Advanced Water Quality

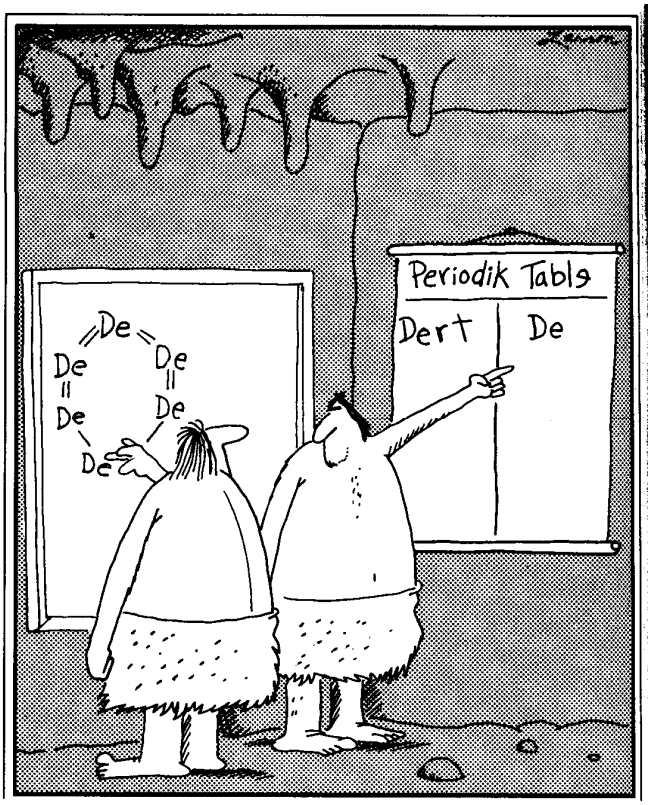
Class 20:

Organic Chemicals III

This week's objectives

- ❑ Introduction to organic pollutants
- ❑ Environmental fate governed by structural influence on interconnected processes
- ❑ **Organic chemical classification and nomenclature**
- ❑ Important fate-controlling processes in aquatic systems

Classification & Nomenclature



Early chemists describe the first dirt molecule.

- **Classify by structure**
  - Triazines, carbamates
- **Classify by properties**
  - VOCs, HOCs, EDCs,
- **Classify by use**
  - fungicides, antibiotics, PPCPs
- Systematic nomenclature: see organic chem text
- Environmental Chemistry
  - Common names (atrazine, chlorpyrifos)
  - Incorrectly-applied nomenclature common

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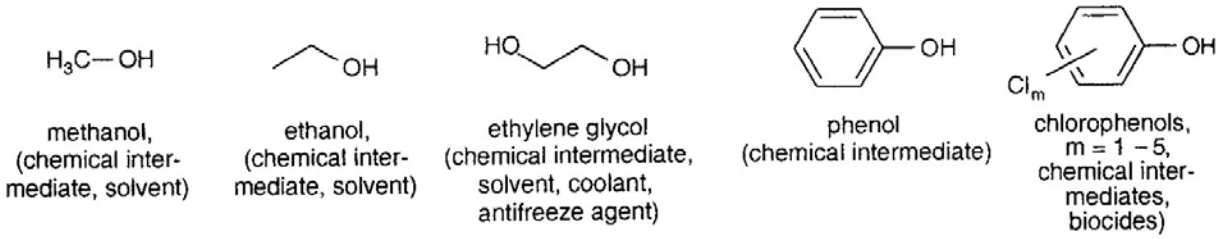
Useful Terms to Know

- Saturated vs. unsaturated
- Primary vs secondary vs tertiary
- Aliphatic (alkane, alkyl groups, *n*-alkanes, etc)
- Aromatic (*ortho, meta, para*)
- *cis* vs. *trans*

O-Containing Functional Groups

alcohols (R—OH) and phenols (Ar—OH)



methanol, (chemical intermediate, solvent)

ethanol, (chemical intermediate, solvent)

ethylene glycol (chemical intermediate, solvent, coolant, antifreeze agent)

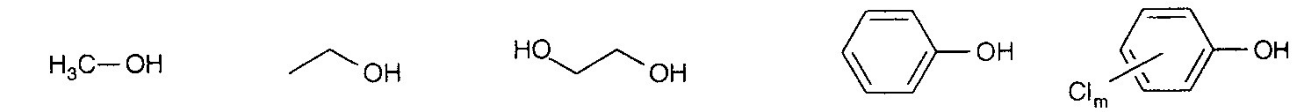
phenol (chemical intermediate)

chlorophenols, m = 1 – 5, chemical intermediates, biocides)

- Alcohols (R-OH)
- Phenols (Ar-OH)

O-Containing Functional Groups

alcohols (R—OH) and phenols (Ar—OH)



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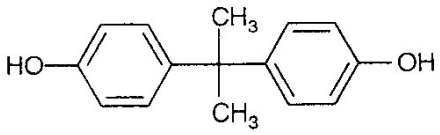
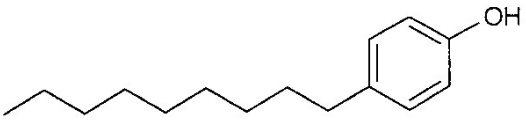
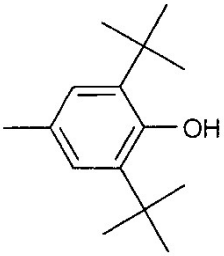


2,2-bis-(4-hydroxy-phenyl)-propane ("bisphenol A," chemical intermediate)

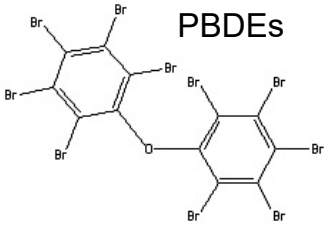


4-nonylphenol (metabolite of nonionic surfactants)



2,6-di-*t*-butyl-*p*-cresol (DBPC, antioxidant)

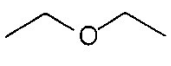
O-Containing
Functional Groups



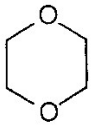
PBDEs

•Ethers

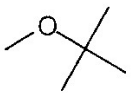
ethers (R_1—O—R_2)



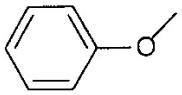
diethyl ether
(solvent)



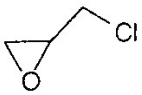
1,4-dioxane
(solvent)



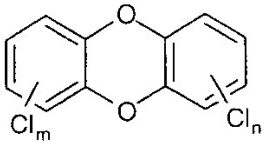
methyl-*t*-butyl-ether
(MTBE, gasoline
additive)



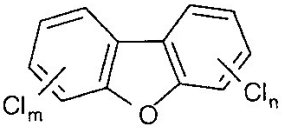
methyl-phenyl-ether
(anisole, methoxy-benzene)



1-chloro-2,3-epoxy-propane
(epichlorohydrine,
chemical intermediate)



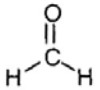
polychlorinated dibenzo-
p-dioxines (PCDDs,
175 possible congeners)



polychlorinated dibenzo-
furans (PCDFs,
135 possible congeners)

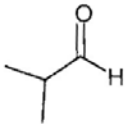
Aldehydes & Ketones

aldehyde and *keto* *functions*

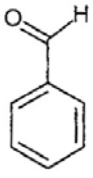


formaldehyde
(disinfectant,
chemical intermediate)

acetaldehyde
(chemical intermediate,
solvent)



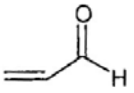
isobutylaldehyde
(chemical intermediate,
solvent, desinfection
byproduct in drinking water)



benzaldehyde
(chemical intermediate,
solvent)

