Organic Contaminants in the Marine Environment

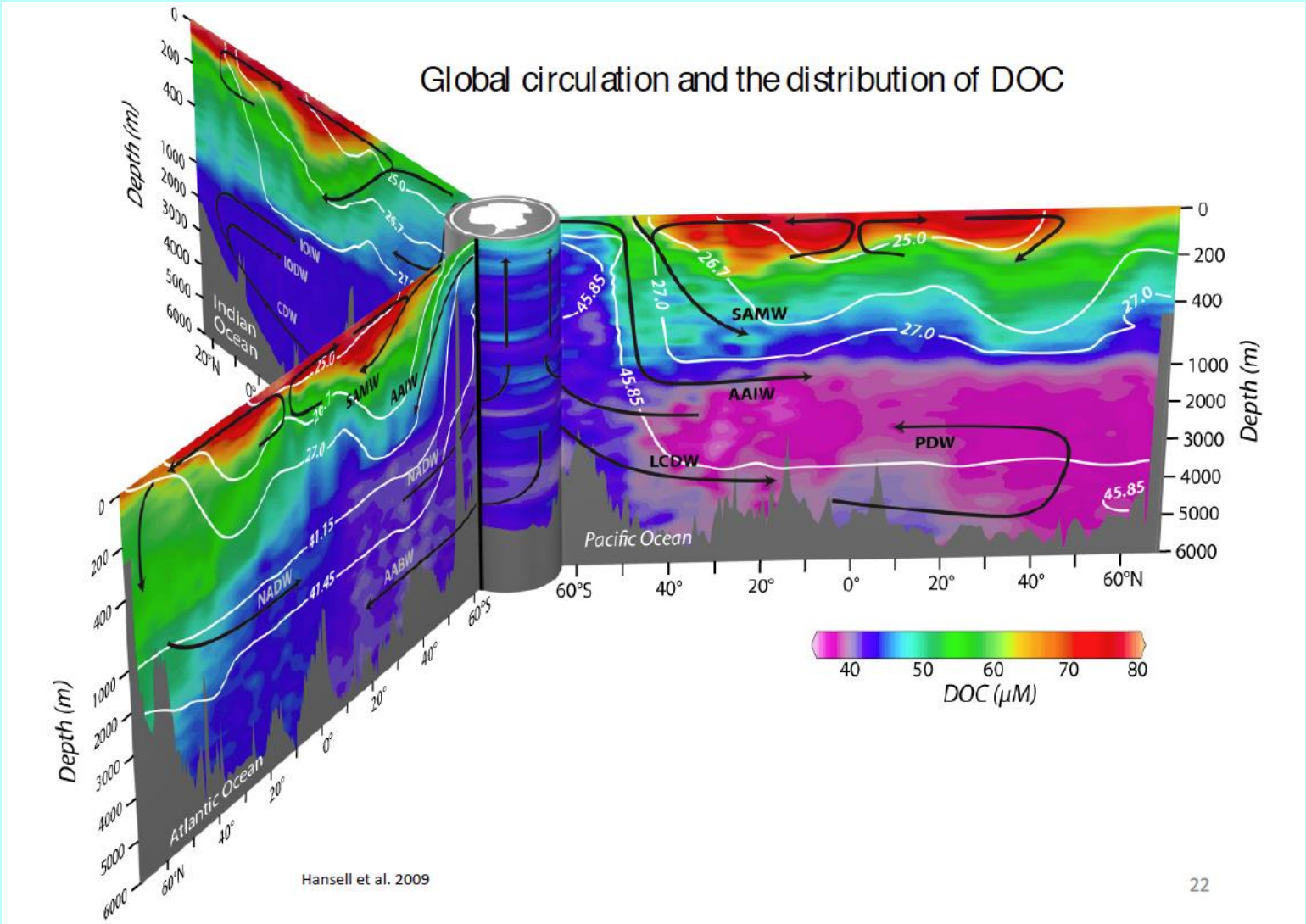
26 August 2015

Regional Maritime University

Overview

- Marine Dissolved Organic Matter
- Structure of Organic Molecules
- Phase Partitioning
- Molecular Transformations
- Case Study: Estrogens in Wastewater

