Aquatic Environmental Science

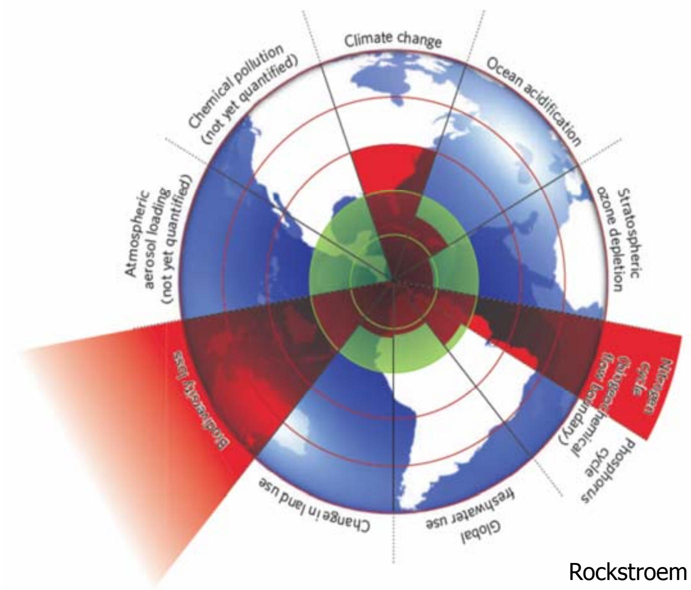
13. Fate and Transport of Pollutants

Present ecosystems

- Anthropogenic modification

- Natural system

Global Environmental Problem & Sustainability

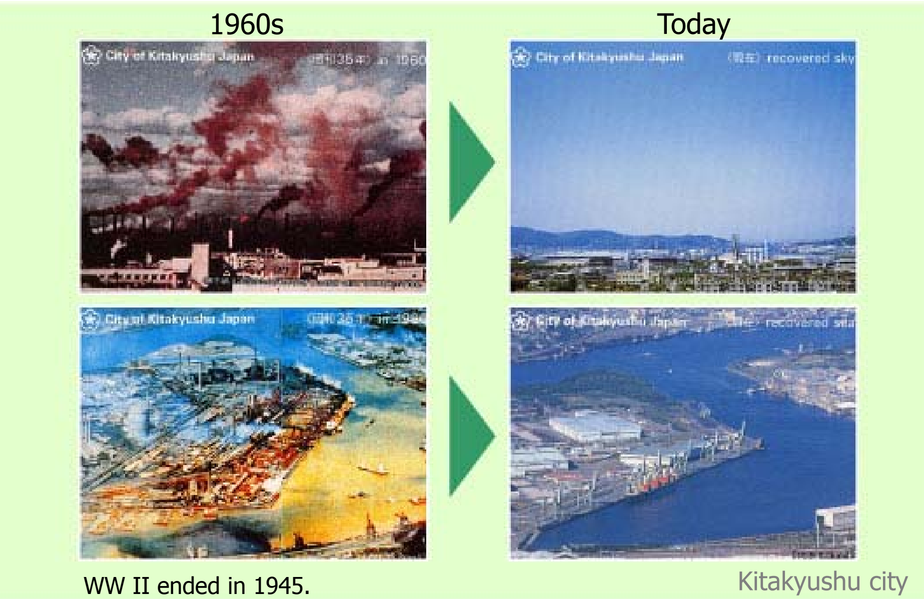


Rockstroem et al., 2009

What is pollution?

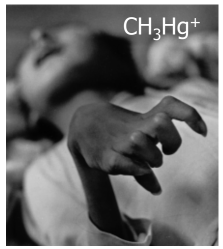
1. Discharging chemical substances
2. Discharging warmer water than environment
3. Introduction of exotic species
4. Channelizing natural streams
5. Abstracting water from rivers
6. Harvesting fish extensively

Case of Japan | Kitakyushu



Major Pollution Diseases of Japan

Name	Year	Cause	Source
Itai-itai disease	1912	Cd	Mining in Toyama Prefecture 185 persons
Minamata disease	1932 - 68	CH_3Hg^+	Chisso Chemical Factory 3000 persons
Yokkaichi Asthma	1961	SO_2, NO_2	Air Pollution in Yokkaichi
Niigata Minamata disease	1965	CH_3Hg^+	Shōwa Electrical Works



Major Pollutants in Environment

Organic substance

Nutrient

Toxic chemical

Pollutants

Heavy metal

Endocrine disrupter

Pathogens

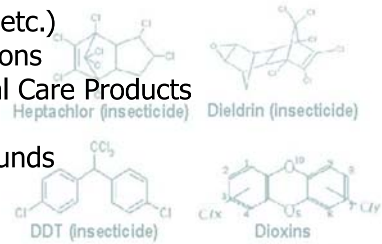
Radioactive substance

POPs: Persistent Organic Pollutants
（残留性有機汚染物質）

- Long-range transport
- Bioaccumulate in human and animal tissue
- Biomagnify in food chains