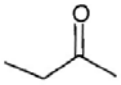
Aldehydes & Ketones

aldehyde (R—C(=O)—H) and *keto* (R$_1$—C(=O)—R$_2$) *functions*

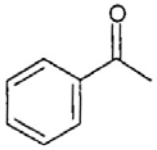


acrolein
(chemical intermediate
for polymer production)

acetone
(chemical intermediate,
solvent)



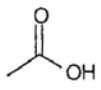
2-butanone
(solvent)



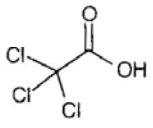
methyl phenylketone
(acetophenone; chemical
intermediate, solvent)

Carboxylic acids & esters

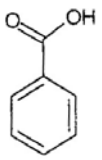
carboxyl (R—C(=O)—OH) and *carboxylic acid ester* (R$_1$—C(=O)—OR$_2$) *functions*



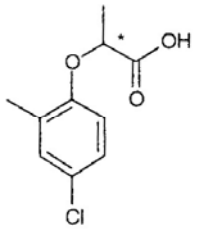
acetic acid



trichloroacetic acid
(herbicide, atmospheric
breakdown product of
chlorinated solvents)



benzoic acid (food
preservative,
additive, chemical
intermediate)

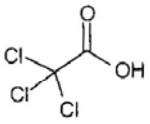


(R,S)-2-(4-chloro-2-methyl
phenyl) - propionic acid
((R,S)-mecoprop; herbicide)

Carboxylic acids & esters

carboxyl (R—C(=O)—OH) and *carboxylic acid ester* (R_1—C(=O)—OR_2) *functions*

acetic acid



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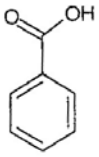

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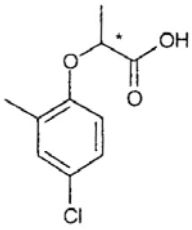
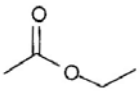
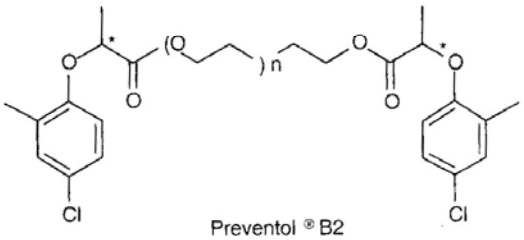


(R,S)-2-(4-chloro-2-methyl phenyl) - propionic acid ((R,S)-mecoprop; herbicide)

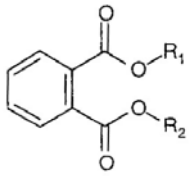


ethylacetate (acetic acid ethyl ester; solvent)



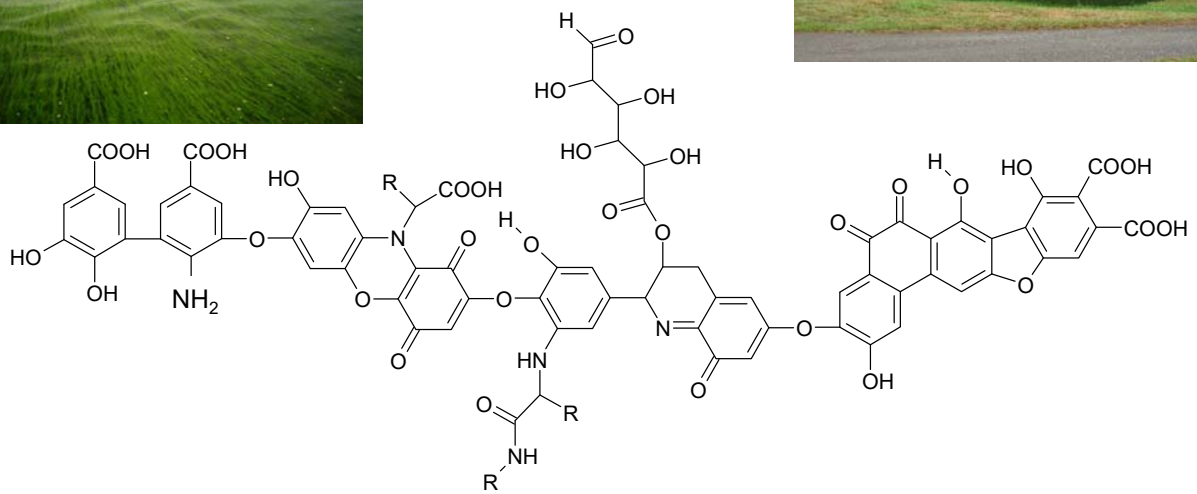
Preventol ® B2

(roof protection agent)



phthalates (R_1, R_2 = C_1, to C_{10}; plasticizers)

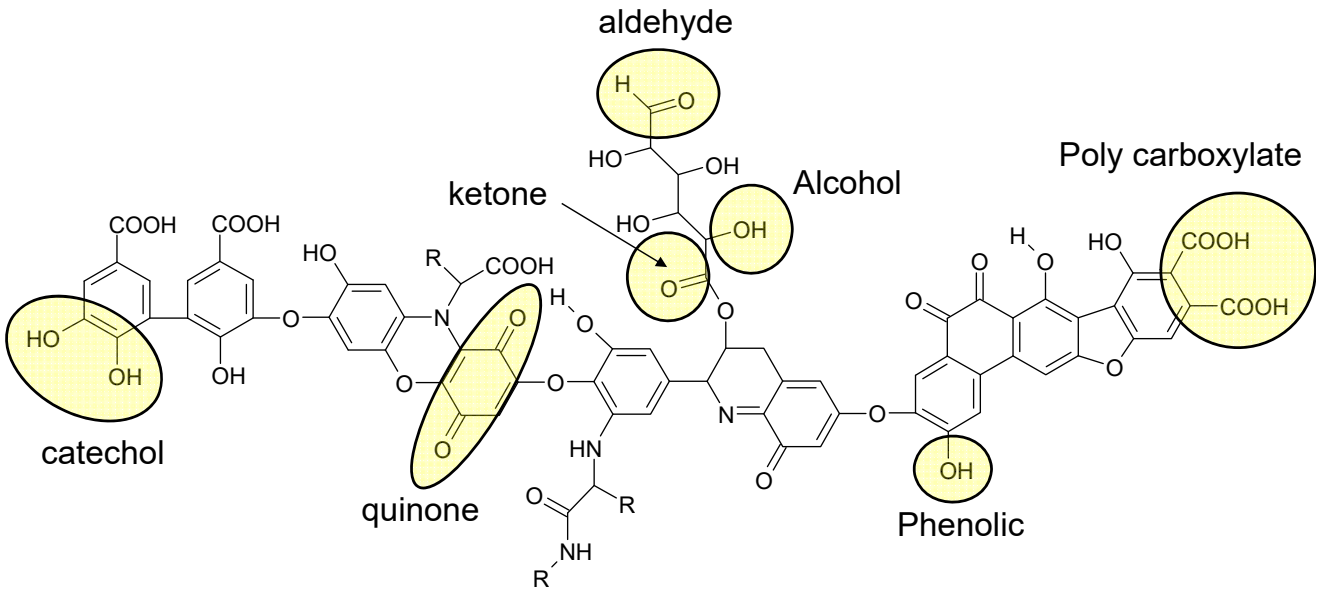
Natural Organic Matter



- Important role in elemental cycling, metal speciation, organic sorption to soil and sediments
- Contains important natural ligands for metal ion complexation
- Affects water quality of drinking water