Global Distributions of Dissolved Organic Carbon

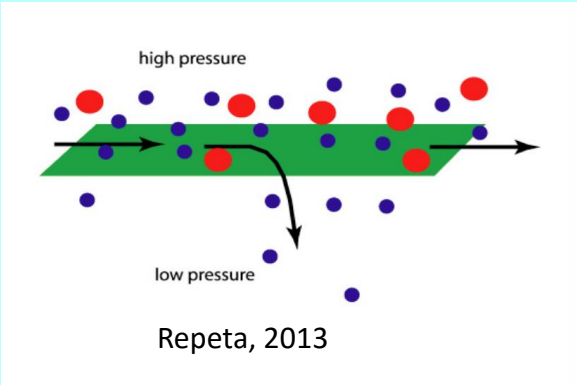


Hansell et al. 2009

Marine Organic Matter

- Operationally defined:
  - High molecular weight organic matter
  - Low molecular weight organic matter

- Ultrafiltration (> 1000 Da)



Repeta, 2013

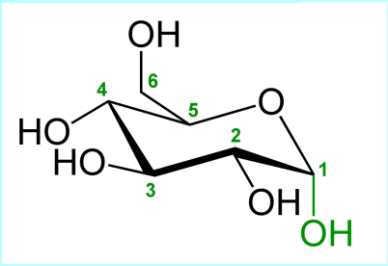
- Solid phase extraction

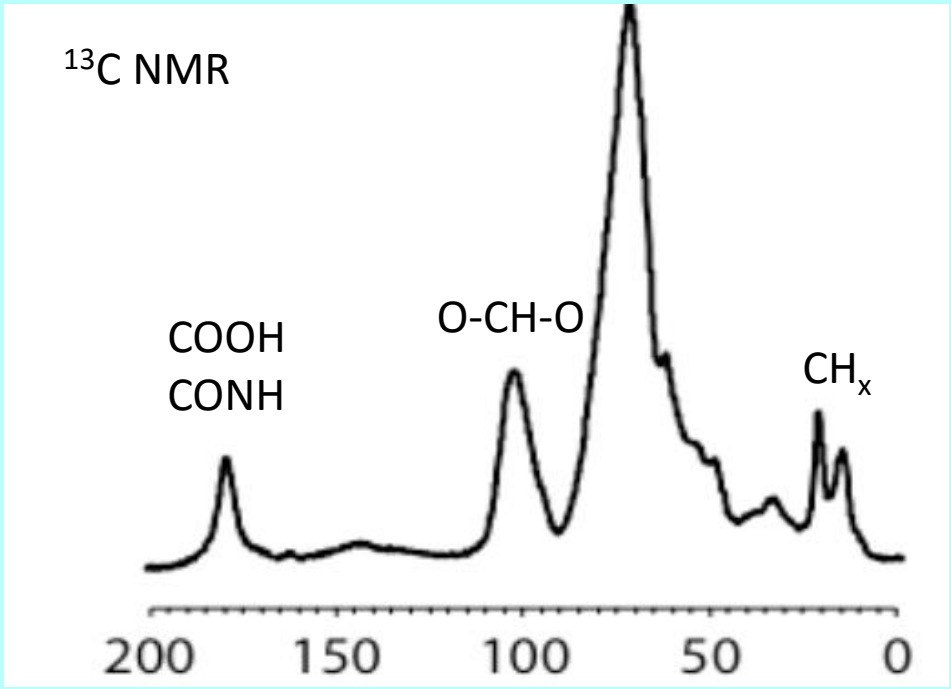
(< 1000 Da)