→ Potential significant impacts on human health and ecosystems

POP includes…
- Pesticides and other chemical substances (PCBs, DDT, HCHs, chlordane, etc.)
- PAH: Polycyclic Aromatic Hydrocarbons
- PPCP: Pharmaceuticals and Personal Care Products
- EDCs: Endocrine Disrupting Compounds

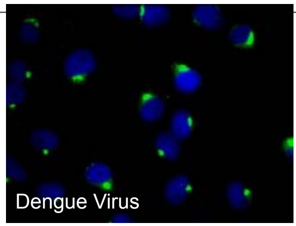


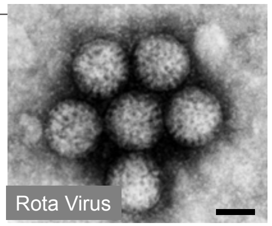
Recently discovered pathogenic microbes

AGENT	MODE OF TRANSMISSION	DISEASE / SYMPTOMS
Rotavirus	Waterborne	Diarrhea
Legionella	Waterborne	Legionnaire's disease
Escherichia coli O157:H7	Foodborne Waterborne	Enterohemorrhagic fever, kidney failure
Hepatitis E virus	Waterborne	Hepatitis
Cryptosporidium	Waterborne Foodborne	Diarrhea
Calicivirus	Waterborne Foodborne	Diarrhea
Helicobacter pylori	Foodborne Waterborne	Stomach ulcers
Cyclospora	Foodborne Waterborne	Diarrhea