Humic Substances

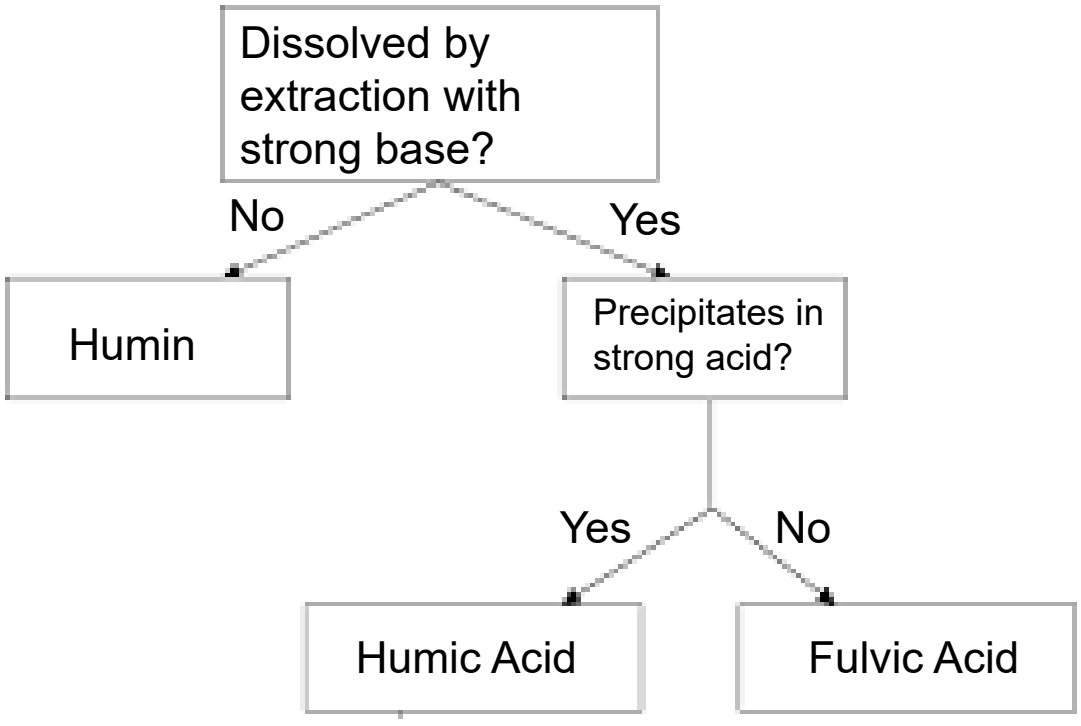
- Macromolecular
- Aliphatic & aromatic regions
- Wide range of O-functional groups



- Carboxylate and phenol/catechol groups are major weak acid groups, bind metal ions in aquatic systems

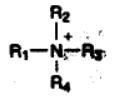
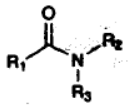
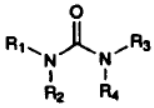
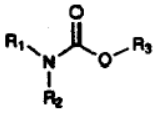
Stevenson (1982) Humus Chemistry

Fractionation of Humic Materials



Nitrogen-Containing Functional Groups

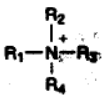
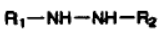
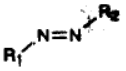
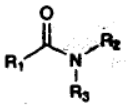
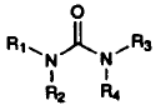
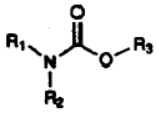
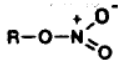
Table 2.5 Some Important Nitrogen-Containing Functio
Compounds

Group	Name (oxidation state of nitrogen)
	ammonium (-III)
	amino[a] (-III) (amine)
	carboxylic acid amide[a] (-III)
	cyano, nitrilo (-III)
	urea (-III)
	carbamate (-III)

[a]Primary if $R_2 = R_3 = H$; secondary if $R_2 = H$ and $R_3 \neq H$; tertiary i

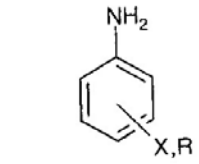
Nitrogen-Containing Functional Groups

Table 2.5 Some Important Nitrogen-Containing Functional Groups Present in Anthropogenic Organic Compounds

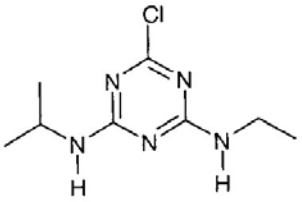
Group	Name (oxidation state of nitrogen)	Group	Name (oxidation state of nitrogen)
	ammonium (-III)		hydrazo (-II)
	amino[a] (-III) (amine)		azo (-I)
	carboxylic acid amide[a] (-III)		hydroxyl-amine (-I)
	cyano, nitrilo (-III)		nitroso (+I)
	urea (-III)		nitro (+III)
	carbamate (-III)		nitrato (+V) (nitrate)

More oxidized

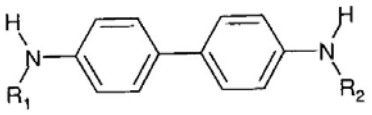
[a]Primary if $R_2 = R_3 = H$; secondary if $R_2 = H$ and $R_3 \neq H$; tertiary if $R_2 \neq H$ and $R_3 \neq H$.



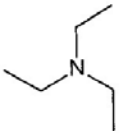
aniline and substituted anilines (chemical intermediates)



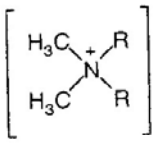
atrazine (a triazine herbicide)



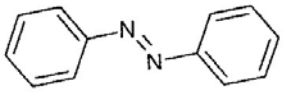
N,N'-dialkyl/aryl *p*-phenylendiamines (antioxidants)



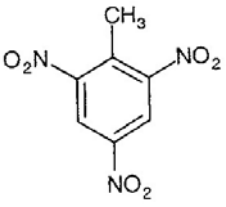
triethylamine (solvent, wetting agent, corrosion inhibitor, propellant)



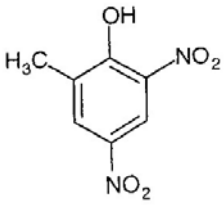
quaternary ammonium salts (cationic surfactants)



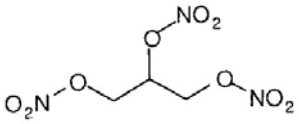
azobenzene (chemical intermediate, pesticide)



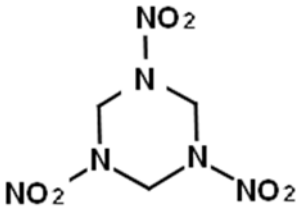
2,4,6-trinitrotoluene (TNT, explosive)



2,4-dinitro-*o*-cresol (DNOC, herbicide)



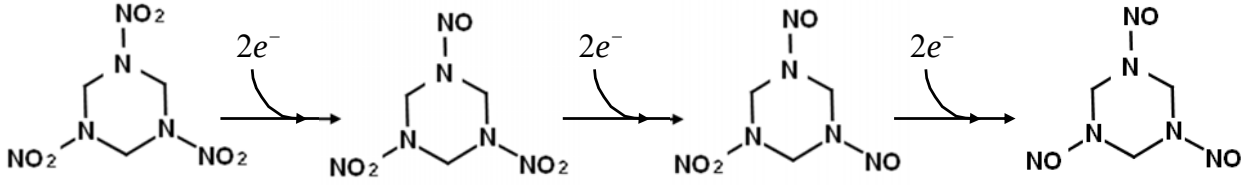
"nitroglycerin" (explosive)