High Molecular Weight Organic Matter Composition

Surface, North Pacific Subtropical Gyre

Carboydrate Example:
Glucose



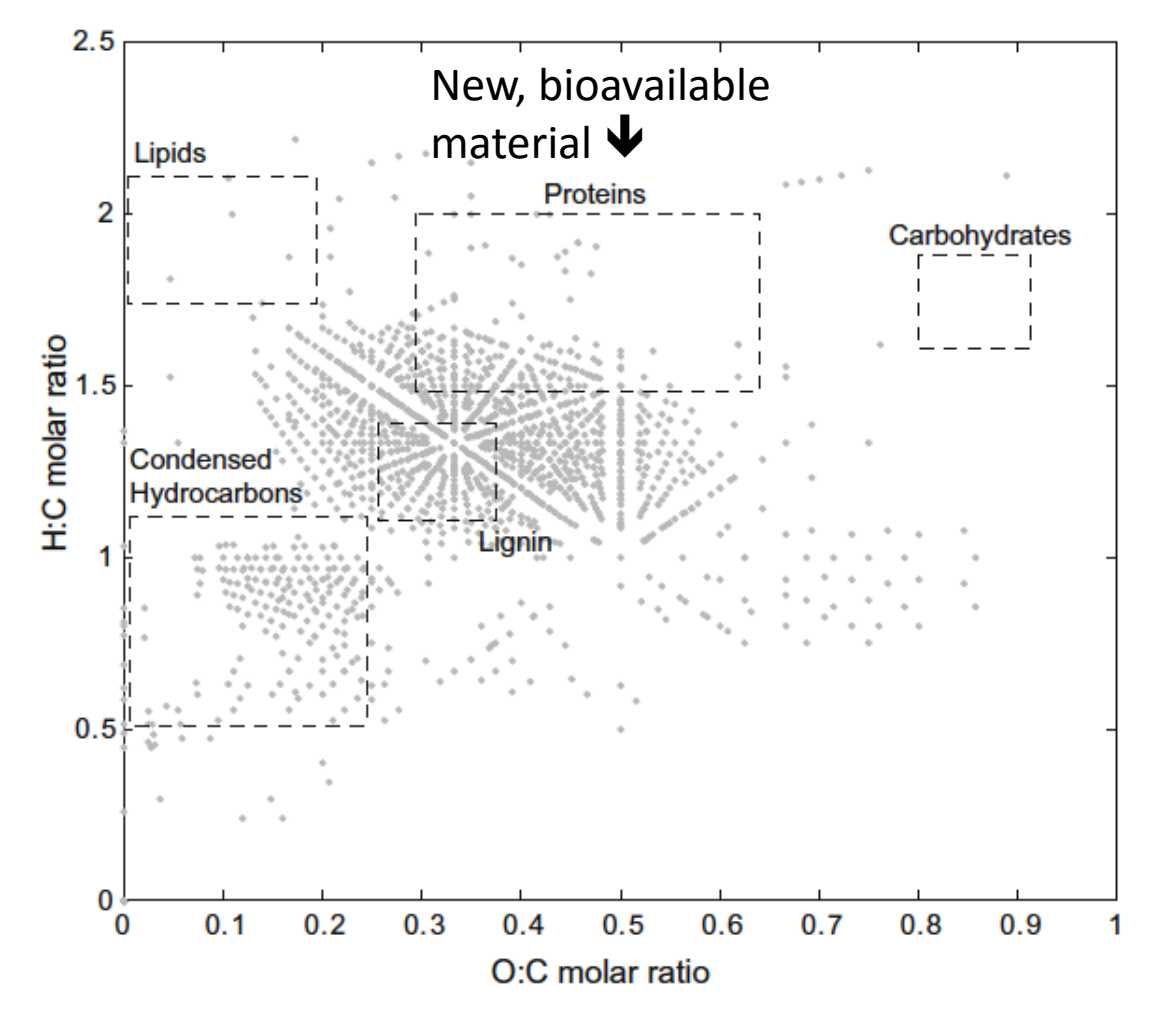


Major peaks are from carbohydrate functional groups (70-90%)

