Advanced Water Quality

Class 18:

Intro to Organic Chemicals

Review of Last Class – Metal Ion Chemistry: Coordination Chemistry and Precipitation

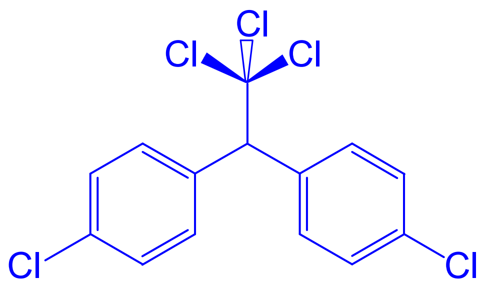
- Metal Ions (Lewis acids) and Ligands (Lewis bases)
- Different ways of representing metal complexation and metal ion hydrolysis equilibria
  - K_i, $^*K_i$, β_i, $^*\beta_i$
  - Solving for $[M^{n+}]$ as a master variable
- Metal precipitation
  - Hydr(oxide) solids
  - Other solids
  - Multiple solids
    - the one predicting the lower $[M^{n+}]$ will control solubility

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

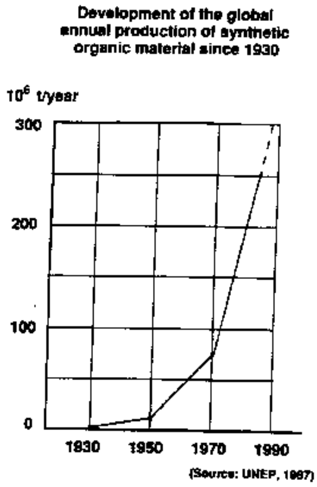
Organic Contaminants

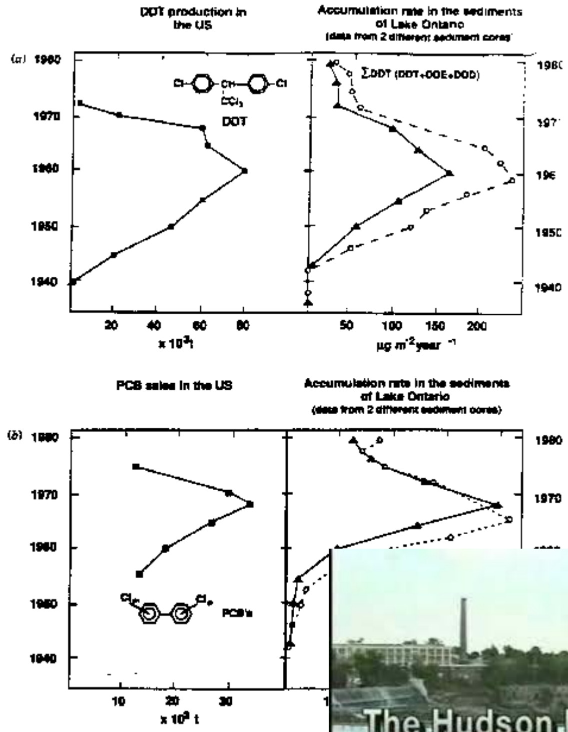
- Rachel Carson (1962)
  - ***Silent Spring***
  - DDT
  - world-wide distribution
  - accumulating in organisms



DDT: 2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane

Organic Contaminants





- Many organics disperse over large distances from origin
- Found in arctic wildlife
- Production continues to grow

Organic Contaminants

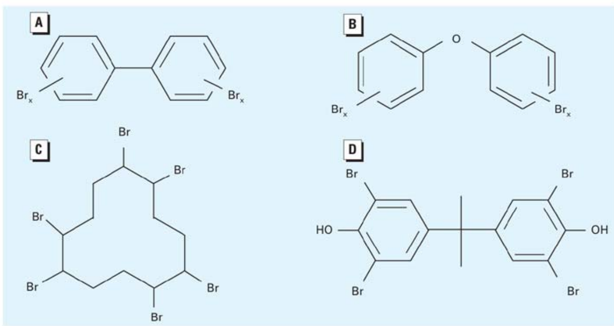
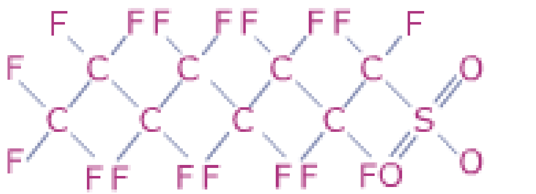


Figure 1. Chemical structures of (*A*) PBBs, (*B*) PBDEs, (*C*) HBCD, and (*D*) TBBPA.



PFOS (Perfluorooctane sulfonate)

$C_8F_{17}SO_3$

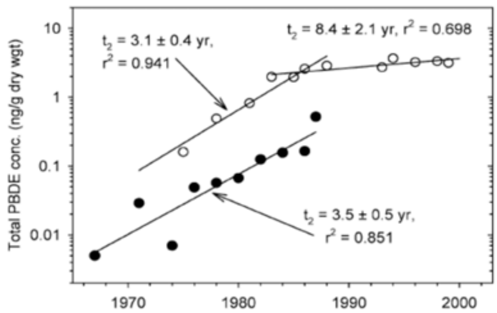


FIGURE 7. ΣPBDE concentrations in two sediment cores (in ng/g dry weight) shown as a function of depth in the core expressed as the year in which the sediment was deposited; see Table 8. The bottom line with filled symbols represents samples from the Baltic Sea (*18*), and the top line with open symbols represents data from Drammenfjord, Norway (*19*). Regressions for the two data sets are shown separately; the doubling times of the pre-1985 data sets are not significantly different.

