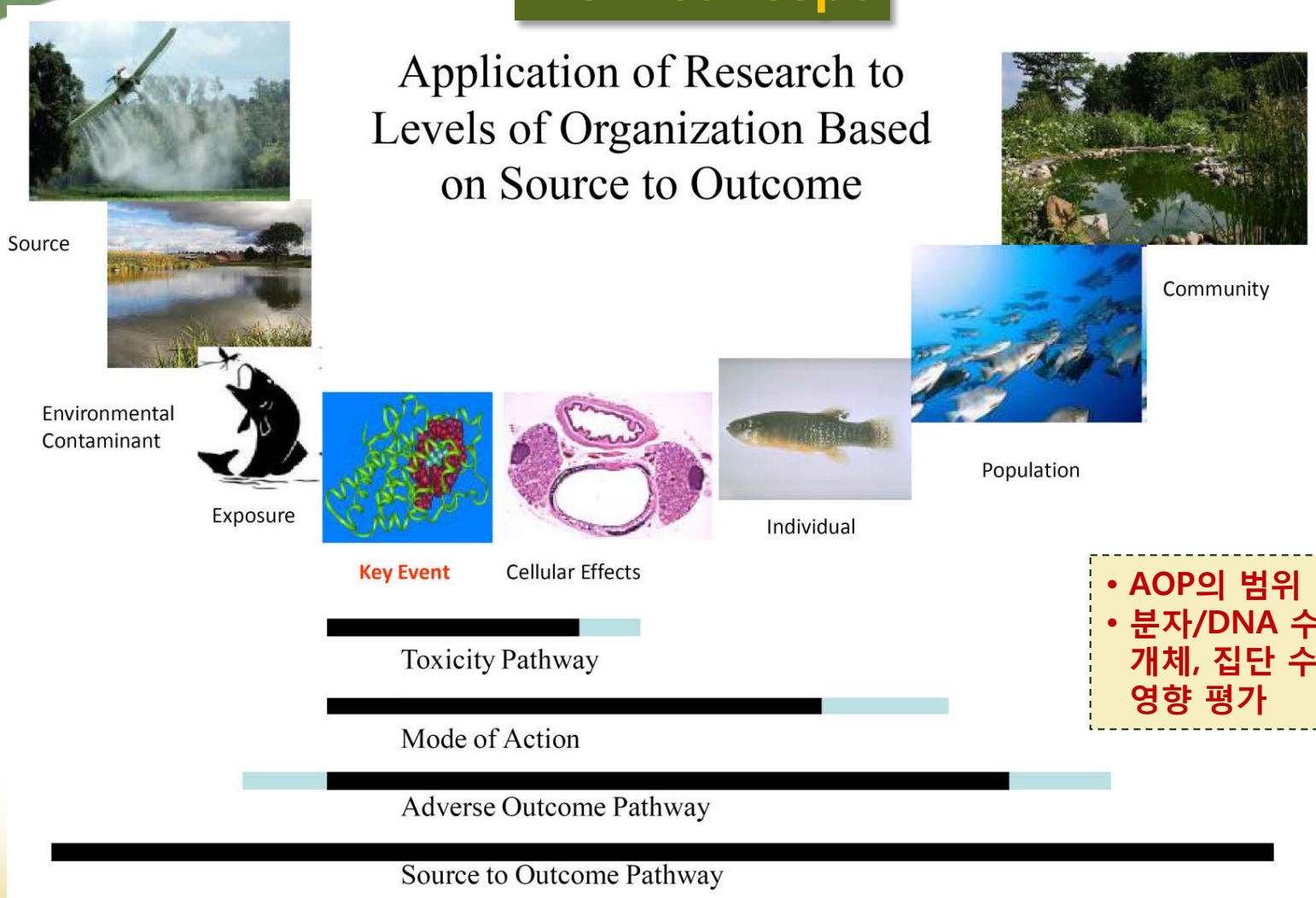
Effect-directed identification of toxicants



Hecker and Hollert, 2009. Environ. Sci. Pollut. Res. 16, 607-613

Adverse Outcome Pathways

AOP concept



- AOP의 범위
- 분자/DNA 수준부터 개체, 집단 수준까지의 영향 평가

Perkins 2011 Mixtures and Cumulative Risk Assessment

Adverse Outcome Pathways

AOP 적용 연구사례

- 해양포유류의 서식밀도, 개체 수 감소
- Predater 감소로 인한 Prey 군집 영향
- 생태계 불균형 초래
- 왜 해양포유류 개체수가 감소하였는가?