Repeta, 2013

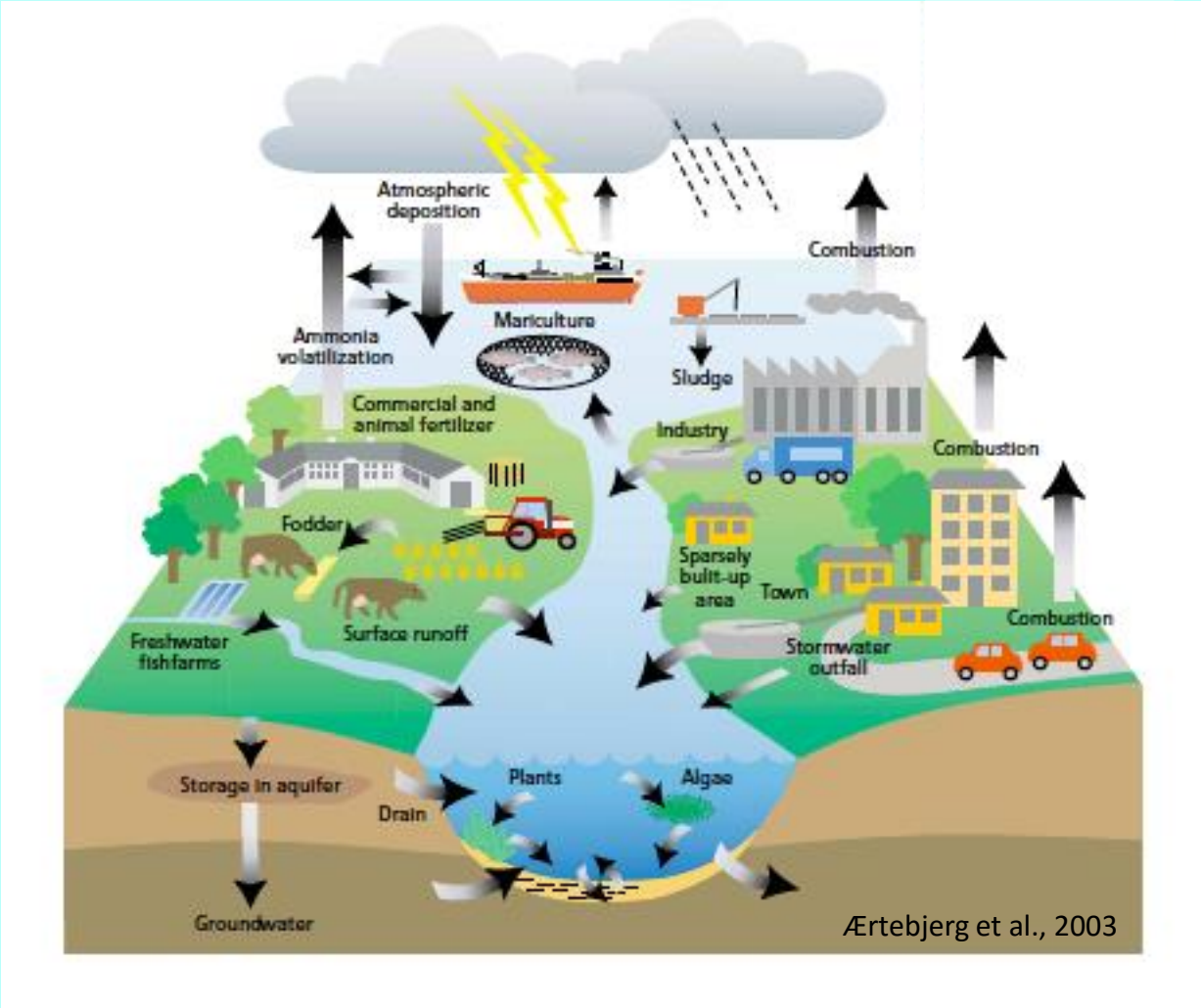
Low Molecular Weight Organic Matter Composition