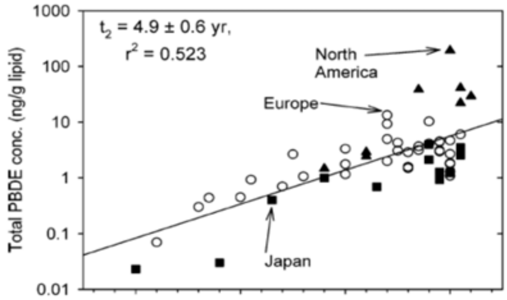


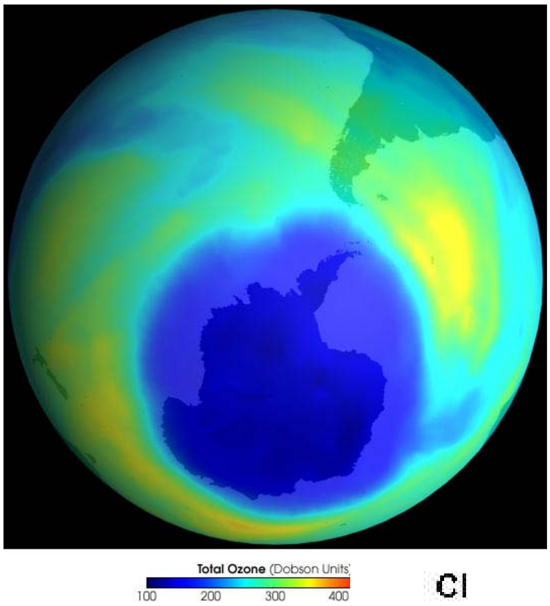
FIGURE 1. Total PBDE concentrations (ΣPBDE) in human blood, milk, and tissue (in ng/g lipid) shown as a function of the year in which the samples were taken; see Table 2. The three symbol types indicate the location from which the samples were collected. The overall regression is shown.

Hites (2004) ES&T 38, 945

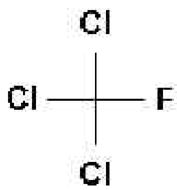
Organic Contaminants

- Love Canal (1978)
  - Hooker Chemical buried wastes in canal
  - residential construction on site
  - chlorinated hydrocarbons seeping into homes, schools
  - first large-scale EPA intervention
  - led to Superfund legislation

Organic Contaminants

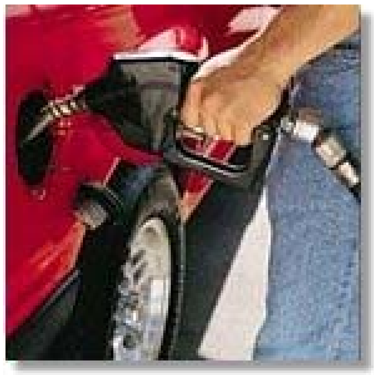


- **CFCs** (when good chemicals go bad!)
  - 1920s: Developed as safer refrigerant to NH_3, $Cl\text{-}CH_3$, SO_2
  - Also used as repellent in bug spray, hair spray, etc…
  - Inert in lower atmosphere

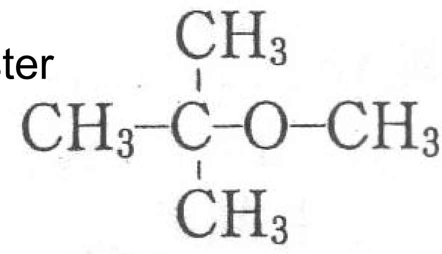


- 1974: Rowland & Molina show that CFCs destroyed in stratosphere by UV light, releasing inorganic chlorine
  - Awarded Nobel Prize in 1995
- 1 atom of chlorine catalytically destroys up to 100,000 atoms of ozone, which shields us from harmful UV-B radiation
- 1987: Montreal Protocol – treaty to reduce production of CFCs

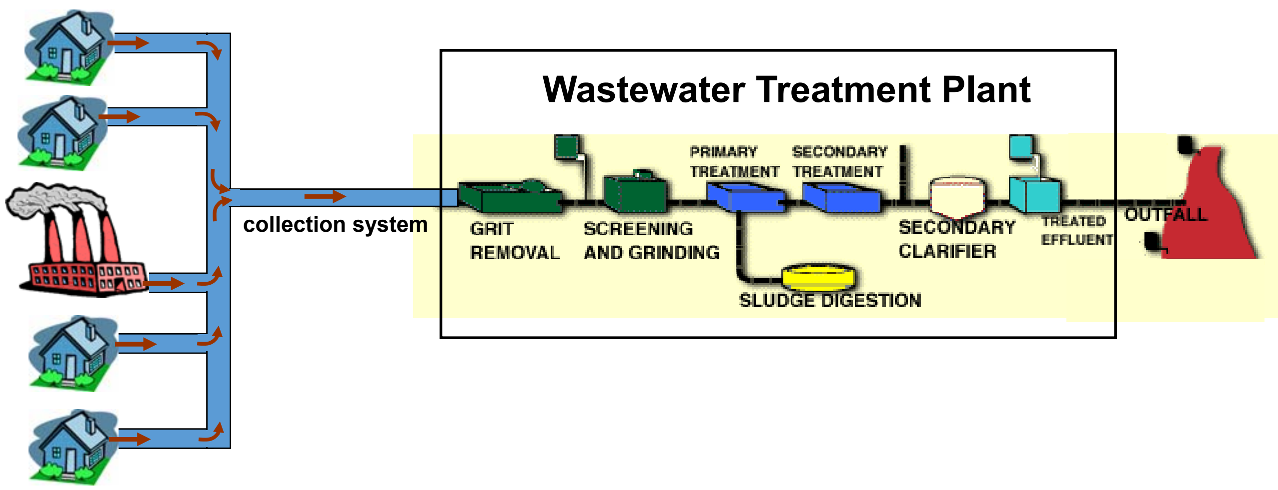
Organic Contaminants



- Reformulated Gasoline Program (1995)
- MTBE (An environmental solution?)
  - Oxygenate fuel additive improves combustion
  - Replacement for lead additives
  - 200,000 barrels per day produced
  - Reduces atmospheric concentrations of smog-forming chemicals
  - Widespread groundwater contamination
  - Very slow degradation
  - High water solubility, migrates faster than other gasoline components



Wastewater-Derived Micropollutants



- Many "emerging" organic micropollutants detected in municipal wastewater effluent
- Conventional treatment processes designed to remove SS, BOD, and sometimes pathogens and nutrients
  - *Not designed to address specific chemical micropollutants*

Wastewater-Derived Micropollutants

The New York Times
nytimes.com

March 10, 2008

Drug Traces Common in Drinking Water

By THE ASSOCIATED PRESS

Filed at 6:34 a.m. ET

A vast array of pharmaceuticals -- including antibiotics, anti-convulsants, mood stabilizers and sex hormone -- have been found in the drinking water supplies of at least 41 million Americans, an Associated Press investigation shows.

in source water but not in treated drinking water.
** Drinking water in Austin, Texas, was tested for only one prescription drug, a synthetic birth control chemical.