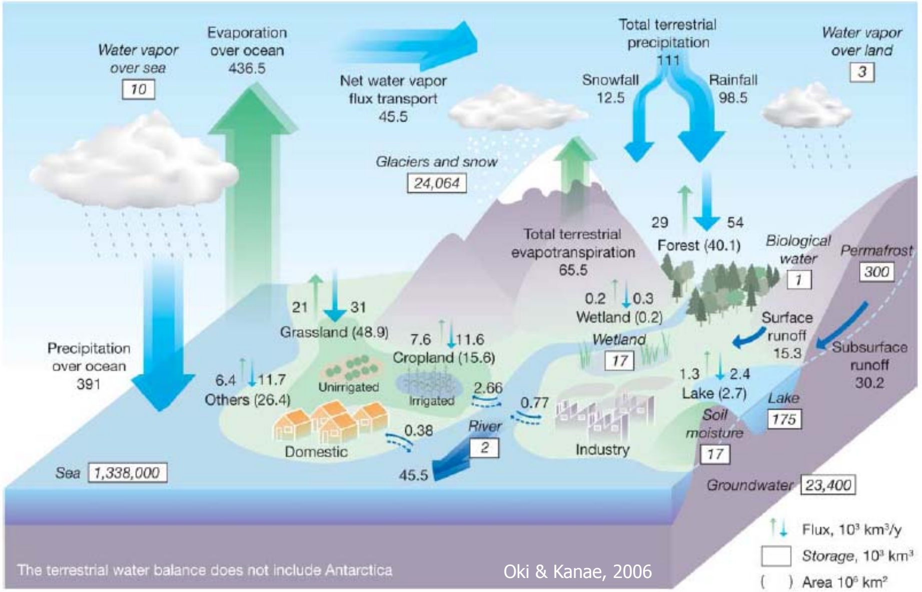
Pepper et al., 2006

Size of virus: 20-970nm





Fate & Transport

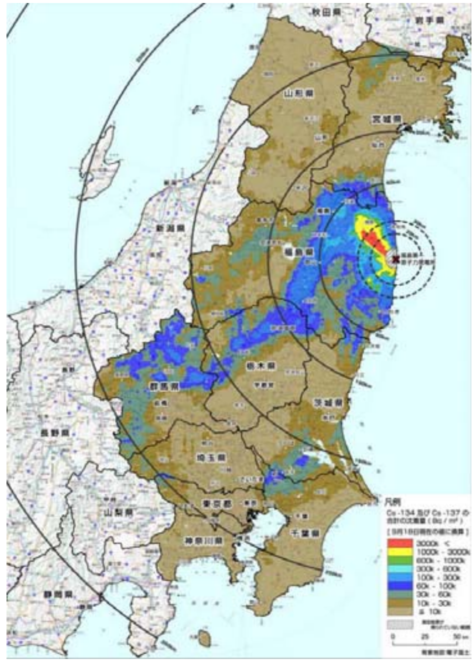


Radioactive Cesium Deposition

^{137}Cs

<u>Half life: 30.17 y</u>

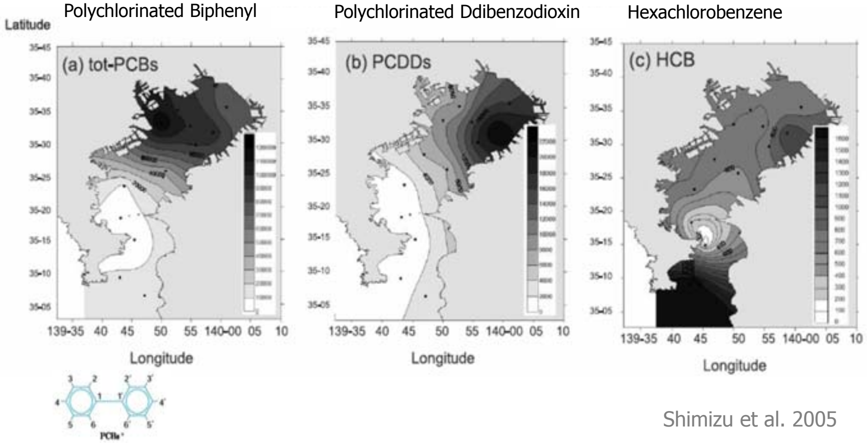
MEXT, Japan
14-18, Sep. 2011



POPs in Tokyo Bay

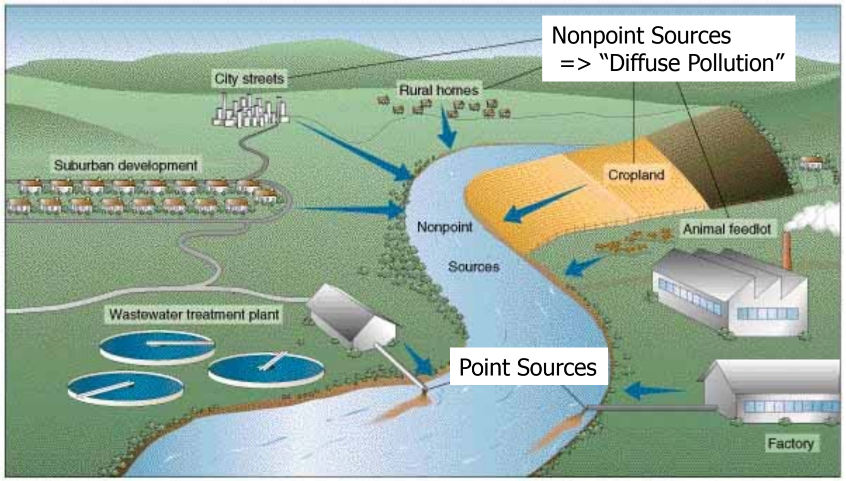
Surface layer (0-5cm) of bottom sediment (pg/g = 10^{-12} g/g)

Polychlorinated Biphenyl | Polychlorinated Ddibenzodioxin | Hexachlorobenzene



Shimizu et al. 2005

Point and Nonpoint Sources



Nonpoint source pollution generally results from land runoff, precipitation, atmospheric deposition, drainage, seepage or hydrologic modification.

http://apesnature.homestead.com/chapter17.html

Understanding Fate & Transport

1. Source
2. Transport & Diffusion
3. Speciation & Distribution
4. Reactivity
5. Bioaccumulation & Bioconcentration

\+ Toxicity test

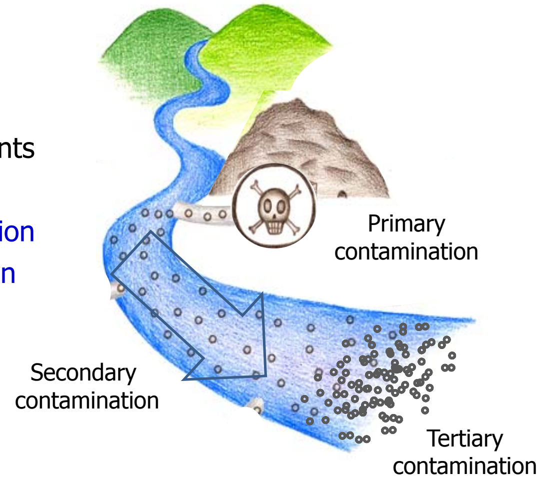
Environmental Risk Assessment

Control

2. Transport & Diffusion

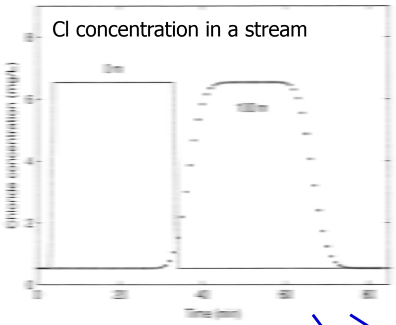
Transport of Pollutants

- Advection
- Turbulent dispersion
- Molecular diffusion



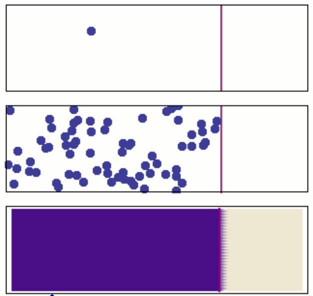
2. Transport & Diffusion

- Advection
- Turbulent dispersion



- Molecular diffusion

Fick's law of diffusion



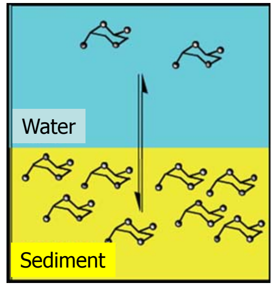
$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} = k\frac{\partial^2 C}{\partial x^2} + f(C)$$

