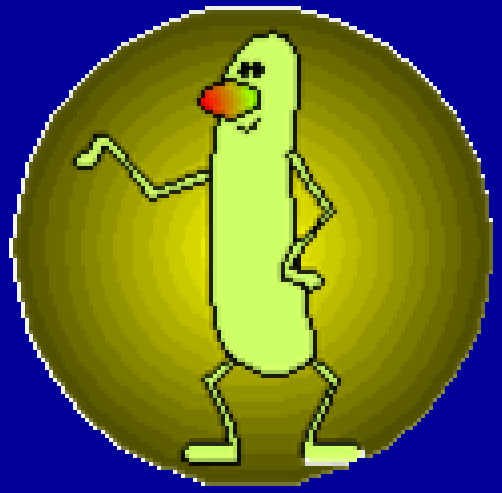
# GEOCHEMISTRY REFRESHER

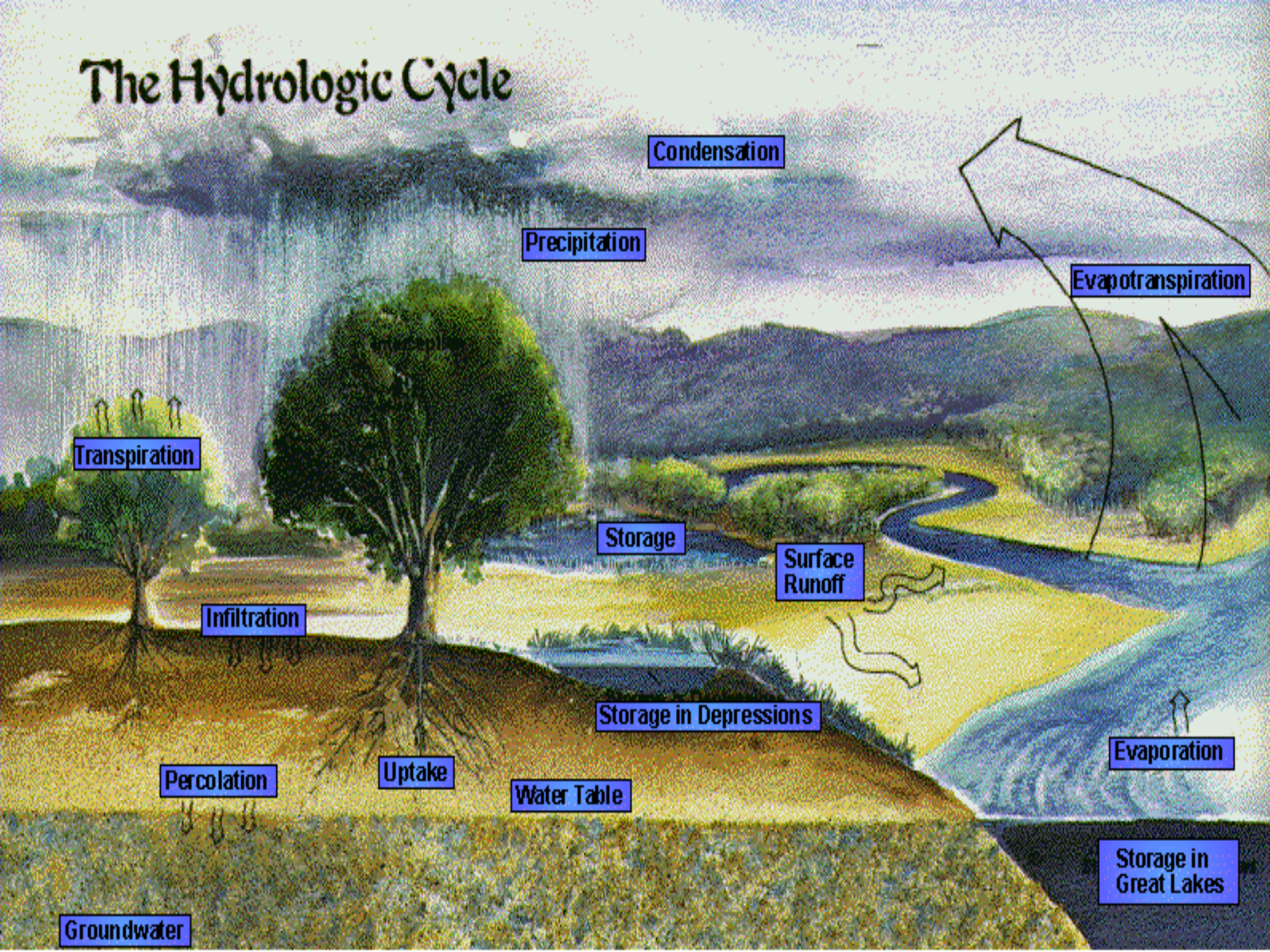
# And

# POLLUTION STUDY APPLICATIONS



Dr. Laine Vignona, University of Wisconsin-River Falls

Assistant Professor of Environmental Science & Management


The Hydrologic Cycle
Condensation
Precipitation
Evapotranspiration
Transpiration
Storage
Surface Runoff
Infiltration
Storage in Depressions
Evaporation
Percolation
Uptake
Water Table
Storage in Great Lakes
Groundwater