NOTE: All places include some surrounding areas except: Albuquerque, N.M.; Arlington, Texas; Long Beach, Calif.; Los Angeles; New Orleans.

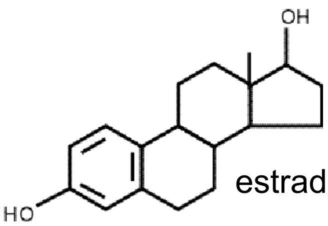
SOURCES: Drinking water providers' responses to Associated Press questions; AP review of scientific literature. AP

AP Associated Press

Source: http://www.msnbc.msn.com/id/26662637/ Sep.2008

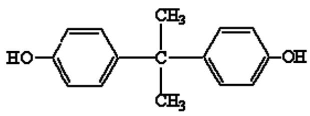
Organic Contaminants

- Endocrine disrupting compounds (EDCs):
  - ***natural or synthetic chemicals that interfere with or mimic the hormones responsible for growth and development of an organism***
  - ***Natural and synthetic steroid hormones have high EDC activity***



estradiol

  - ***Bisphenol-A is key intermediate in polymer production. Recent concerns about BPA leaching from Nalgene polycarbonate water bottles***

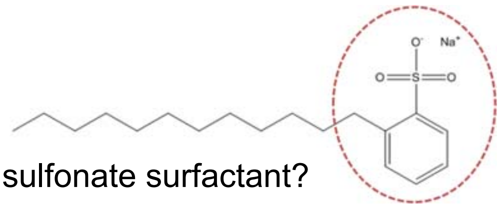


Bispenol-A (BPA)

Deepwater Horizon

- Gulf oil rig explosion in April 2010 resulted in continuous oil for >3 months
- Largest accidental marine spill in petroleum industry (53 – 62,000 barrels/day)
- Extensive damage to marine and wildlife habitats
- Also concerns about use of dispersants (e.g., Corexit EC9500A and 9527A)

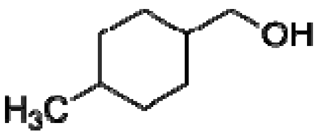
2-butoxyethanol



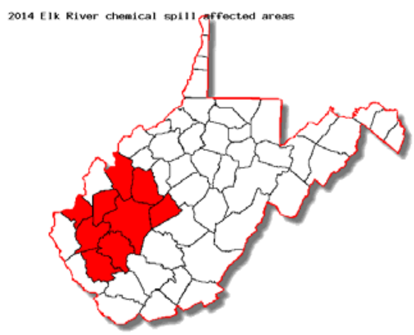
sulfonate surfactant?

Elk River Chemical Spill (WV)

- 7,500 GAL 4-methylcyclohexanemethanol (MCHM) released to Elk River on Jan 9, 2014



- Drinking water supply for 300,000 residents in Charleston, WV contaminated



The Denver Post

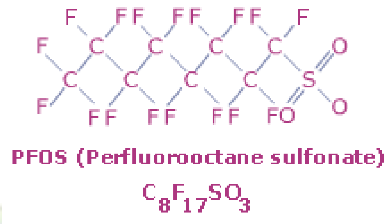
Water contamination issues grip Colorado Springs-area residents

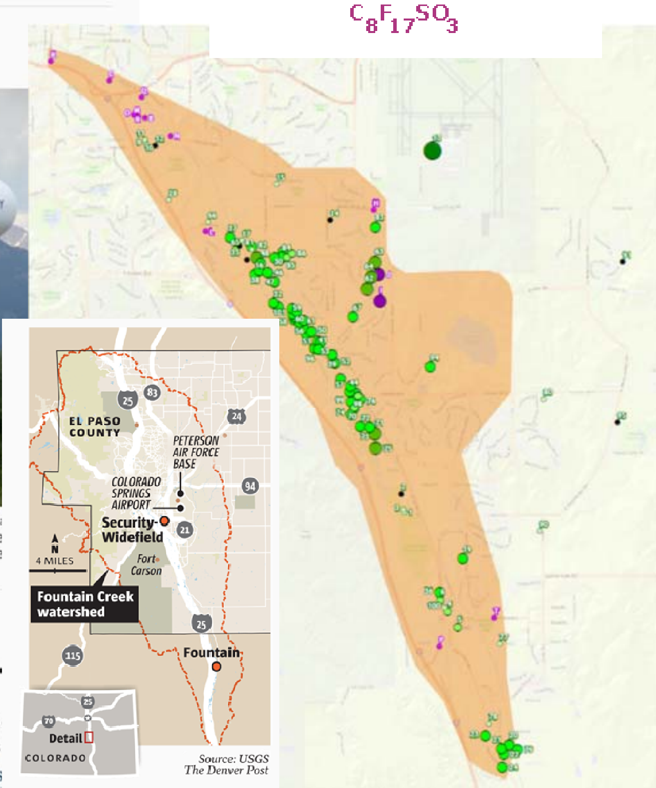
Meeting at high school addresses PFC levels in wells in Widefield, Security and Fountain

A water tower overlooks the community of Security in the foreground of Pike's Peak on June
invisible toxic chemical has been discovered in the drinking water that affects 70,000 people
communities south of Colorado Springs.