Advection Diffusion Equation

3. Distribution & Speciation

- Speciation / Solubility
- Henry's Law
- Partition (or distribution) Coefficient (k_d)
- Octanol / Water Partition Coefficient (k_{OW})

Hydrophilic / Hydrophobic

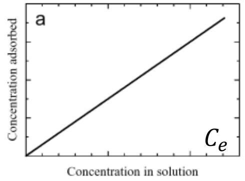


$$k_d = \frac{[A]_{\text{solid}}}{[A]_{\text{water}}} = \frac{[A]_s \left(mg\ kg^{-1}\right)}{[A]_w \left(mg\ L^{-1}\right)} \left(L\,kg^{-1}\right)$$

$$k_{ow} = \frac{[A]_{\text{octanol}}}{[A]_{\text{water}}}$$

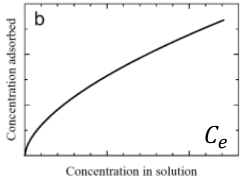
3. Distribution & Speciation

Adsorption Isotherms



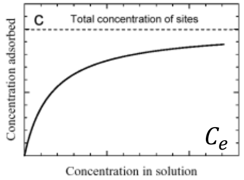
Partition Coefficient
Empirical with 1 parameter

$$q_e = k_d C_e$$



Freundlich Equation
Empirical with 2 parameters

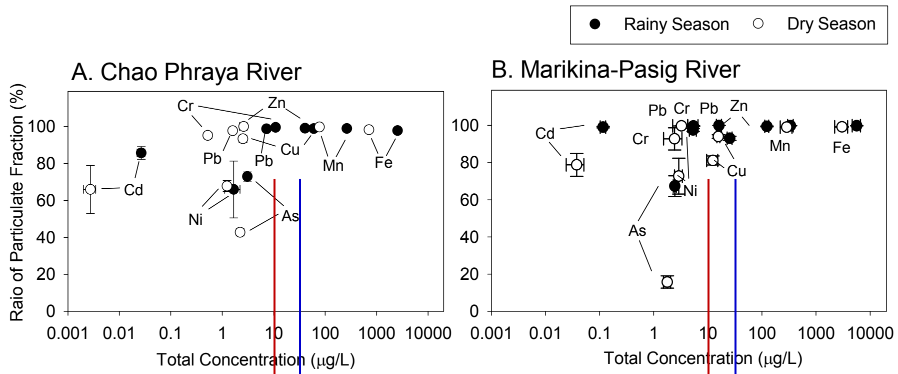
$$q_e = kC_e^{1/n}$$



Langmuir Equation
Monolayer model with 2 parameters

$$q_e = \frac{q_{max} K C_e}{1 + K C_e}$$

Total Metal Concentration



Pb, Cr | Zn | Pb, Cr | Zn

Comparison w

$$EF = \frac{(Metal/Fe)_{sample}}{(Metal/Fe)_{UCC}}$$

Hg, Cd, <u>Pb</u>, <u>Cr</u>, <u>Zn</u>

Metal Content, Geoaccumulation Index,
<u>Enrichment Factor</u>, <u>Sequential Extraction</u>, Model

4. Reactivity (Stability, Degradability)

Reactive, Labile, Biodegradable

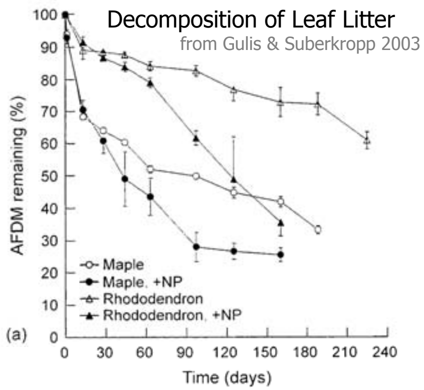
Persistent, Refractory, Recalcitrant

determined by
- Molecular structure
- Speciation / Phase
- Physicochemical condition
- Microbes / Others