# Physical/chemical properties of water

Water always contains natural “impurities”

Acceptability of water for its *defined use*:
physical,chemical, biological properties

Are properties acceptable or “modifiable”?

# Some physical properties of natural waters

- COLOR:
  - dissolved minerals, humic acids
- TURBIDITY
  - particles scatter/absorb light
- SOLIDS
  - total, suspended, dissolved
  - river values typically 2-200 mg/L TSS
- TEMPERATURE
  - reaction rates depend on temperature & pressure

# What do you remember?

- Molarity
- Normality
- Solubility & Precipitation
- Dissolution of gases
- Vapor pressure
- Free energy
- Chemical equilibrium = “K”
- Oxidation-reduction reactions
- Kinetics

- Normality – alkalinity, conductivity, ionic strength
- Solubility & Precipitation – Mercury
- Dissolution of gases – $O_2$, $CO_2$
- Vapor pressure – Mercury, fossil fuels
- Free energy and K – the equilibrium constants
- Kinetics – decay rates, reaction rates

# Water Quality Assessments
## mass balance, charge balance, toxicity

- GENERAL
  - pH
  - Alkalinity
  - Conductivity
  - Hardness
- SPECIFIC
  - Major ions (ppm)
    - Na, K, Ca, Mg
  - Minor ions (ppb)
  - Heavy Metals
    - Pb, Cu, Zn, Sn
  - Nutrients
  - Organic Compounds

# pH

- A master variable
- pH = - log [H+]
- Depends on:
  - parent rock
  - carbonate concentrations (limestone)
  - exposure to pollutants (NOx, SOx)

# Acid mine drainage

Metals are more mobile at low pH


Discharge of acid mine drainage to the environment

# Alkalinity

- Neutralizing capacity – bases accept acids
- Calculated in equivalents/liter
- Equivalents are a function of charge
- [Alkalinity] =