By BRUCE FINLEY | bfinley@denverpost.com
PUBLISHED: July 7, 2016 at 5:52 pm | UPDATED: July 8, 2016 at 2:39 pm

FOUNTAIN — More than 1,000 people south of Colorado Springs packed
school Thursday night and buffeted government officials with questions
concerns about an invisible toxic chemical contaminating public water s

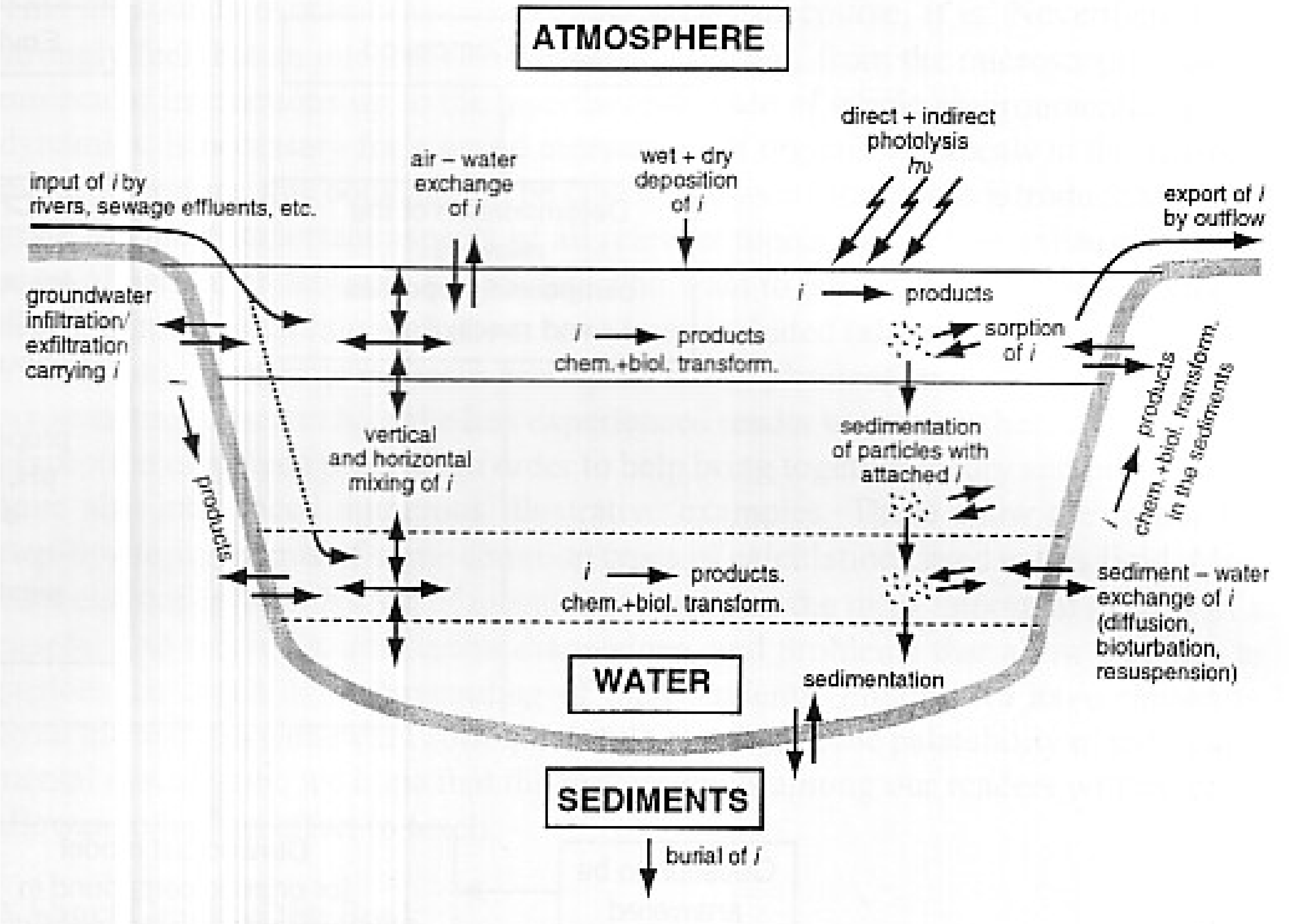




This week's objectives

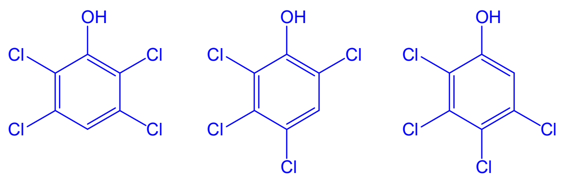
- ❑ Introduction to organic pollutants
- ❑ **Environmental fate governed by structural influence on interconnected processes**
- ❑ Organic chemical classification and nomenclature
- ❑ Important fate-controlling processes in aquatic systems

Organic chemical fate is controlled by interconnected processes



Organic chemical structure heavily influences each fate-controlling process

- Different structure causes different
  - toxicity
  - reactivity
  - Partitioning
  - persistence



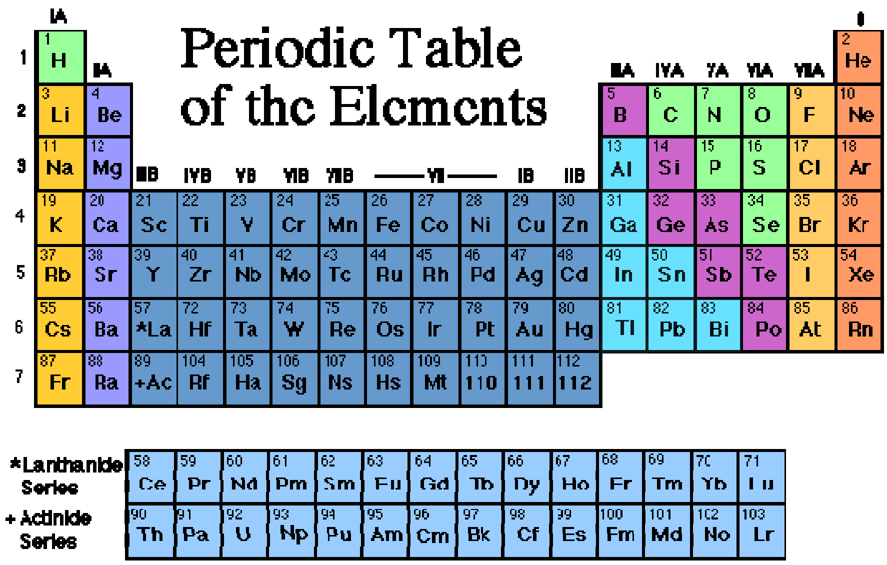
pK_a:	5.04	5.40	6.35
K_d:	10 L kg^{-1}	20 L kg^{-1}	180 L kg^{-1}

sorption to river sediments at pH 7

- Important properties of organic chemicals relevant to environmental fate
  - Formula, structure, and representation
  - Covalent bonding and filling the octet
  - Electronegativity
  - Oxidation State
  - Delocalized electrons