First Order Kinetics
Common model for reactive substances

$$\frac{d[A]}{dt} = -k[A]$$

$$[A] = [A]_0 \exp(-kt)$$



Reactivity in Environment

Organic substance

Nutrient

Toxic chemical

Pollutants

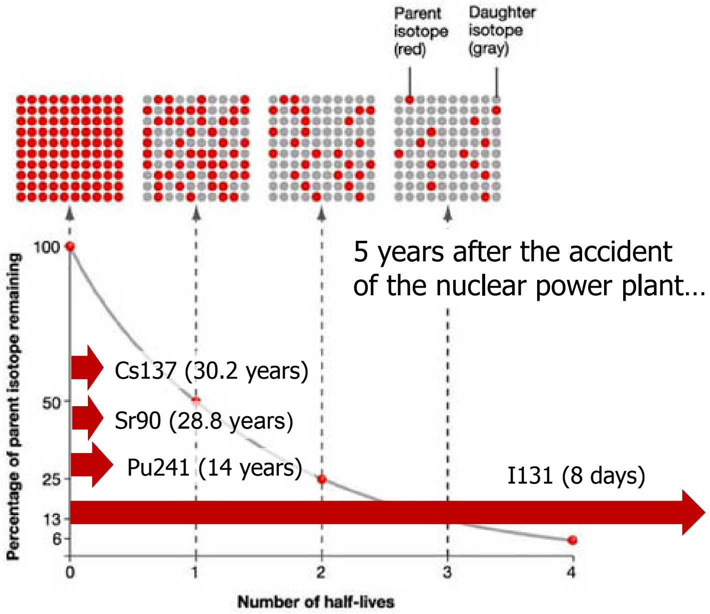
Heavy metal

Endocrine disrupter

Pathogens

Radioactive substance

Kinetics and Half Life

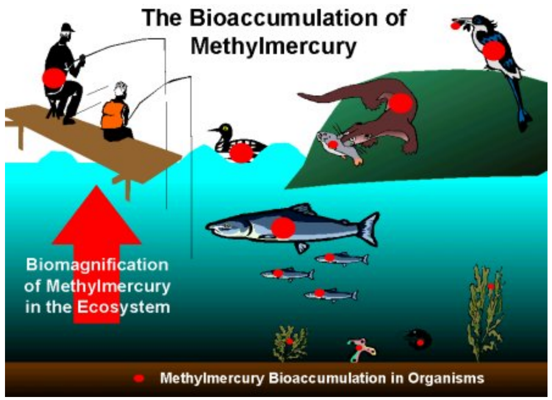


5. Bioaccumulation / Bioconcentration

Pesticide and heavy metal tend to be accumulated/concentrated.

Bioconcentration factor (BCF) =

$$\frac{\text{Concentration in tissue (mg/kg)}}{\text{Concentration in environment (mg/L)}}$$



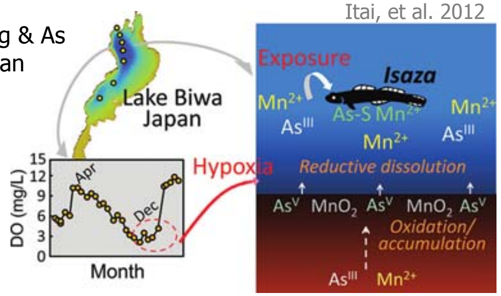
In case of CH_3Hg
BCF = 10^7

Major Pollution Diseases of Japan

Name	Year	Cause	Major Pathway to Human
Itai-itai disease	1912	Cd	
Minamata disease	1932 - 68	CH_3Hg^+	
Yokkaichi Asthma	1961	SO_2, NO_2	
Niigata Minamata disease	1965	CH_3Hg^+	

Case study:
Hypoxia-Induced Exposure to Mg & As at the Bottom of Lake Biwa, Japan

Itai, et al. 2012



1. Source
2. Transport & Diffusion
3. Speciation & Distribution
4. Stability
5. Bioconcentration

Environmental Quality Standard in Japan

Health items

Item	Standard Value	Item	Standard Value
Cadmium	0.01 mg/L or less	1,1,1-trichloroethane	1 mg/L or less
Total cyanide	Undetected	1,1,2-trichloroethane	0.006 mg/L or less
Lead	0.01 mg/L or less	Trichloroethylene	0.03 mg/L or less
Hexavalent chromium	0.05 mg/L or less	Tetrachloroethylene	0.01 mg/L or less
Arsenic	0.01 mg/L or less	1,3-dichloropropene	0.002 mg/L or less
Total mercury	0.0005 mg/L or less	Thiuram	0.006 mg/L or less
Alkylmercury	Undetected	Simazine	0.003 mg/L or less
PCB	Undetected	Thiobencarb	0.02 mg/L or less
Dichloromethane	0.02 mg/L or less	Benzene	0.01 mg/L or less
Carbon tetrachloride	0.002 mg/L or less	Selenium	0.01 mg/L or less
1,2-dichloroethane	0.004 mg/L or less	Nitrate nitrogen & Nitrite nitrogen	10 mg/L or less
1,1-dichloroethylene	0.02 mg/L or less	Fluoride	0.8 mg/L or less
Cis-1,2-dichloroethylene	0.04 mg/L or less	Boron	1 mg/L or less

Living environment items

Item	River	Lake	Sea Area
BOD	≤ 1 - 10 mg/L	-	-
COD-Mn	-	≤ 1 - 8 mg/L	≤ 2 - 8 mg/L
pH	6.0 - 8.5	6.0 - 8.5	7.0 - 8.3
SS	≤ 25 - 100 mg/L etc.	≤ 1 - 15 mg/L etc.	-
DO	2-7.5 mg/L ≤	2-7.5 mg/L ≤	2-7.5 mg/L ≤
Coliform bacteria count	≤ 50 - 5,000 MPN/100 mL	≤ 50 - 1,000 MPN/100 mL	≤ 1,000 MPN/100 mL
N-hexane extracts	-	-	Undetected.
Total nitrogen	-	≤ 0.1 - 1 mg/L	≤ 0.2 - 1 mg/L
Total phosphorous	-	≤ 0.005 - 0.1 mg/L	≤ 0.02 - 0.09 mg/L
All zinc	≤ 0.03 mg/L	≤ 0.03 mg/L	≤ 0.01 - 0.02 mg/L

Standards are devices to keep the lazy mind from thinking.