$$[OH^-] + 2[CO_3^{2-}] + [HCO_3^-] - [H^+]$$

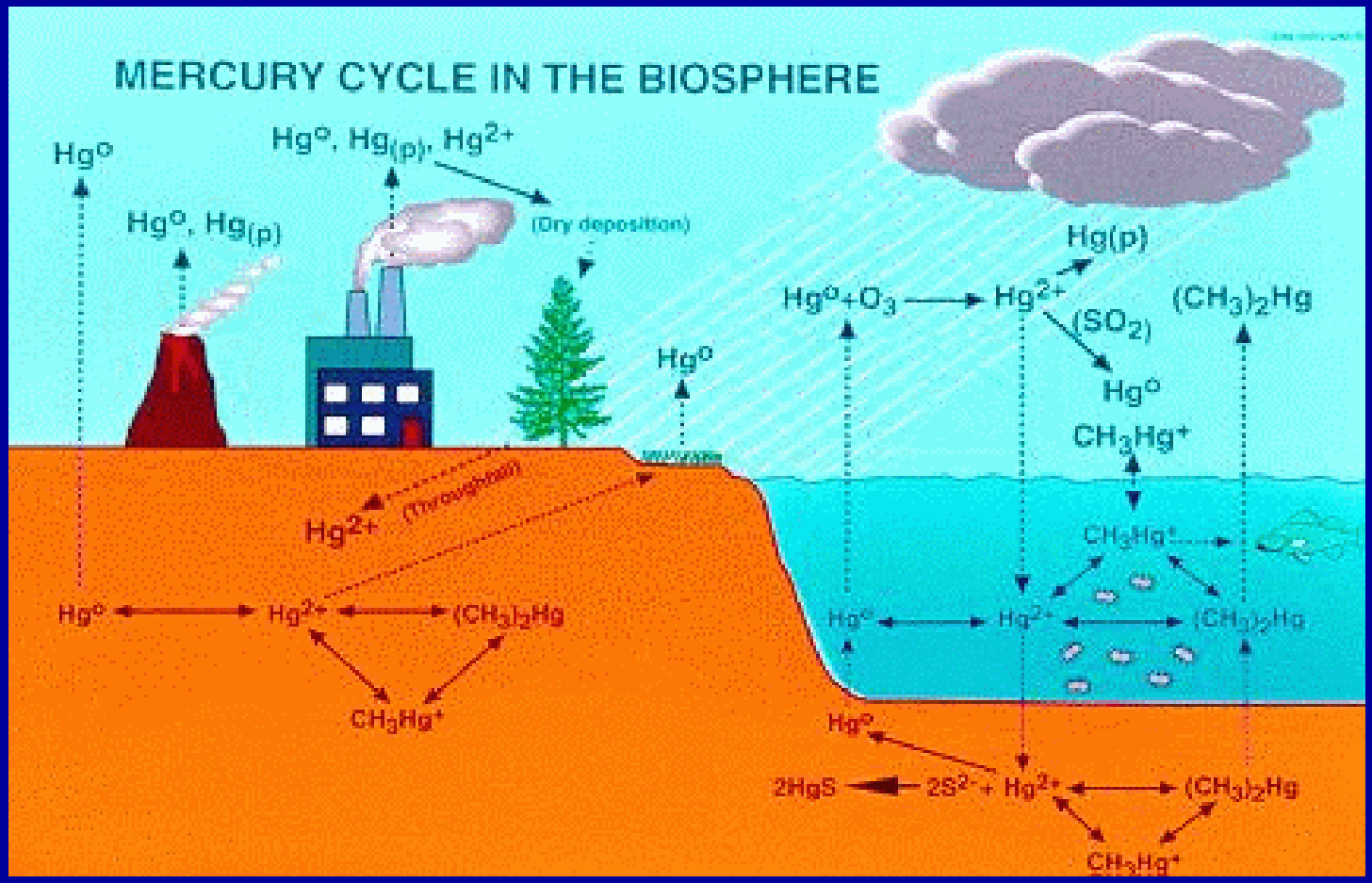
# Conductivity & Ionic Strength

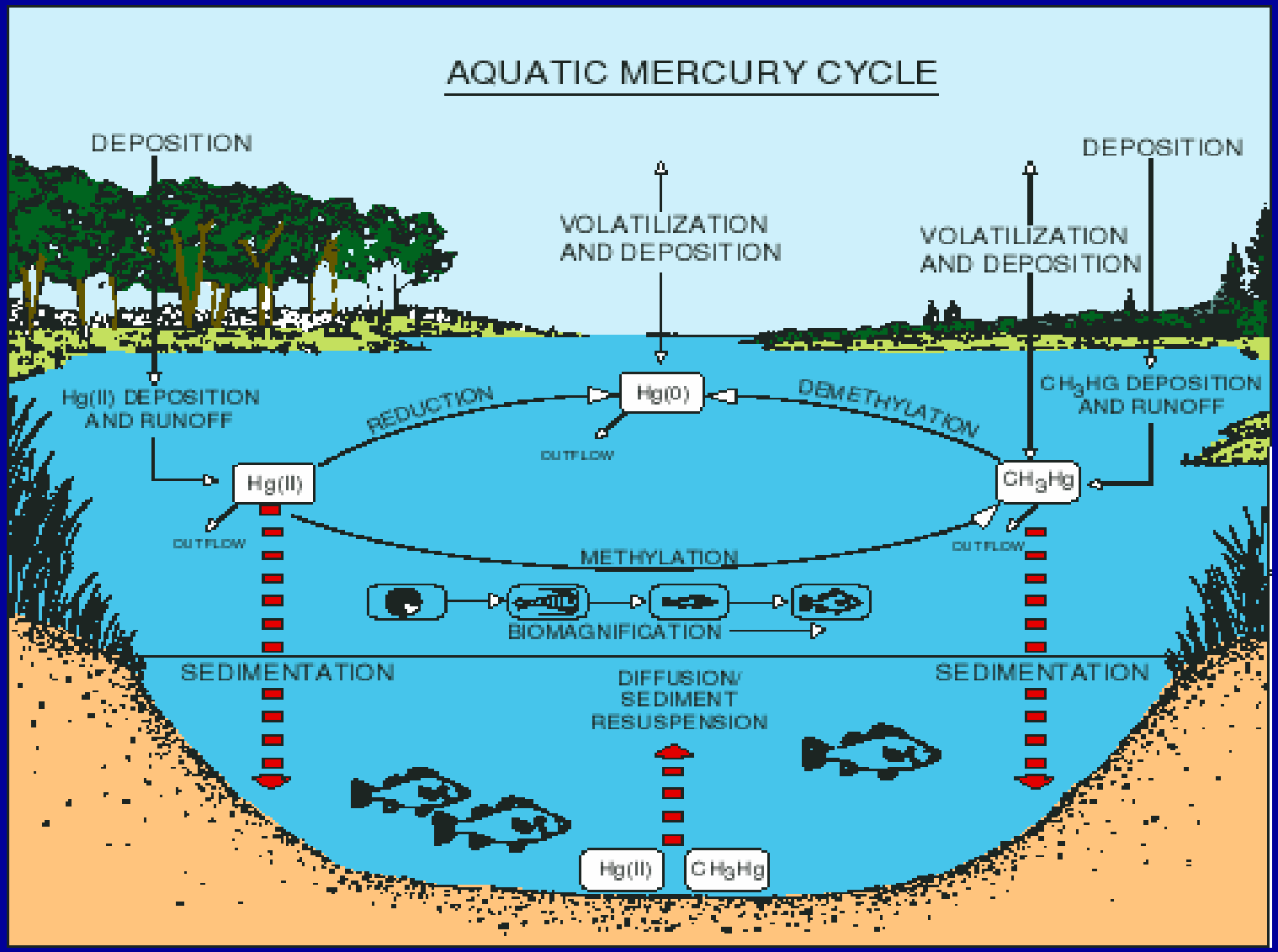
*Conductivity*

- Water conducts an electrical current
- Current is conducted by dissolved ions
- 0.05 uS/cm in pure water
- 40,000 uS/cm in seawater

Ionic strength

- intensity of the electrical field
- IS = ½ sum ($CZ^2$)
- IS = ($1.6 \times 10^{-5}$) (conductivity)


MERCURY CYCLE IN THE BIOSPHERE
Hg°
Hg°, Hg(p)
Hg°, Hg(p), Hg2+
(Dry deposition)
Hg°
Hg2+ (Throughfall)
Hg° ↔ Hg2+ ↔ (CH3)2Hg
CH3Hg+
Hg°+O3 → Hg2+
Hg(p)
(SO2)
Hg°
CH3Hg+
(CH3)2Hg
CH3Hg+
Hg° ↔ Hg2+ ↔ (CH3)2Hg
Hg°
2HgS ← 2S2- + Hg2+ ↔ (CH3)2Hg
CH3Hg+


AQUATIC MERCURY CYCLE
DEPOSITION
VOLATILIZATION AND DEPOSITION
VOLATILIZATION AND DEPOSITION
DEPOSITION
Hg(II) DEPOSITION AND RUNOFF
REDUCTION
Hg(0)
DEMETHYLATION
CH3HG DEPOSITION AND RUNOFF
OUTFLOW
Hg(II)
CH3Hg
OUTFLOW
OUTFLOW
METHYLATION
BIOMAGNIFICATION
SEDIMENTATION
DIFFUSION/ SEDIMENT RESUSPENSION