– hexahydro-1,3,5-trinitro-1,3,5-triazine

– Synthesized energetic explosive compound

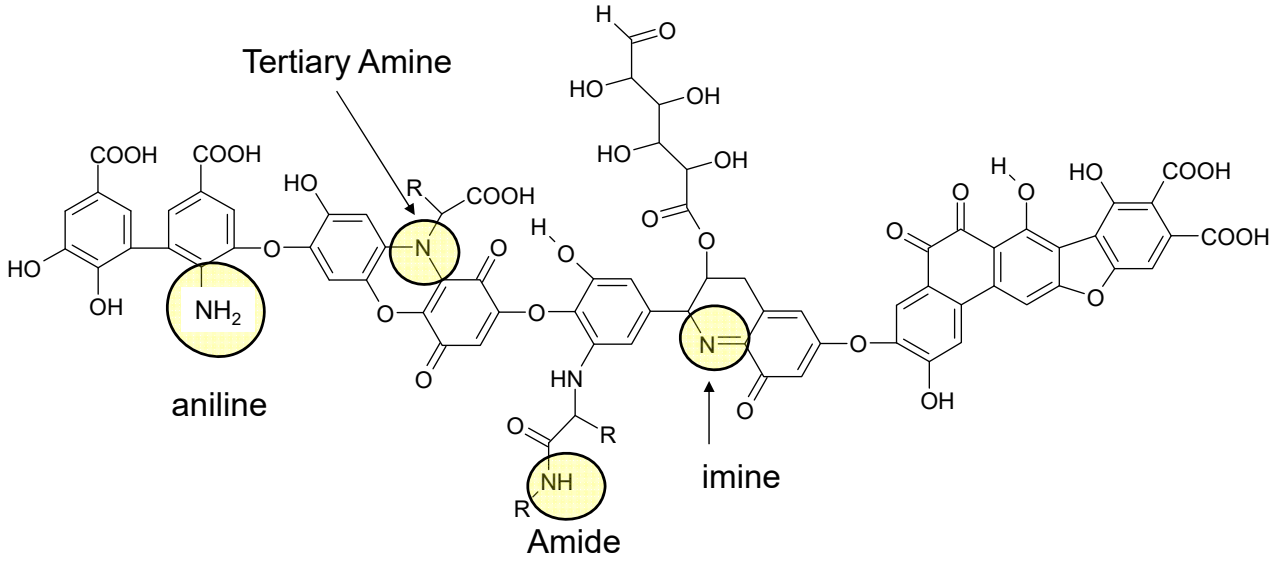
RDX (Royal Demolition Explosive)



RDX **MNX** **DNX** **TNX**

Humic Substances

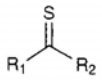
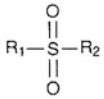
- N-containing groups second most important acid/base groups in NOM
- Derived from decay of proteinaceous source materials



Stevenson (1982) Humus Chemistry

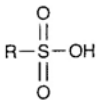
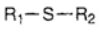
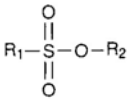
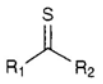
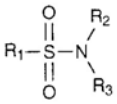
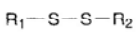
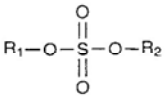
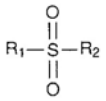
Sulfur-Containing Functional Groups

e 2.6 Some Important Sulfur-Containing Functional g

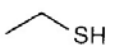
Group	Name (oxidation state of sulfur)
R—SH	thiol, mercaptan (-II)
R_1—S—R_2	thioether, sulfide (-II)
	thiocarbonyl (-II)
R_1—S—S—R_2	disulfide (-I)
	sulfoxide (0)
	sulfone (+II)

Sulfur-Containing Functional Groups

e 2.6 Some Important Sulfur-Containing Functional groups Present in Anthropogenic Organic Compound

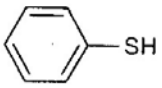
Group	Name (oxidation state of sulfur)	Group	Name (oxidation state of sulfur)
	thiol, mercaptan (-II)		sulfonic acid (+IV)
	thioether, sulfide (-II)		sulfonic acid ester (+IV)
	thiocarbonyl (-II)		sulfonic acid amide, sulfonamide (+IV)
	disulfide (-I)		sulfuric acid ester, sulfate (+VI)
	sulfoxide (0)		
	sulfone (+II)		

More oxidized

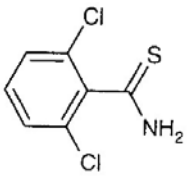


ethylmercaptan (ethanethiol) (odorant, chemical intermediate)

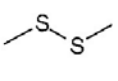
dimethylsulfide (solvent, important biogenic sources)



thiophenol (chemical intermediate)

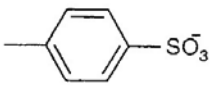


chlorthiamide (herbicide)

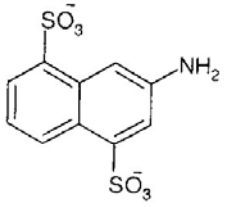


dimethyldisulfide (important biogenic source)

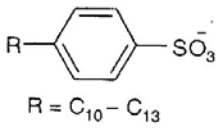
dimethylsulfoxide (solvent)



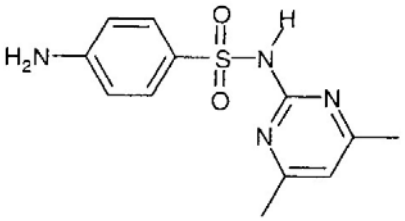
p-toluenesulfonate (hardener, stabilizer)



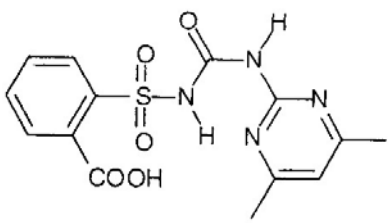
2-amino-naphthalene-4,8-disulfonate (azo dye component)



linear alkylbenzene sulfonates (LAS) (surfactants)



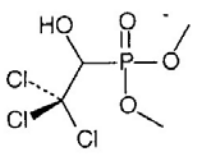
sulfadiazine (a therapeutical drug)



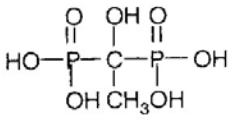
sulfomethuron (a "sulfonylurea" herbicide)

Phosphorus-Containing Functional Groups

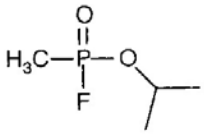
phosphonates



trichlorfon
(insecticide)

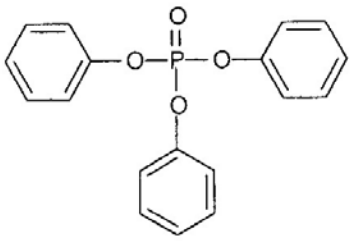


1-hydroxyethyl-
1,1-diphosphonic acid
(HEDP, complexing agent)

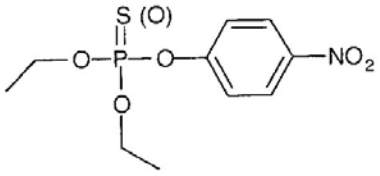


sarin
(nerve poison)

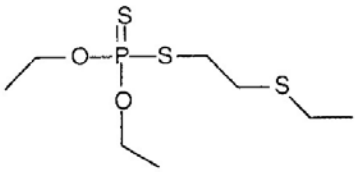
phosphates and thiophosphates



triphenylphosphate
(plasticizer, fire retardant)



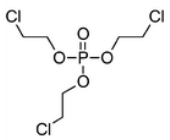
parathion (paraoxon)
(insecticide, acaricide)



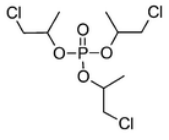
disulfoton
(insecticide, acaricide)

Organophosphate Flame Retardants (replacement for PBDEs)

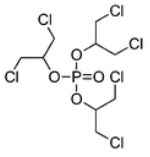
Tris(2-chloroethyl) phosphate
TCEP
S_w: 7820 mg L^{-1}
Log K_{ow}: 1.7
Log K_{oc}: 2.48



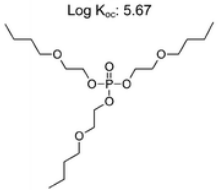
Tris(2-chloro-1-methylethyl) phosphate – isomer 1
TCPP
S_w: 1080 mg L^{-1}
Log K_{ow}: 2.6
Log K_{oc}: 3.11