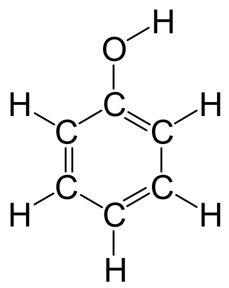
Organic Chemistry Review

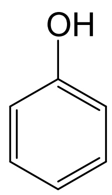
- What elements make up organic compounds?
  - C, H, O, N, S, P
  - Halogens: F, Cl, Br, I

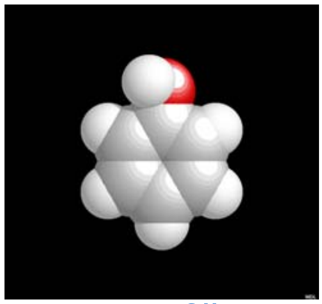


Formula and Structure

- What is the molecular formula of phenol?
  - C_6H_6O
- What is a structural formula of phenol?
  - C_6H_5OH
- What is the structure of phenol?

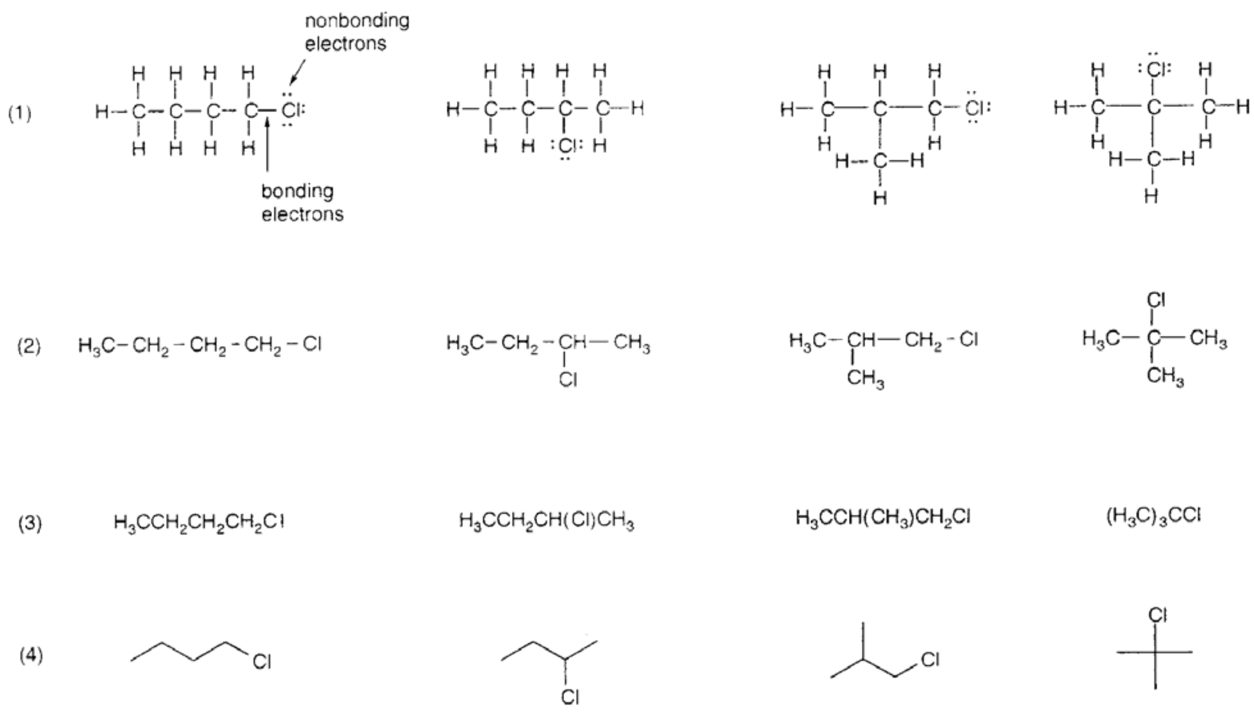






space-filling

Ways of representing organic structures

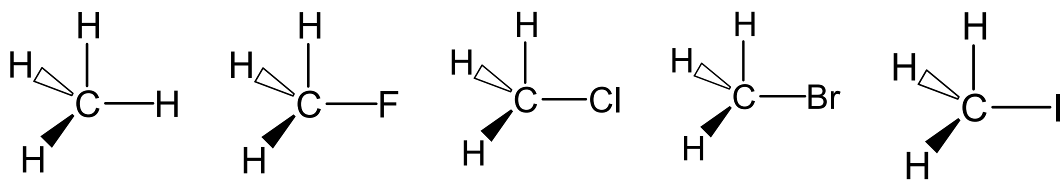


Organic chemical structures built by forming covalent bonds to fill the octet

- What is a covalent bond?
  - a sharing of a pair of electrons between two elements in a molecule – by sharing the e-, both contributing atoms can fulfill their octet
  - single, double, triple covalent bonds
  - Bond strengths: hundreds kJ mol^{-1}
- Missing electrons in outer (valence) shell?
  - H: 1 (of 2 in K), F: 1 (of 8 in L), Cl: 1 (of 8 in M), …
  - C: 4 (of 8 in L)
  - N: 3 (of 8 in L), P: 3 (of 8 in M)
  - O: 2 (of 8 in L), S: 2 (of 8 in M)