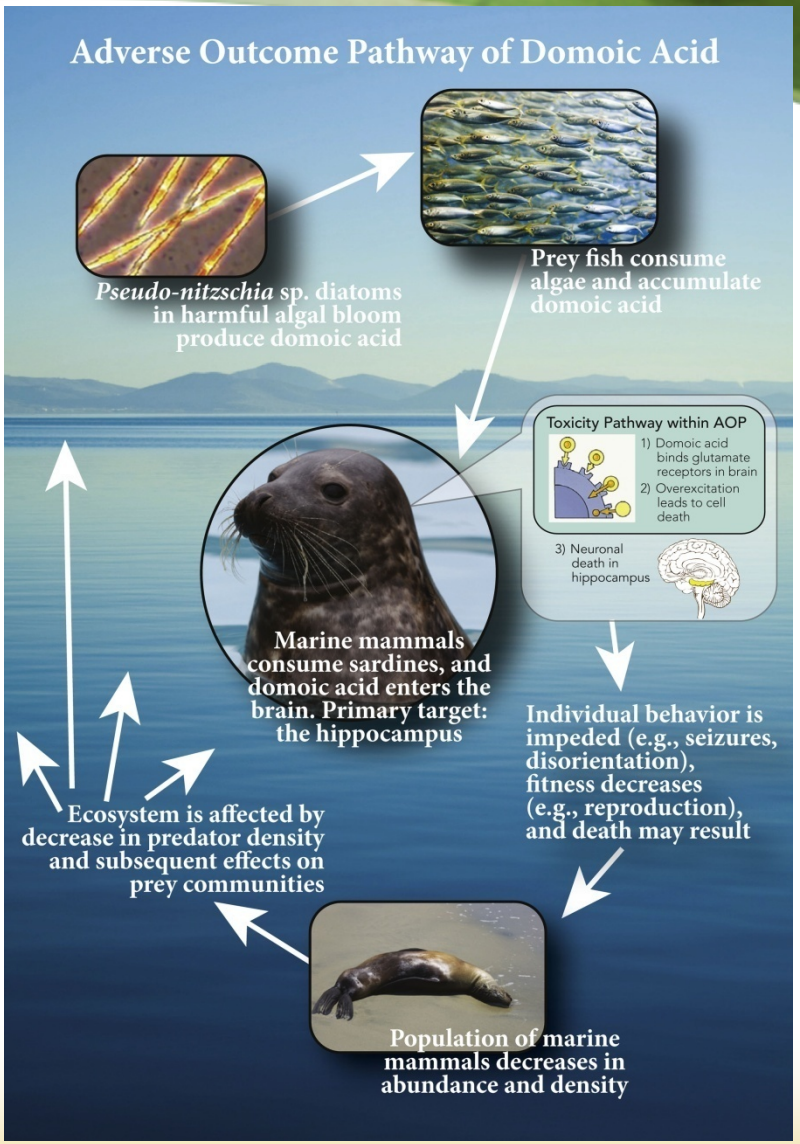
↓

- HAB 과정에서 생성된 domoic acid
- 식물플랑크톤을 섭식하는 물고기 체내에 축적됨
- 해양포유류는 물고기를 섭식

↓

- 해양포유류 체내로 유입된 domoic acid 가 뇌로 들어가 glutamate receptor 와 결합하여 세포손상 야기
- 개체 수준에서 행동장애(발작, 방향감각 상실), 체력감소(생식장애), 치사 등의 영향 나타남.