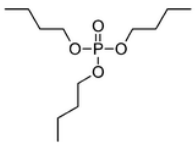
Tris(1,3-dichloro-2-propyl) phosphate
TDCP
S_w: 18.1 mg L^{-1}
Log K_{ow}: 3.8
Log K_{oc}: 3.96



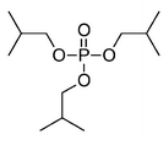
Tris(2-butoxyethyl) phosphate
TBEP
S_w: 1300 mg L^{-1}
Log K_{ow}: 3.8
Log K_{oc}: 5.67

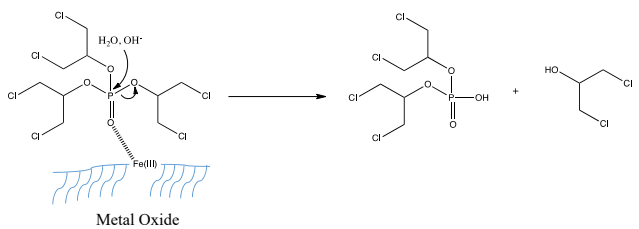


Tri-n-butyl phosphate
TnBP
S_w: 400 mg L^{-1}
Log K_{ow}: 4.0
Log K_{oc}: 3.28

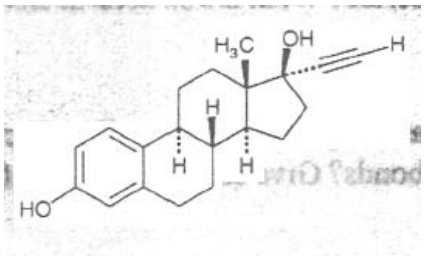


Tri-iso-butyl phosphate
TiBP
S_w: 265 mg L^{-1}
Log K_{ow}: 3.6
Log K_{oc}: 3.05

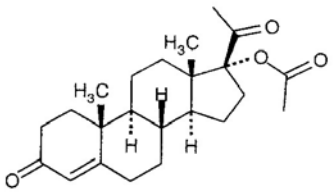




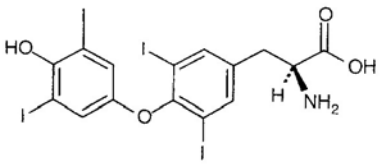
Emerging Contaminants (More Complex)



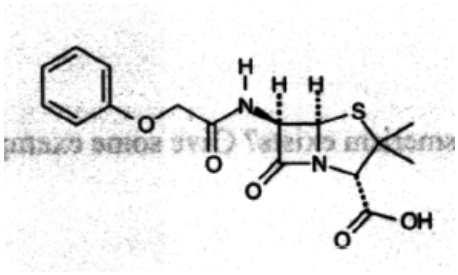
17-ethynyl estradiol
(hormone, birth control pill)



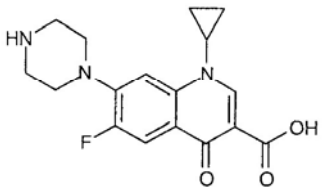
17α-acetoxy-progesterone
(hormone)



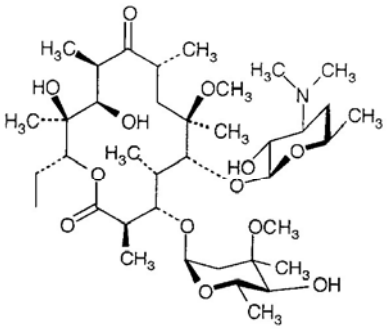
levothyroxine
(hormone)



penicillin V
(β-lactam antibiotic)



ciprofloxacin
(fluoroquinolone antibiotic)