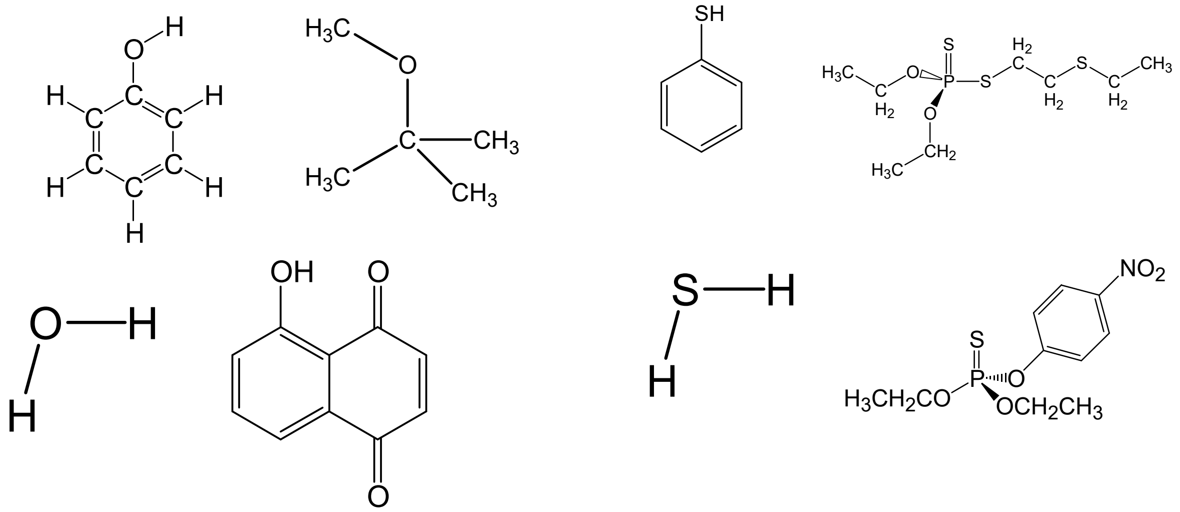
Covalent Bonds

- Which element(s) form monovalent bonds?
  - H, F, Cl, Br, I
  - missing 1 electron in outer shell



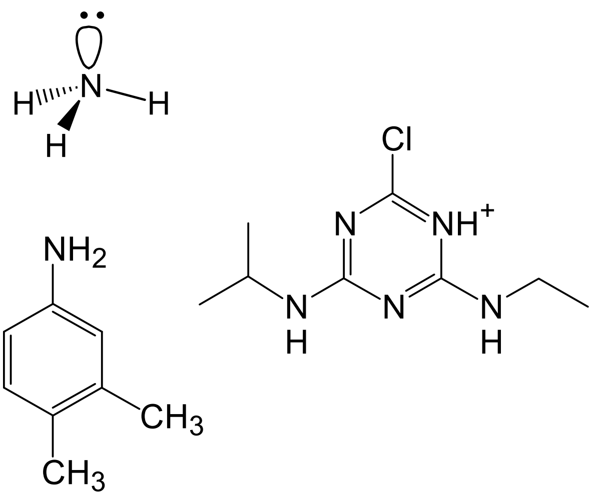
Covalent Bonds

- Which element(s) form 2 covalent bonds?
  - O, S (in the –II oxidation state)
  - missing 2 electrons in outer shell



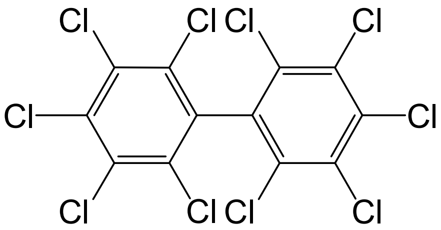
Covalent Bonds

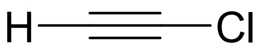
- Which element(s) form 3 covalent bonds?
  - N (in the –III oxidation state)
  - Missing 3 electrons in the outer shell

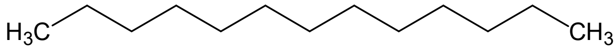


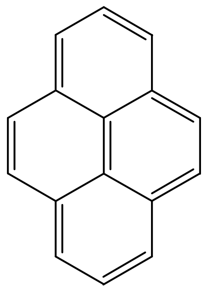
Covalent Bonds

- Which element(s) form 4 covalent bonds?
  - C (missing 4 electrons in outer shell)



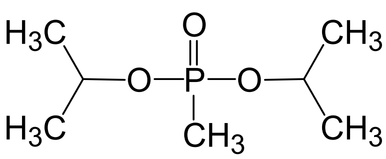


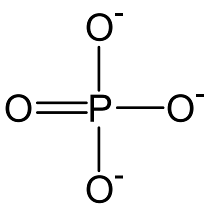


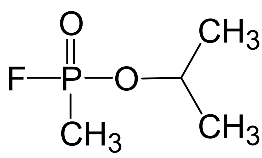


Five Covalent Bonds

- Which element(s) form pentavalent bonds?
  - P (in the +V oxidation state)
  - missing 5 electrons in the outer shell