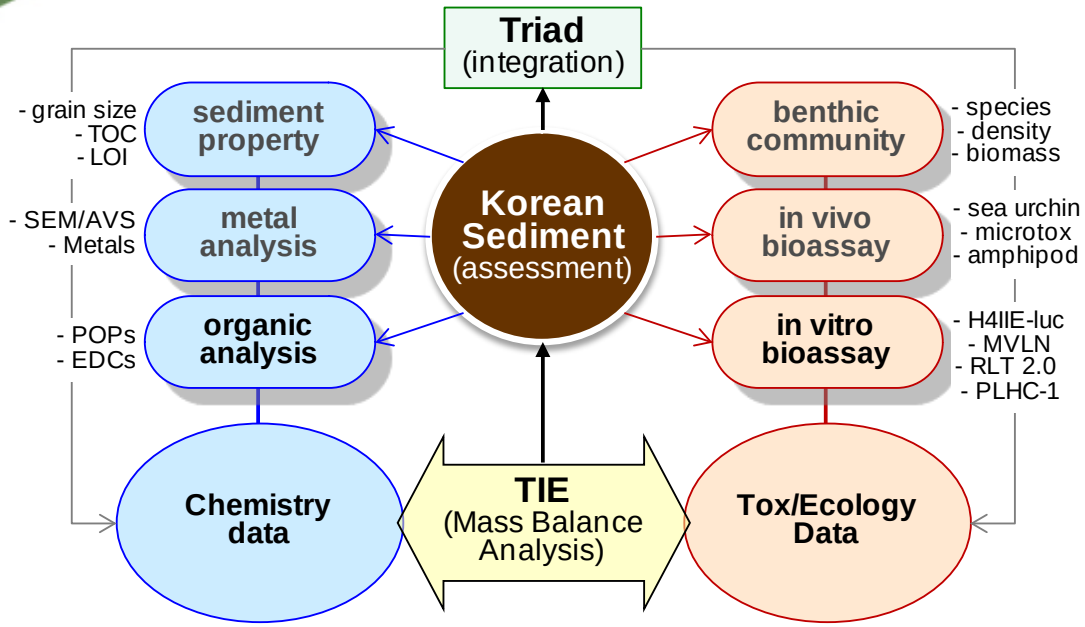
AOP concept

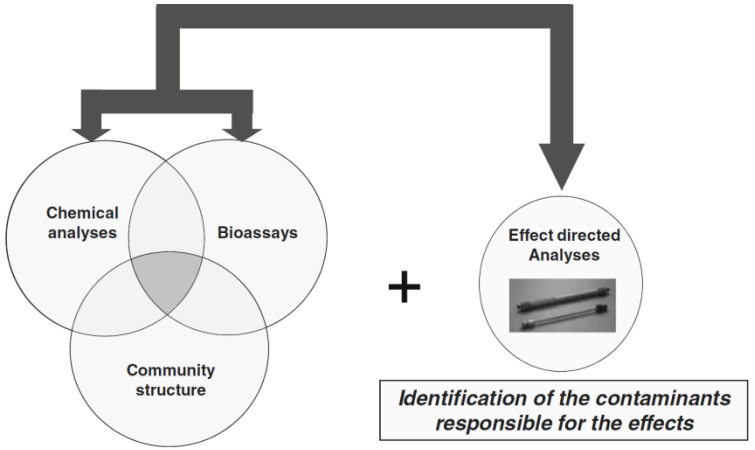


Villeneuve and Garcia-Reyero 2011 ET&C 30 1-8
Watanabe et al 2011 ET&C 30 9-21

Research Example
Integrated Assessment

Integrated Approach – Activity Summary





Integrated assessment

Triad

- practiced since 1996
- samples: >1,000

research items
1) chemical analysis
2) bioassay response
3) benthic community

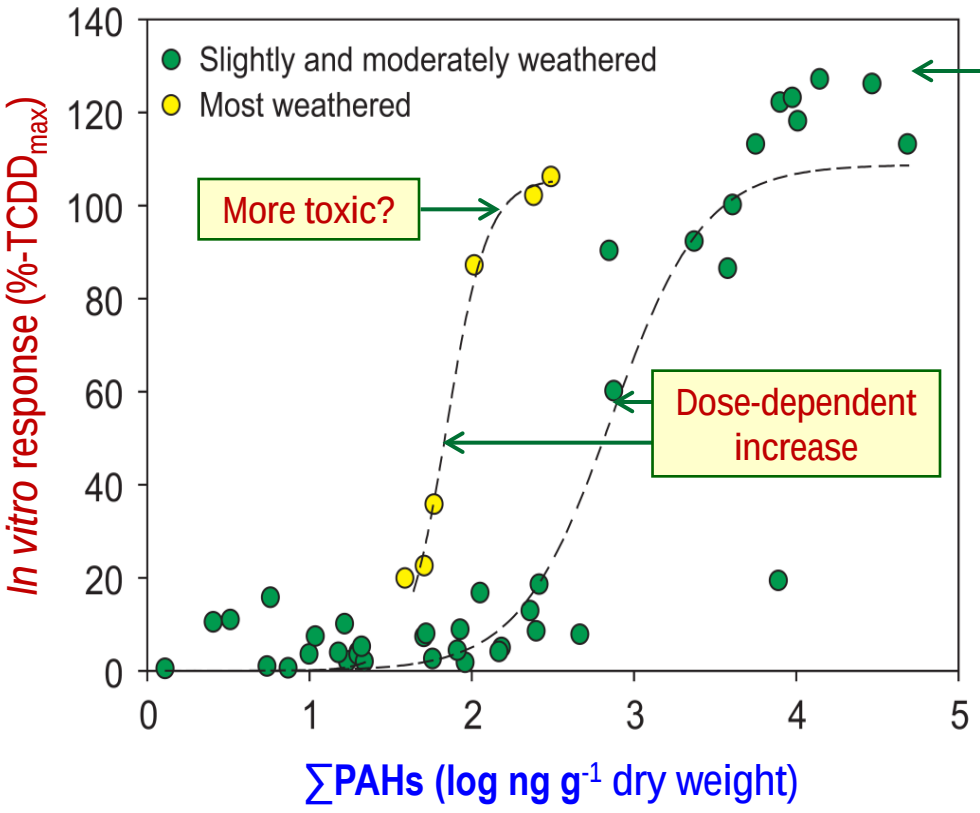
TIE

- highlighted since 1998
- samples: >200

main subjects
1) organic analysis
2) in vitro bioassay
3) mass balance

Recent Example: Taean Study
EDA-Triad-ATT Considered??