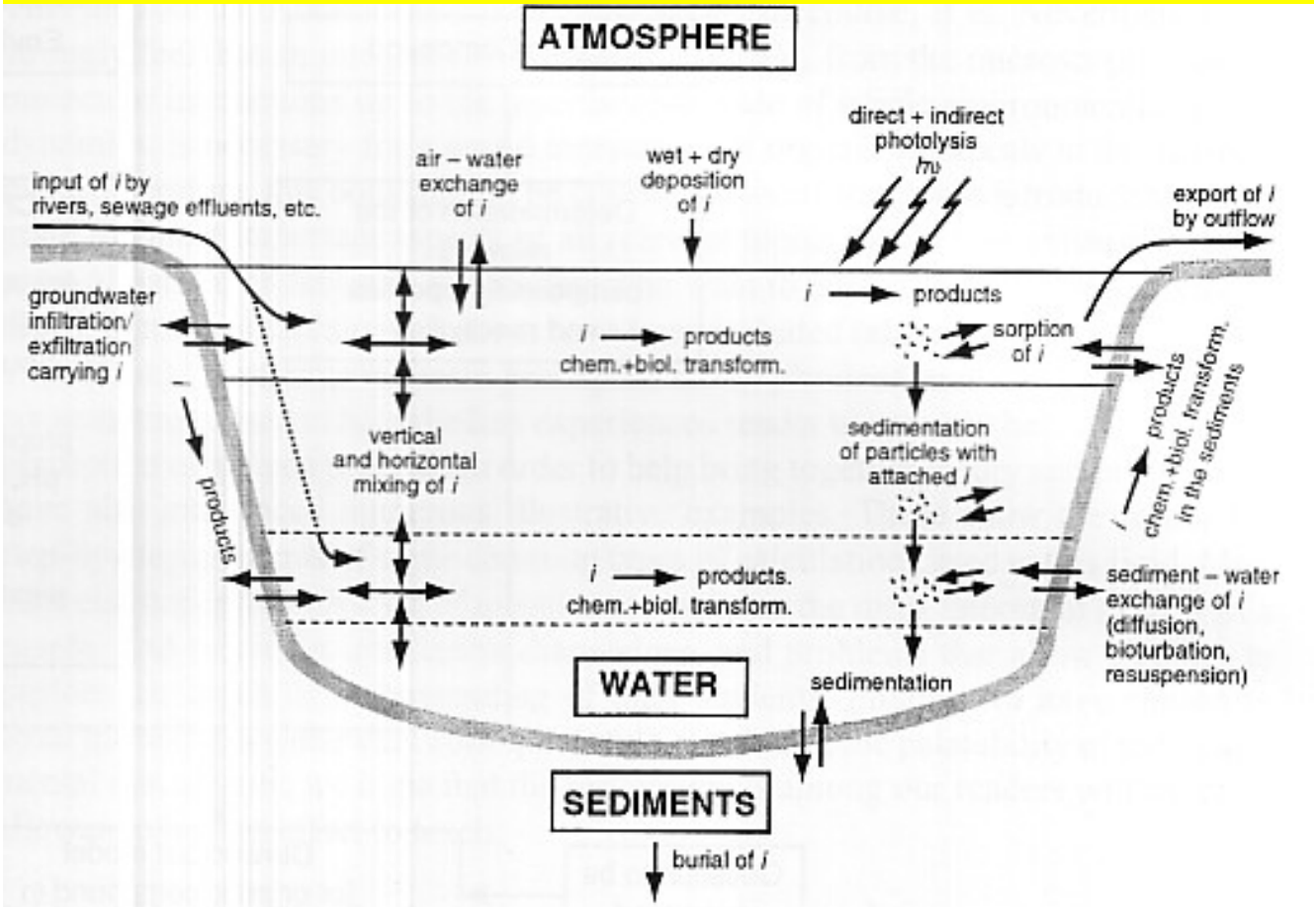


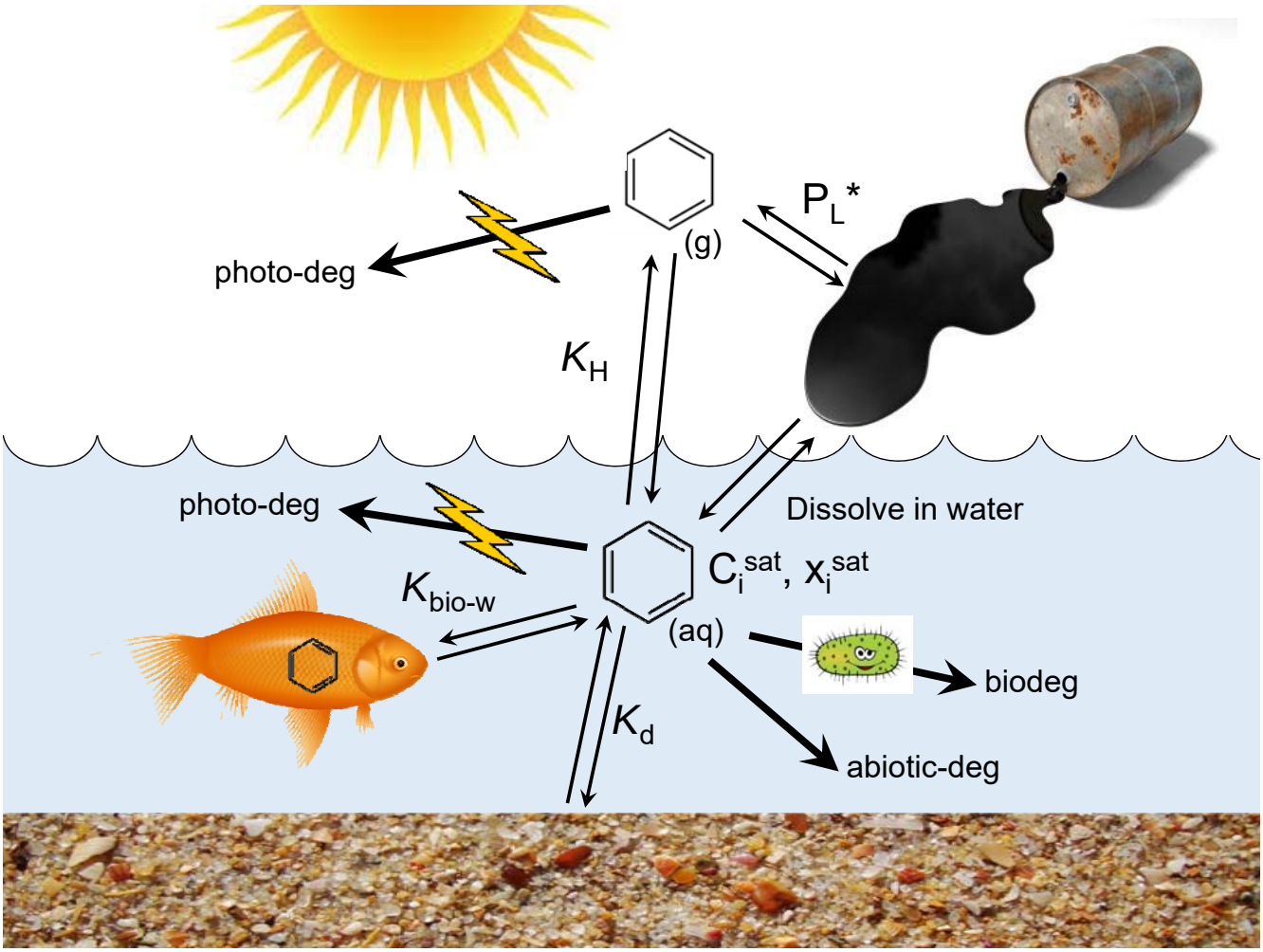
clarithromycin
(macrolide antibiotic)

Today's objectives

- ❑ Introduction to organic pollutants
- ❑ Environmental fate governed by structural influence on interconnected processes
- ❑ Organic chemical classification and nomenclature
- ❑ **Important fate-controlling processes in aquatic systems**

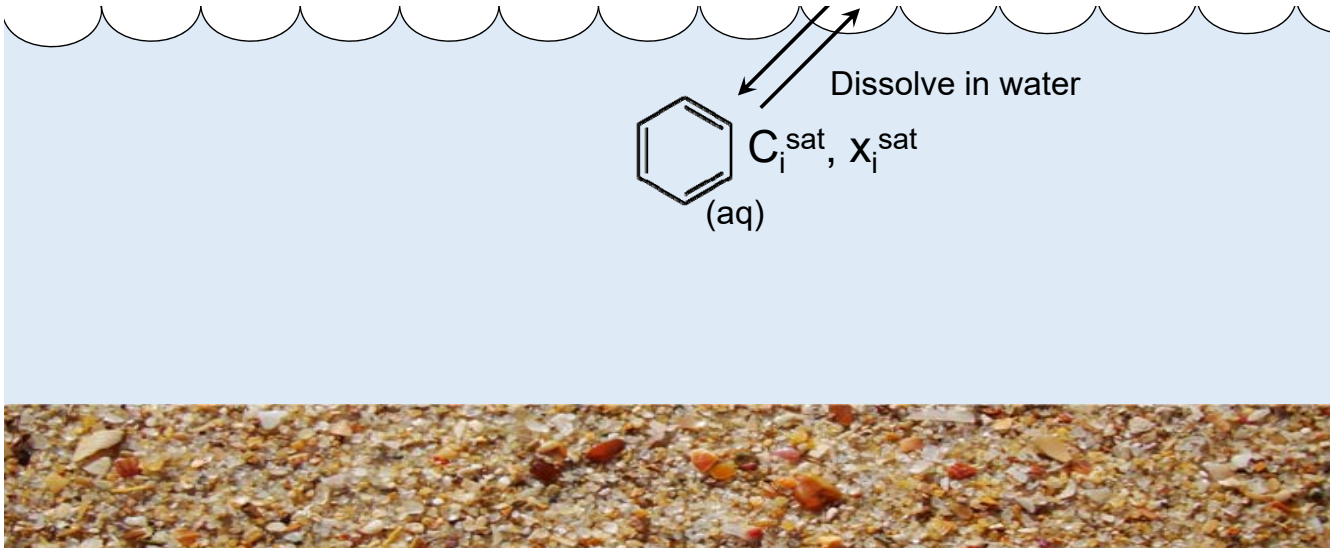
Organic chemical fate is controlled by interconnected processes

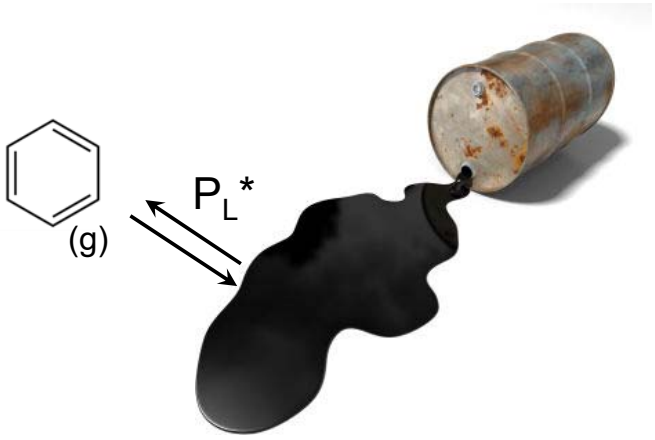




C_i^{sat} = saturation aq solubility (mol/L)
x_i^{sat} = saturation aq solubility (mol fraction)

- Influenced by structure
- ↓ with ↑ molecule size
- ↑ with introduction of polar/ionic or H-bonding functional groups
- Predict from LFERs, fragment approach, SPARC, EPI-Suite





Saturation Vapor Pressure (P_L^*, atm)