Old, refractory material ➔

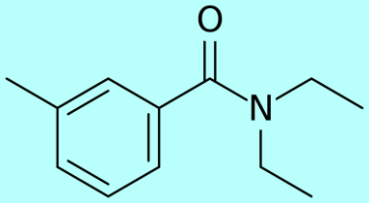


Kujawinski et al., 2009

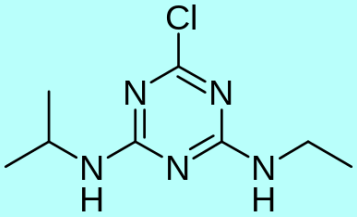
Sources of Contamination



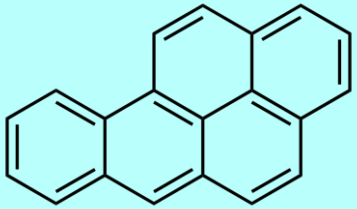
Organic Pollutants



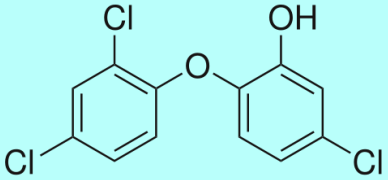
DEET
Insect repellent



Atrazine
herbicide

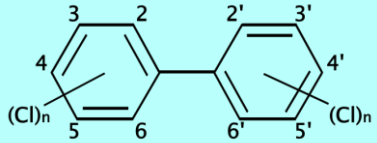


Polycyclic Aromatic
Hydrocarbons (PAHs)
Oil or incomplete combustion



Triclosan
Anti-bacterial

Lindane
pesticide

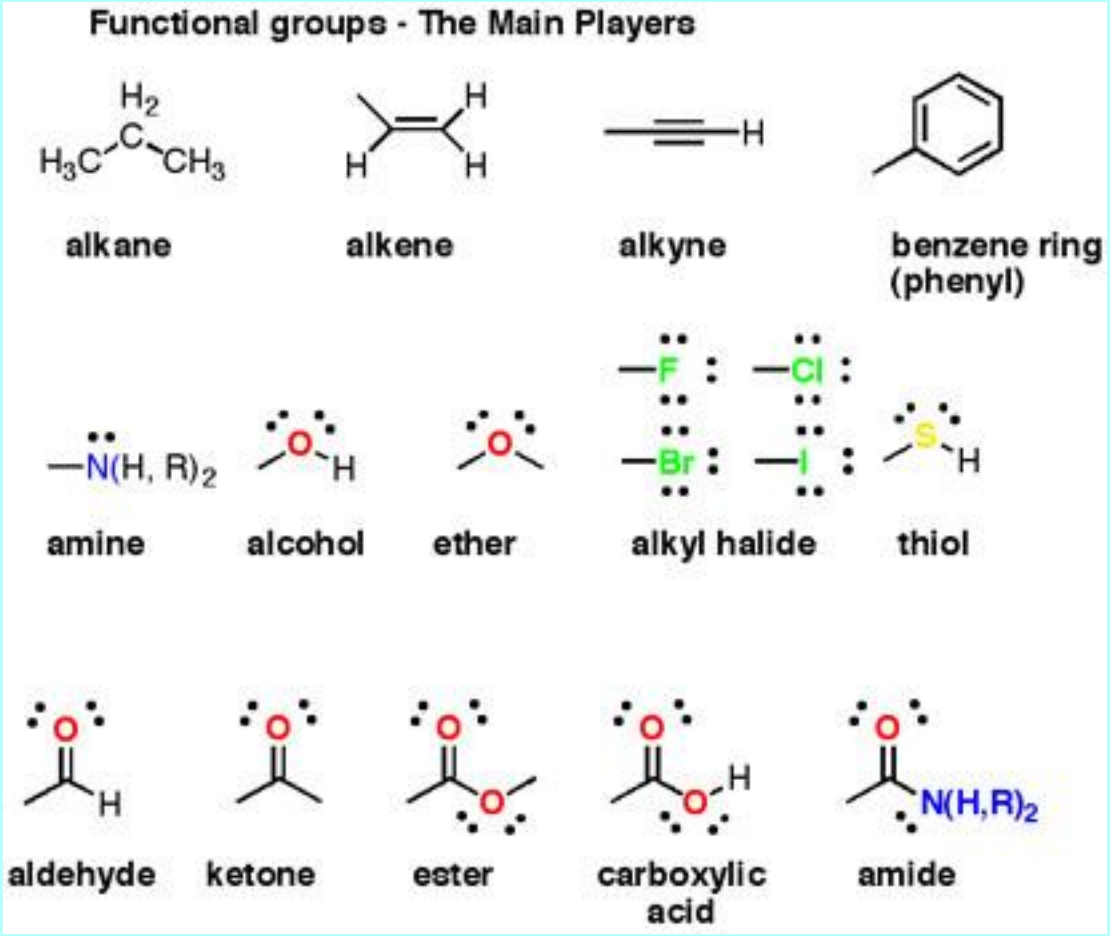


Polychlorinated biphenyls (PCBs)
Various industrial applications

Partitioning between Phases

Molecular Transformations