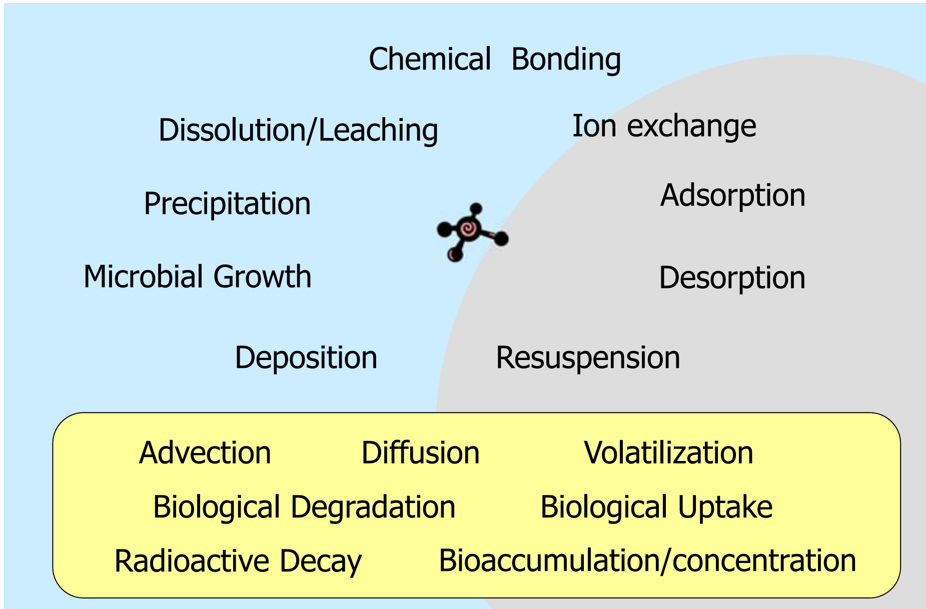
Williams Sedgwick (1855-1921)

They are not perfect, so be careful…

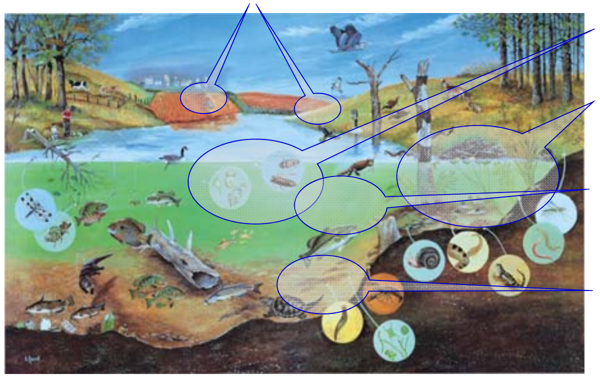
Ecosystem Service

Millennium Ecosystem Assessment, 2005

Relevant Processes of Fate & Transport of Pollutants



Water Quality Management in Lakes and Reservoirs



Lecture schedule

1) June 13, Mon., Guidance to aquatic environmental science
2) June 16, Thu., Present state and properties of water
3) June 20, Mon., Watershed hydrology and aquatic ecosystem
4) June 23, Thu., Sediment and habitat dynamics
5) June 27, Mon., pH and redox potential
6) June 30, Thu., Dissolution and Kinetics
7) July 4, Mon., Particle and adsorption (with a guest speaker)
8) July 7, Thu., Mid-term exercise
9) July 11, Mon., Primary production (with a guest speaker)
10) July 14, Thu., Nutrient cycle
11) July 18, Mon., Organic carbon dynamics and microbial community
12) July 21, Thu., Biodiversity and species distribution (with a guest speaker)
13) July 25, Mon., Fate and transport of pollutants
14) July 28, Thu., Management of aquatic environments
15) August 1, Mon., Exam (Presentation and Report)

Next Class

Grazing in Vernal Pools
Restoration Management Decisions

The Situation

The U.S. Fish and Wildlife Service has recently acquired 200 acres of open land in the Central Valley of California. This land once supported vernal pools that were home to many endemic and endangered flora and fauna. Unfortunately, over the last decade human activities such as off-road driving have significantly degraded the landscape. Because of this degradation invasive species have taken over both the uplands and the pool basins.