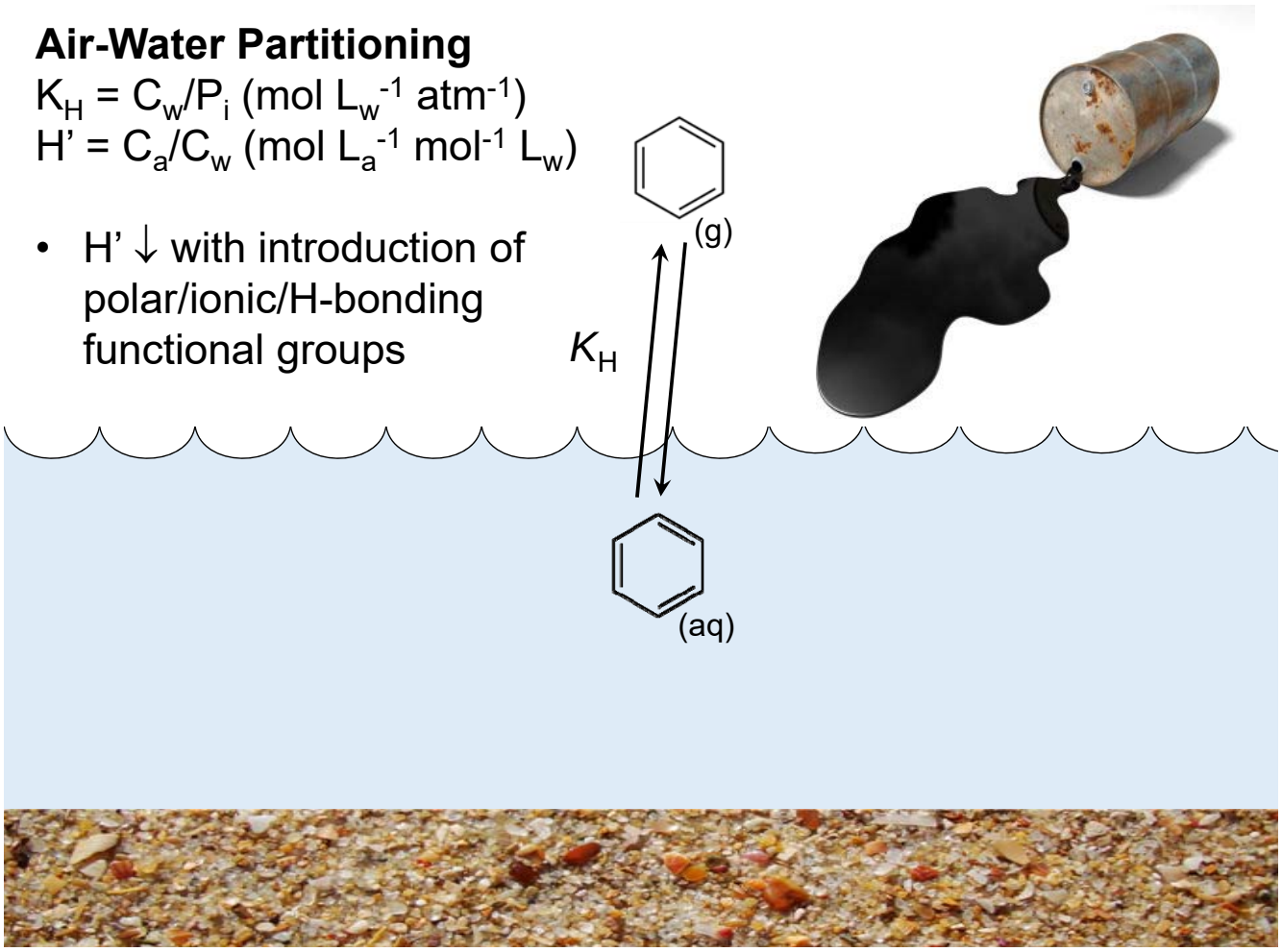
- ↓ with ↑ molecular size
- ↓ with introduction of (bi)polar/ionic/H-bonding functional groups

Air-Water Partitioning

$K_H = C_w/P_i$ (mol L_w^{-1} atm^{-1})

$H' = C_a/C_w$ (mol L_a^{-1} mol^{-1} L_w)

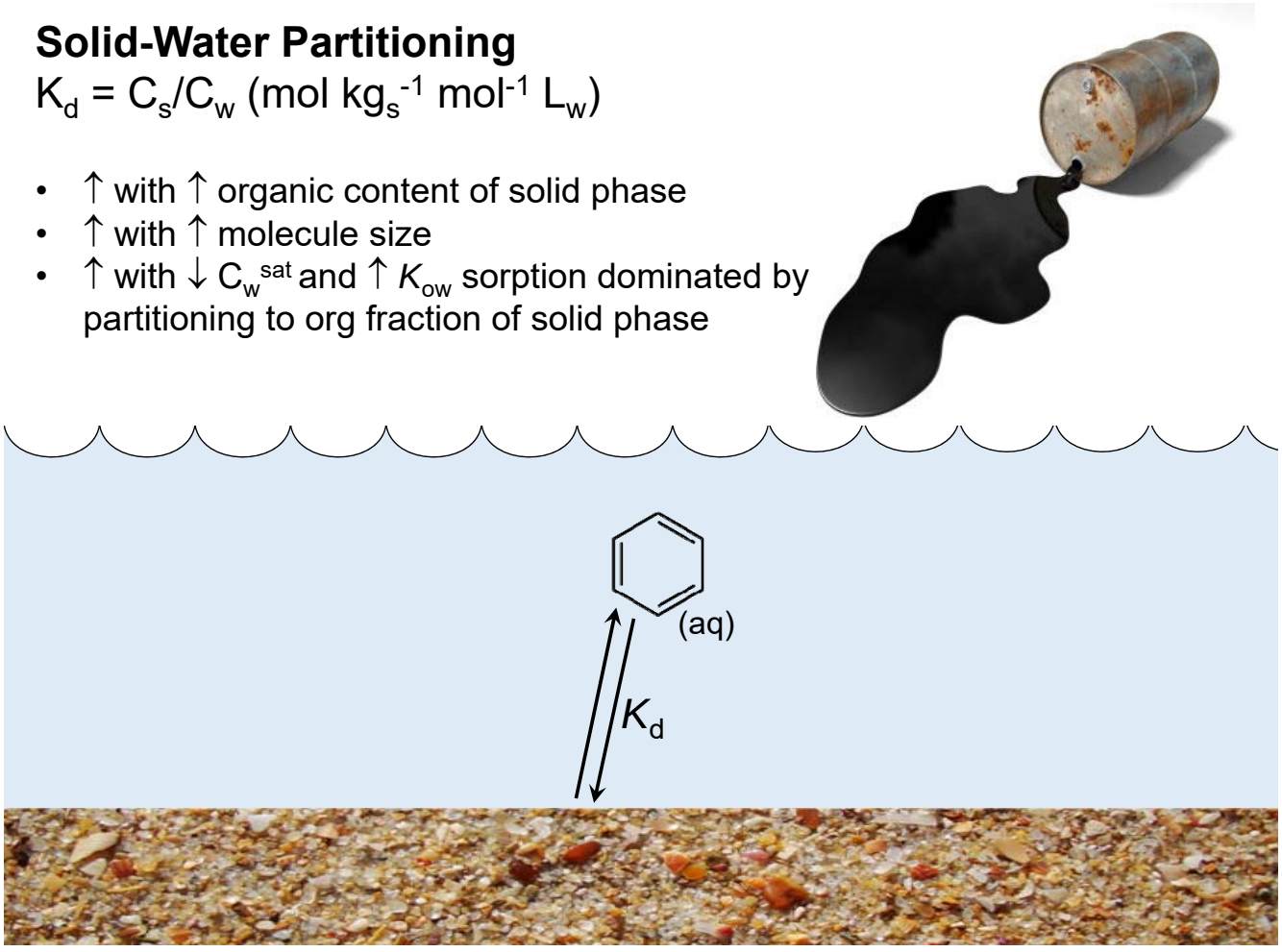
- H' ↓ with introduction of polar/ionic/H-bonding functional groups