Two years after the *Hebei Spirit* oil spill, Taean, South Korea



Potential Toxic Effects of Oil-contaminated Sediments

NEXT STEP

Towards integrated sediment assessment

Chemistry

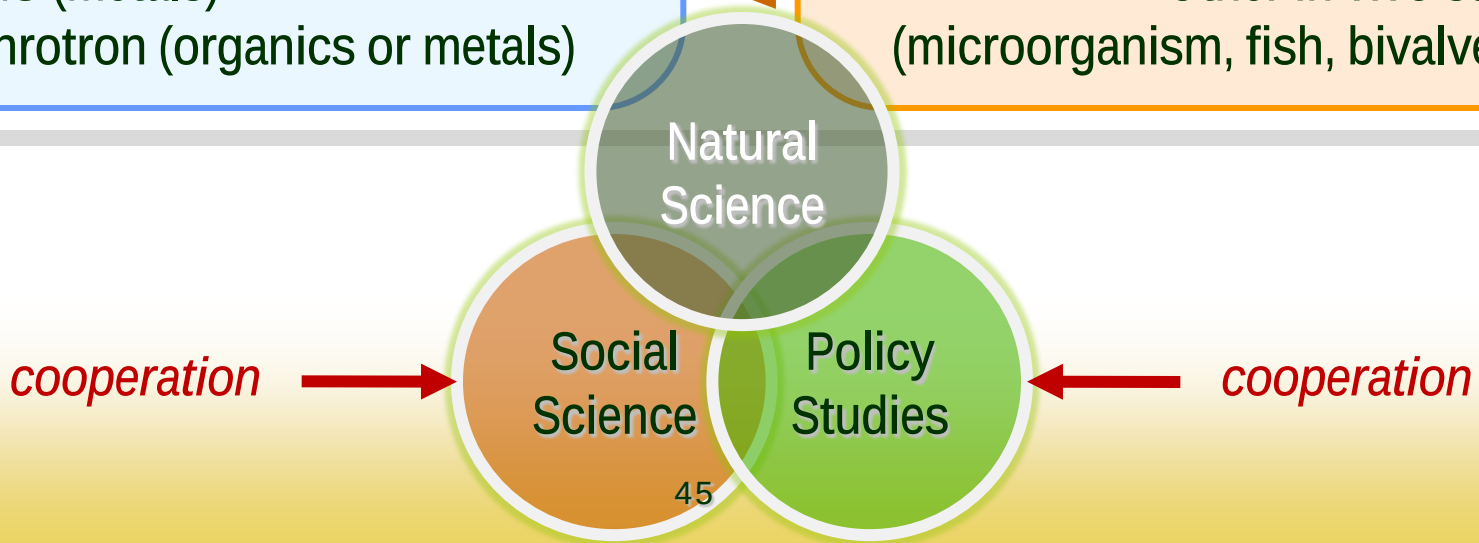
Ecology
Community indices

Toxicology

Instrumental analyses using
LC (PFCs, Hormones)
GC (PAHs, APs, BPA)
HRGC (PCDD/DFs, co-PCBs, PBDEs)
CIC (Total F)
ICP-MS (metals)
Synchrotron (organics or metals)

V S

Bioassays using
Dioxin-like activities (HII4E-luc)
Estrogenicity (MVLN)
Steroidogenesis (H295R)
Mutagenicity (Mutatox®)
Other in vivo studies
(microorganism, fish, bivalve etc.)



Thank you!

Enjoy the summer