SEDIMENTATION
Hg(II)
CH3Hg

Oil Spill at Sea

LOOKS LIKE PETROLEUM CONTAMINATION

# *K is an equilibrium constant*

- Acid-base reactions: $K_a$ in the carbonate system
- Gas exchange between water & the atmosphere: $K_H$
- Precipitation/dissolution: the solubility product $K_{sp}$
- Adsorption-desorption: the partition coefficient $K_p$ or $K_{oc}$
- Complexation: dissolved complex formation $K_f$

# PHREEQC modeling capabilities
# speciation, batch-reaction, (1D) reactive-transport (USGS)

**Applications:**

Mine drainage
Radioactive-waste isolation
Contaminant migration
Natural and engineered aquifer remediation
Aquifer storage and recovery
Water treatment
Natural systems
Laboratory experiments

# Partition coefficients: $K_p$ and $K_{oc}$

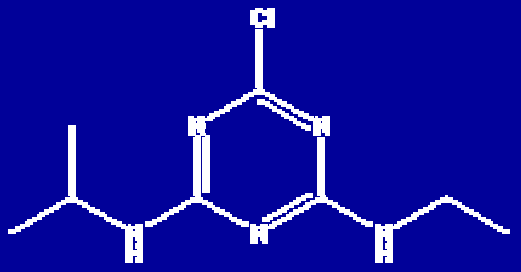
- Critical in the study of subsurface pollution

- There's advection
- There's dispersion
- There's diffusion and *then*
- There's partitioning due to adsorption