Solid-Water Partitioning

$K_d = C_s/C_w$ (mol kg_s^{-1} mol^{-1} L_w)

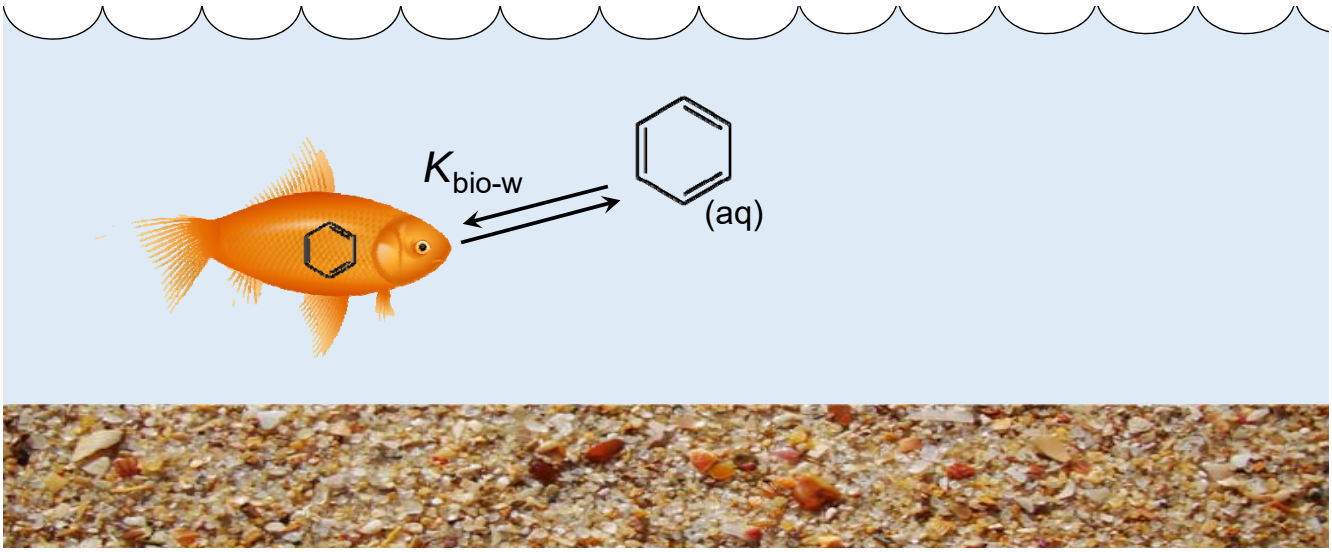
- ↑ with ↑ organic content of solid phase
- ↑ with ↑ molecule size
- ↑ with ↓ C_w^{sat} and ↑ K_{ow} sorption dominated by partitioning to org fraction of solid phase



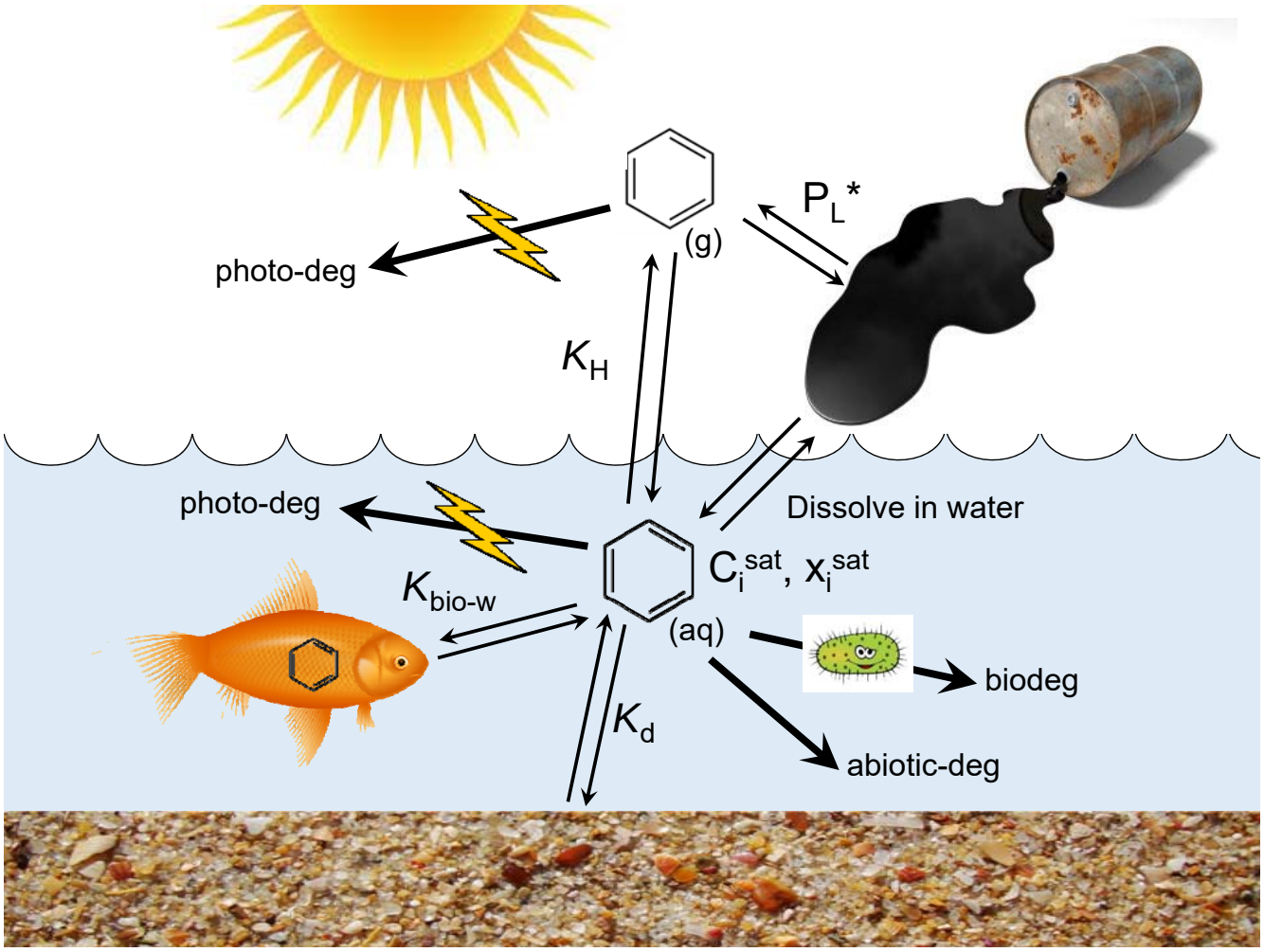
Biota-Water Partitioning

$K_{biota\text{-}w} = C_{biota}/C_w$ (mol kg_{bio}^{-1} mol^{-1} L_w)

- Varies with same factors as K_d (partitioning driven by hydrophobic affects)
- ↑ with ↑ lipid content of organism



- Predicting partitioning and speciation of organic chemicals
  - Vapor pressure (P_L)
  - Aqueous solubility (X_w^{sat}, C_w^{sat}) and activity coefficient (γ_w^{sat})
  - Henry's constant (H')
  - Octanol-water partition constant (K_{ow}) as a predictor of sorption to soil/sediment and bioconcentration



For this class, focus on methods for predicting important partitioning processes of different neutral organic molecules