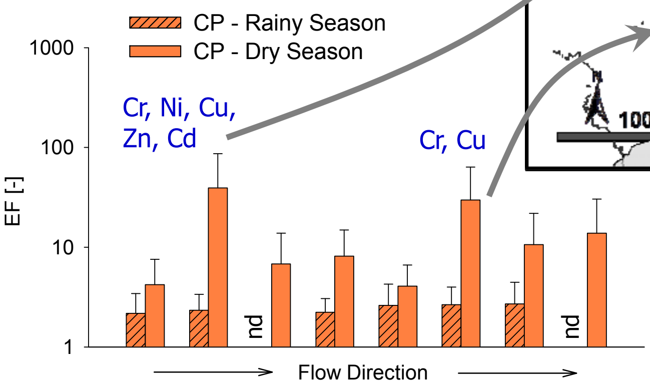
The acquired site has been approved for an active restoration plan that seeks to create …

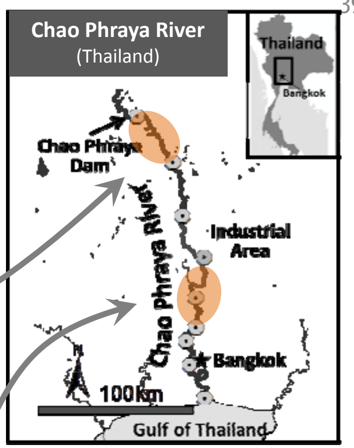
Appendix

Risk Assessment of Pollutants

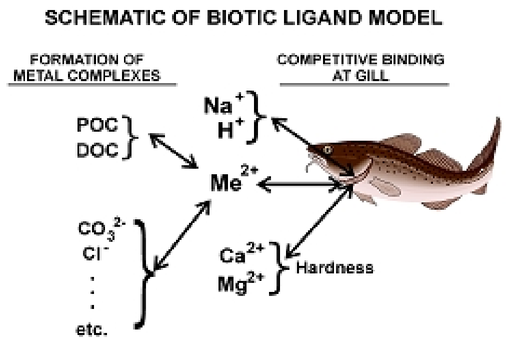
Enrichment Factor along Chao Phraya

Average of Cr, Mn, Ni, Cu, Zn, Cd, Pb

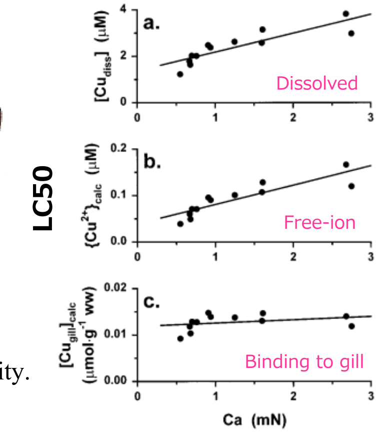




Toxicity | Biotic Ligand Model (BLM)



BLM is developed based largely on acute toxicity.



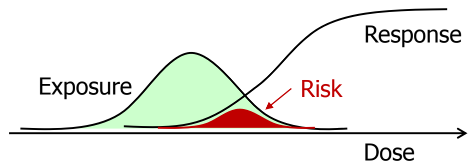
Meyer et al. 1999

Environmental Risk

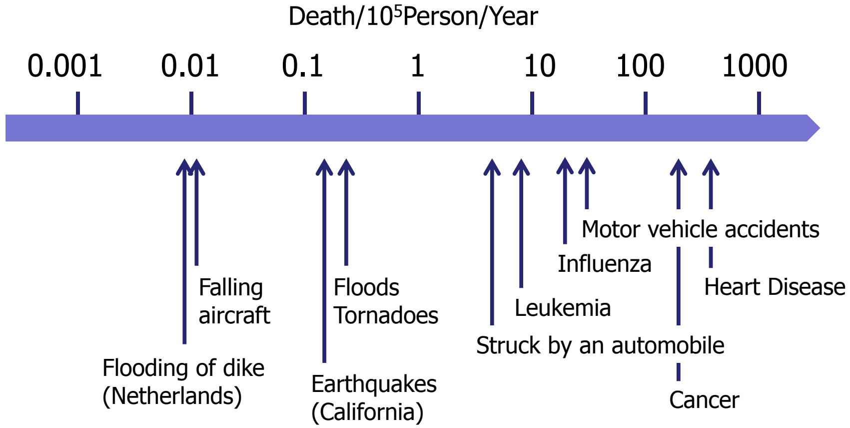
- Health Risk
- Ecological Risk

General procedure of risk assessment

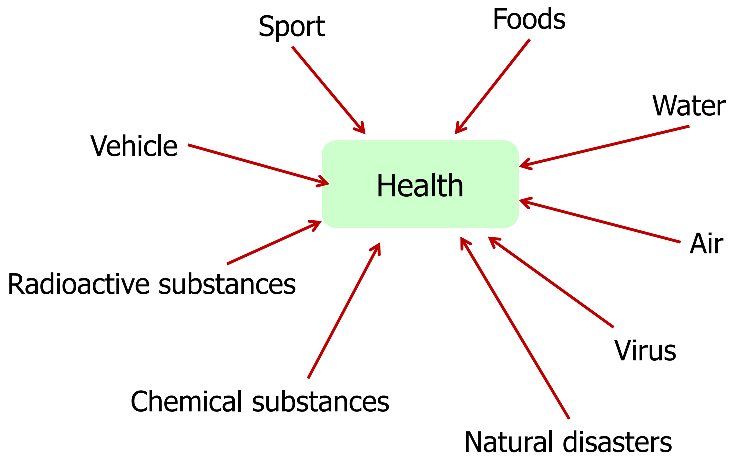
1. Hazard Identification
2. Determination of endpoint
3. Exposure Quantification（曝露解析）
4. Dose-Response Analysis （用量反応解析）
5. Risk characterization



Risks in Reality (Involuntary Risks in US)



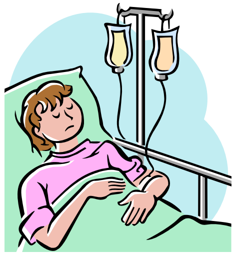
Adapted from Dinman, B.D., The Reality and Acceptance of Risk,
J Am Med Assoc, 244: 1126–1128, 1980.