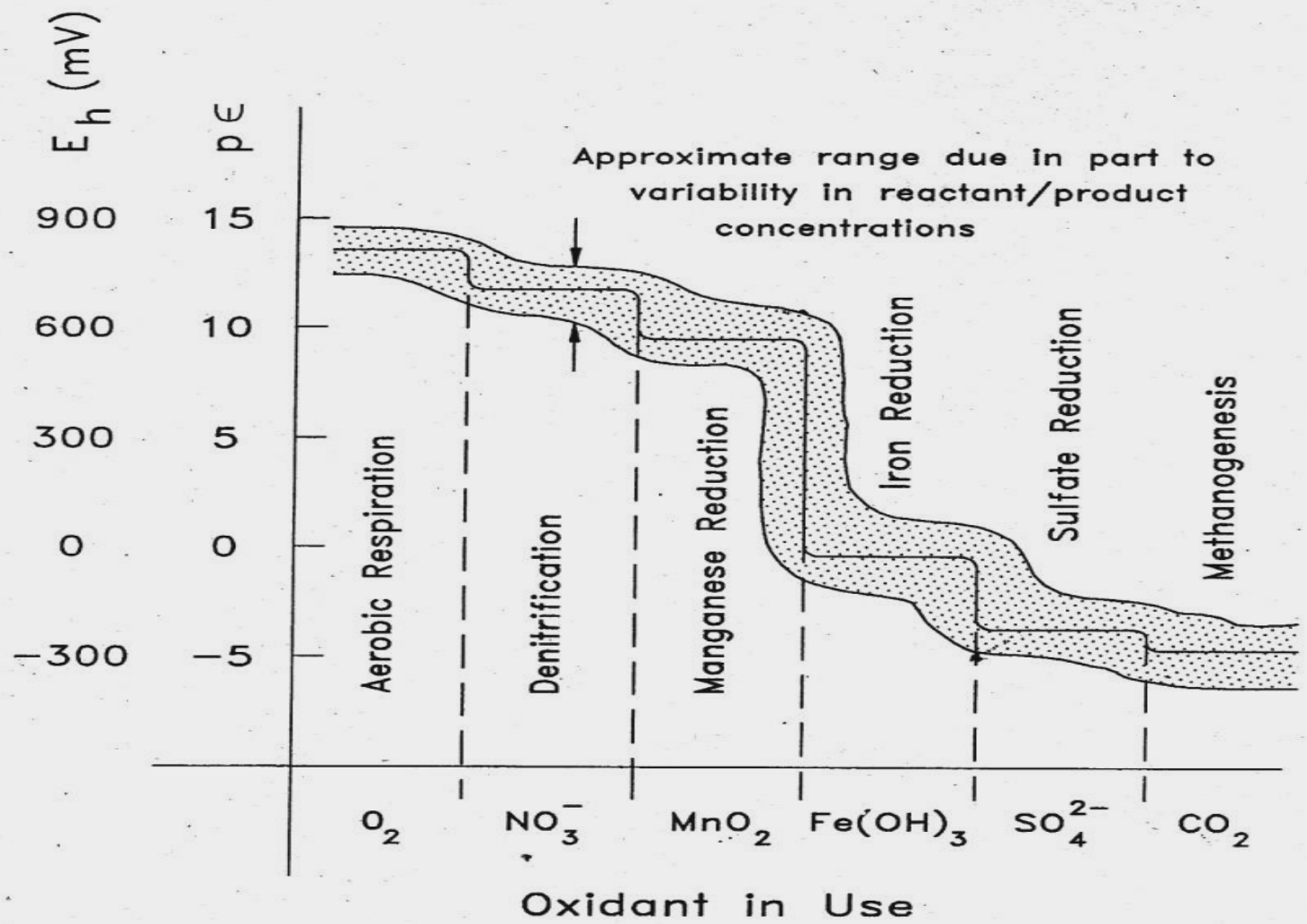
- A major geologic influence on contaminant transport

Many pesticides have high partition coefficients

Atrazine



# Oxidation-Reduction Reaction Sequence




The ecological redox sequence.


Mississippi
Lake
Pontchartrain
Basin
Louisiana
Mississippi River
Gulf of Mexico

# Redox reactions and the role of bacteria

- Bacteria are ubiquitous and are natural degraders
- They carry out biodegradation through oxidation-reduction reactions
- Bugs are used in water, wastewater & hazardous waste treatment
- Aerobic organisms use oxygen to degrade contaminants
- Anoxic organisms don’t use oxygen to degrade

# Issues

- Mercury in water
  - Analyze mercury in soil
  - Analyze mercury in groundwater
  - Inform the public
- Pharmaceuticals in water
  - Surface and groundwater
  - Then what?