Structure: Functional Groups

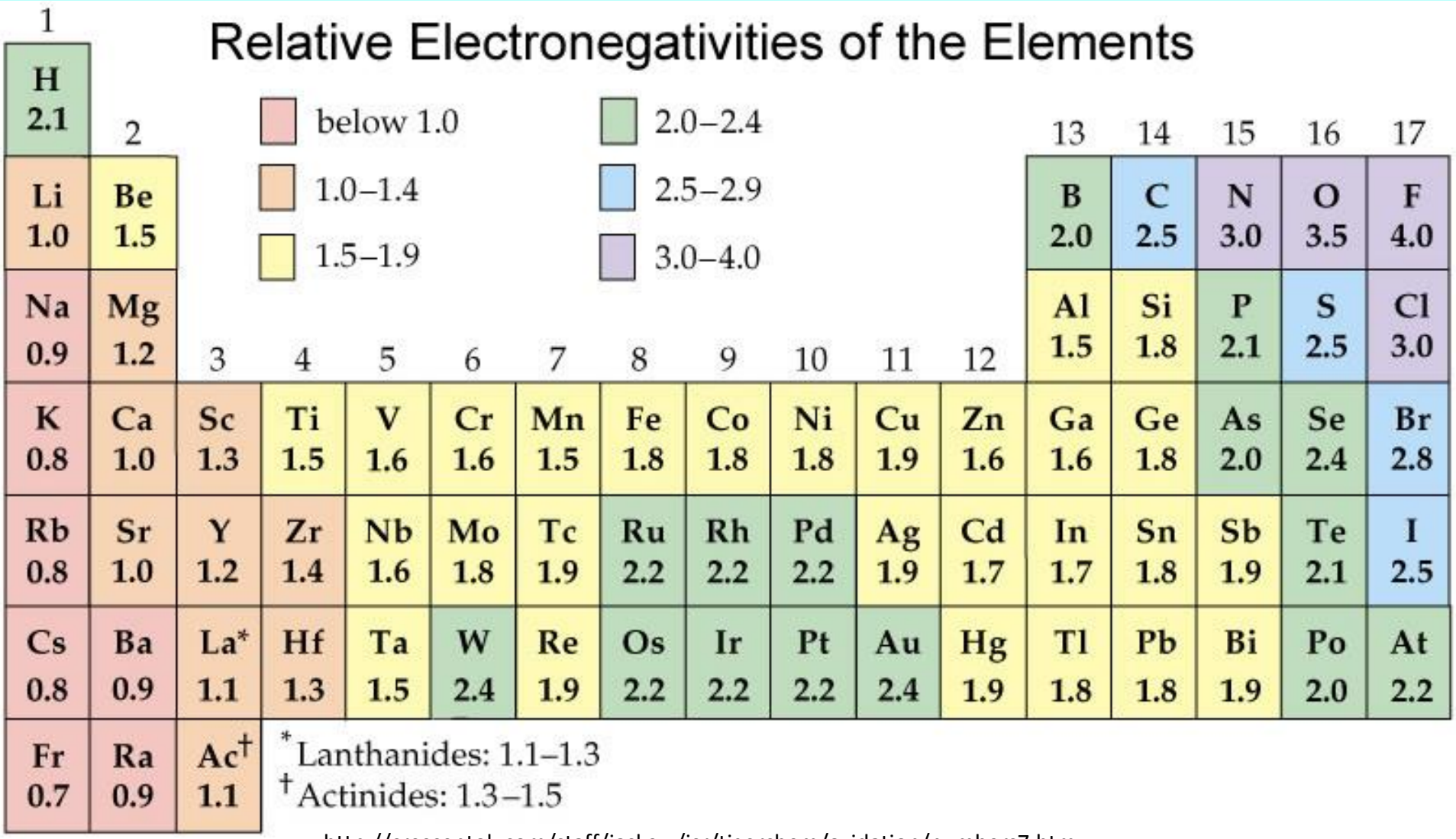


http://www.masterorganicchemistry.com/2010/10/06/functional-groups-organic-chemistry/

Some Structural Considerations

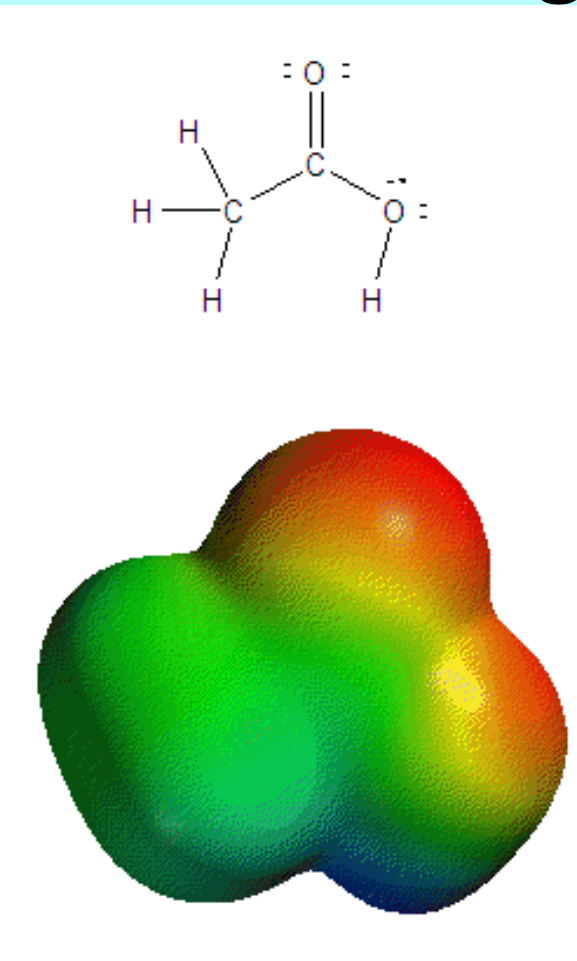
- Electronegativity / Polarity
- Spatial Arrangement
- Delocalized Electrons (aromaticity, resonance)