Environmental Risk

Actual or potential threat of adverse effects on living organisms and environment by effluents, emissions, wastes, resource depletion, etc., arising out of an organization's activities.

1. Risk assessment
2. Risk management



1. Hazard Identification

To determine the qualitative nature of the potential adverse consequences of the contaminant (chemical, radiation, noise, etc.) and the strength of the evidence it can have that effect.

Example	Aircraft	Smoking	Water environment
Hazard			

2. Determination of endpoint

Hazard

Endpoint

Outcome of adverse effects to be considered for probability in risk assessment

Example	Aircraft	Smoking	Water environment
Hazard	Crash	Tar	Heat
Endpoint			

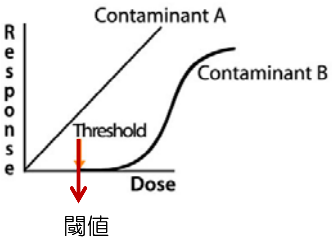
3. Exposure Quantification（曝露解析）

- To determine the amount of a contaminant (Dose, 用量) that individuals and populations will receive.
- Particular care is taken to determine the exposure of the susceptible population(s). (Sensitivity)
- As different location, lifestyles and other factors likely influence the amount of contaminant that is received, a range or distribution of possible values is generated in this step.

Example	Aircraft	Smoking	Water environment
Hazard	Crash	Tar	Heat
Endpoint	Death	Lung cancer	Loss of species
Exposure			

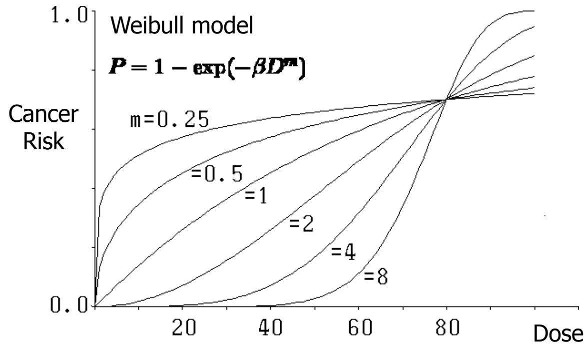
4. Dose-Response Analysis（容量反応解析）

Dose = Exposure



NOAEL: No Observed Adverse Effect Level

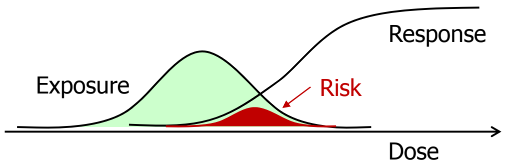
- To determine the relationship between dose and the probability or the incidence of effect.
- The complexity of this step in many contexts derives mainly from the need to extrapolate results from experimental animals to humans, and/or from high to lower doses.
- An alternative to dose-response estimation is to determine an effect unlikely to yield observable effects (NOAEL).
- Safety factor in the estimate of the "safe" dose, is typically 10 for each unknown step.
- Logit model, Weibull model or other models can applied for different hazards and endpoints.



Example	Aircraft	Smoking	Water environment
Hazard	Crash	Tar	Heat
Endpoint	Death	Lung cancer	Loss of species
Exposure	mile/year·per	number/day·kg	Δdegree/year
Dose-Response	Exposure - Endpoint		

5. Risk characterization

- Finally, the results of the 4 steps above are combined to produce an estimate of risk.
- Because of the different susceptibilities and exposures, this risk will vary within a population.



1. Hazard Identification
2. Determination of endpoint
3. Exposure Quantification
4. Dose-Response Analysis
5. Risk characterization

Probability distribution (3. Exposure Quantification, 4. Dose-Response Analysis)

5. Risk characterization

Monte Carlo methods

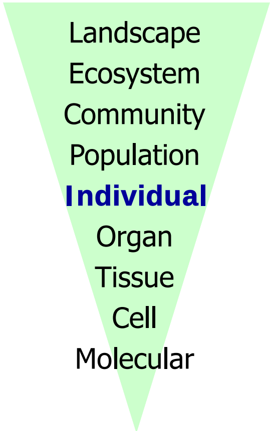
1. Define a domain of possible inputs.
2. Generate inputs randomly from <u>a probability distribution</u> over the domain.
3. Perform a deterministic computation on the inputs.
4. Aggregate the results.

1. Hazard Identification
2. Determination of endpoint
3. Exposure Quantification
4. Dose-Response Analysis
5. Risk characterization

Probability distribution (3. Exposure Quantification, 4. Dose-Response Analysis)

Ecological Risk Assessment

What can be endpoints in ecological risk assessment?



1. Hazard Identification
2. Determination of endpoint
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