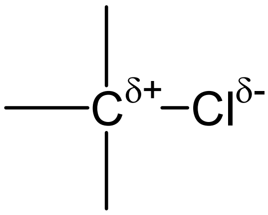


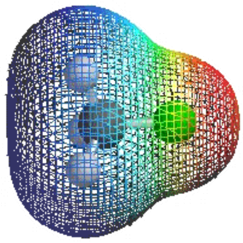




Electronegativity

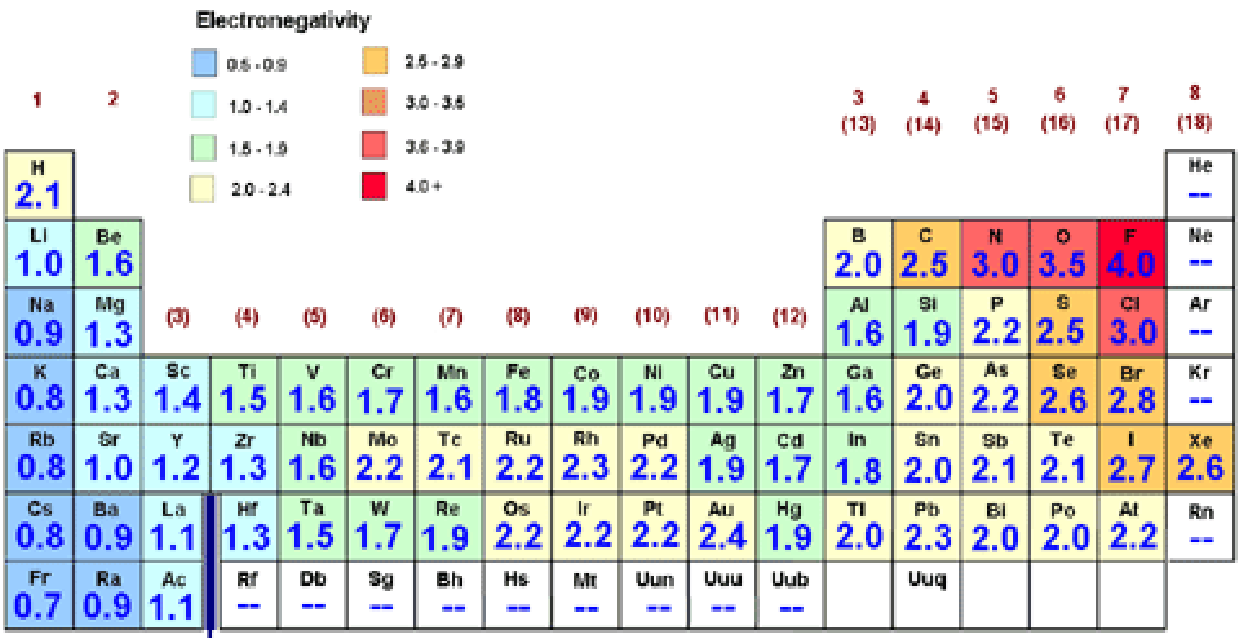
- How does electronegativity affect covalent bonding?
  - The "electron cloud," or average electron position, between the two atoms is shifted toward the atom that more strongly attracts electrons



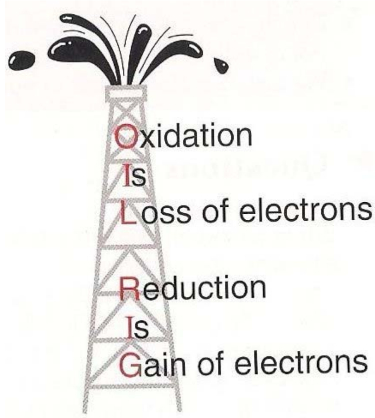


  - Carbon bonding with elements of greater polarity introduces permanent dipoles and increases compound polarity
    - Increased aqueous solubility, interaction with charged species (dissolved metals, surfaces)

Electronegativity



Oxidation State



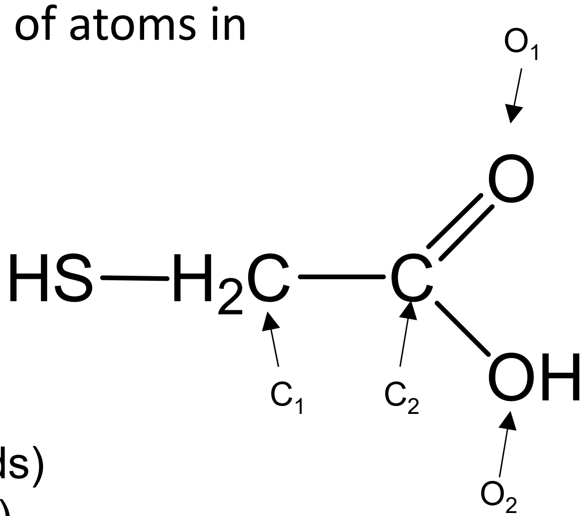
- **Oxidation-Reduction Rxns:** e^- transfer
- **Formal oxidation state** = (protons – electrons assigned)
- **Reduction:** formal oxidation state is "reduced"
- **Oxidation:** formal oxidation state is increased

Rules for Assigning Oxidation State

- 0 = oxidation state of uncharged element
- Oxidation state of monoatomic ion = charge
- Atoms within polyatomic mCs or ions:
  - Give electrons to more electronegative element in covalent bond
  - Add 0 for every bond to same element (e.g., C-C bond)
  - Add -1 for every bond to a less electronegative element
  - Add +1 for every bond to a more electronegative element
  - Add any formal charges localized to that element
  - Note: in C-S, C-I, C-P bonds, assign electrons to the heteroatom

Oxidation State

- What is the oxidation state of atoms in mercaptoacetic acid?



Hydrogens
+1 (H-X bond)
+1

Sulfur
-1 (S-H bond)
-1 (S-C bond)
-2

Carbon 1
0 (C-C bond)
-1 x 2 (C-H bonds)
+1 (C-S bond)
-1

Carbon 2
0 (C-C bond)
+2 (C=O bonds)
+1 (C-O bond)
+3

Oxygen 1
-2 (O=C bond)
-2

Oxygen 2
-1 (O-C bond)
-1 (O-H bond)
-2

Oxidation State

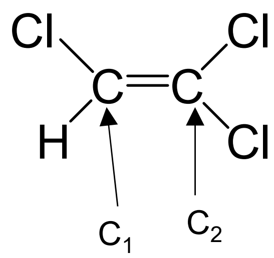
- What is the average oxidation state of atoms in trichloroethylene?

Hydrogen
+1 (H-X bond)
+1

Chlorine
-1 (Cl-C bond)
-1

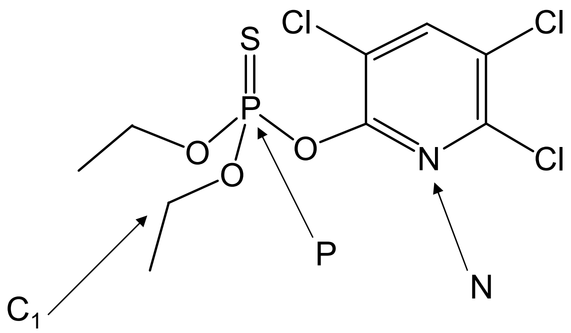
Carbon 1
0 (C=C bond)
+1 (C-Cl bond)
-1 (C-H bond)
0

Carbon 2
0 (C=C bond)
+1 x 2 (C-Cl bonds)
+2

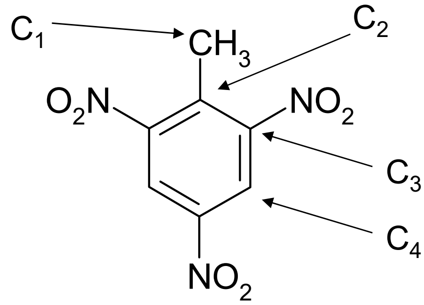


C_2 is more oxidized than C_1: Which will be site of attack by reducing agent?

chlorpyrifos

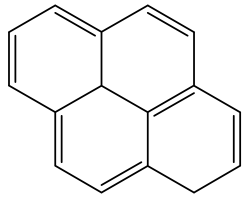


TNT (explosive)

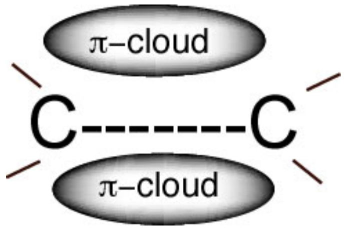


Delocalized Electrons

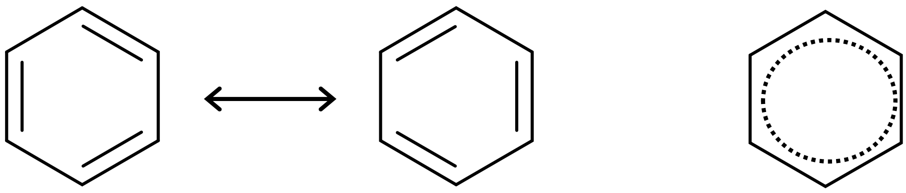
•Do delocalized electrons make a compound more or less stable?



- Delocalized electrons = double, triple bonds = stronger bonds
- Restraints on electron positions diminished, energy levels are lowered, increased stability.
- Resonance of delocalized electrons
  - Conjugated π-bond systems
  - Aromatic systems Non-bonded electrons and π-bond system

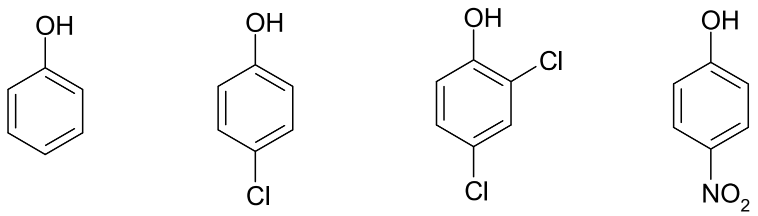


Aromaticity – conjugated db ring systems



Functional Groups “withdraw” and “donate” electron density to core structure

- Some functional groups withdraw electron density from structure

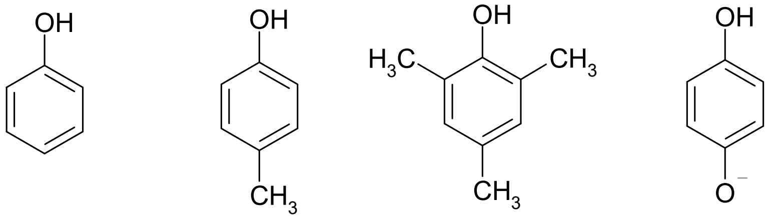


pKa *9.95* *9.29* *7.85* *8.36*

  - Stabilizes negatively charged species (lowers acidic pK_a)
  - Affects other properties like tendency to be oxidized or reduced

Functional Groups “withdraw” and “donate” electron density to core structure

- Some functional groups donate electron density from structure

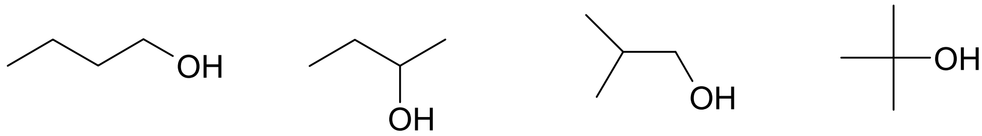


pKa *9.95* *10.25* *10.9* *11.40 (pK_{a2})*

  - Destabilizes negatively charged species (raises pK_a)

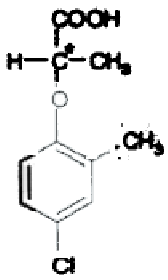
- **Isomers**: compounds with the same molecular formula, but different spatial arrangement

$C_4H_{10}O$:



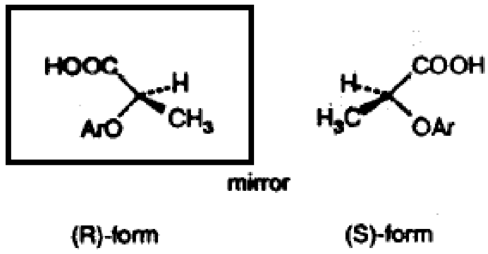
1-butanol (n-butanol) | 2-butanol | isobutanol | *t*-butanol

- **Stereoisomers**: same connectivity, but different spatial arrangement



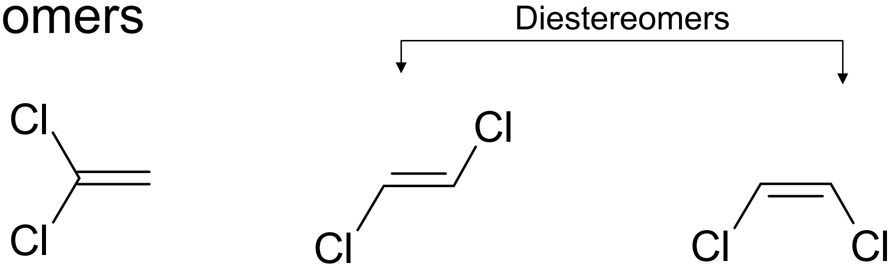
mecoprop

active herbicide



Enantiomers: chiral mirror-image isomers

Dichloroethene Isomers



	1,1-DCE	trans-DCE	cis-DCE
Bp (°C)	32	49	61
C_w^{sat} (mM)	26	65	52
K_{aw}	1.1	0.35	0.16
K_{ow}	30	123	72

$K_{aw} = C_{air}/C_{water}$ $K_{ow} = C_{octanol}/C_{water}$