Electronegativity

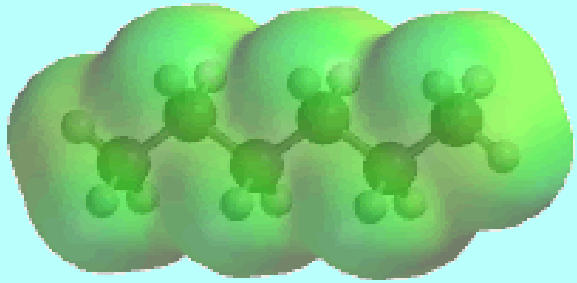


http://crescentok.com/staff/jaskew/isr/tigerchem/oxidation/numbers7.htm

Polarity of Molecules Dictated by Electronegativity of Atoms



Acetic Acid

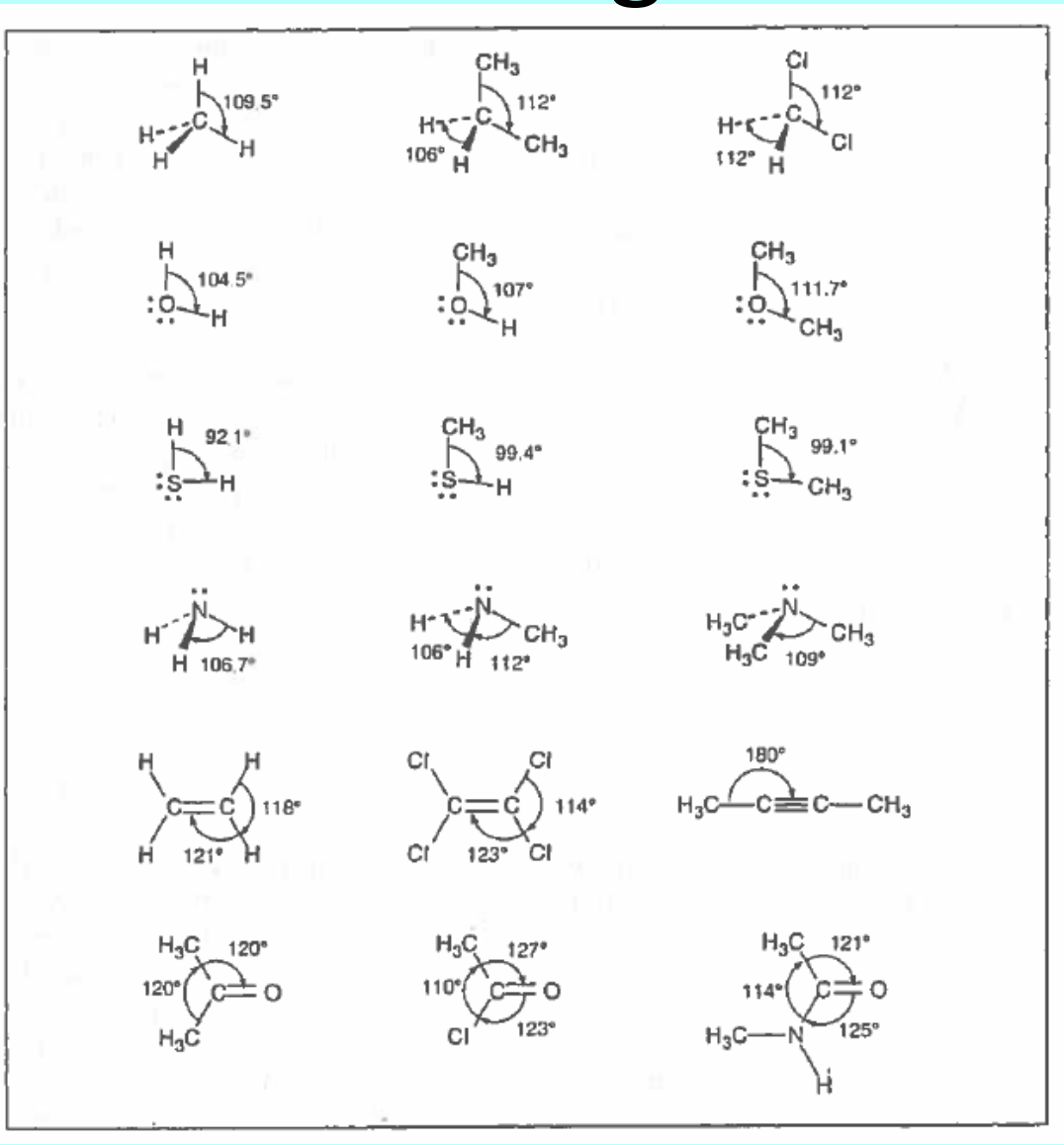


Hexane

http://employees.csbsju.edu/HJAKUBOWSKI/classes/Chem%20and%20Society/Bonding/olbonding.htm

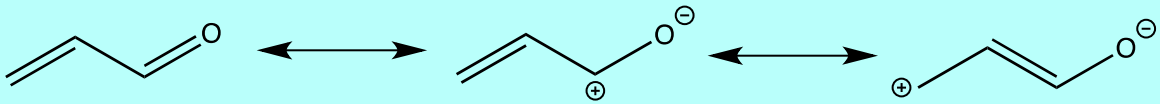
http://www.bestchoice.net.nz/chemistry/913/p14418.htm

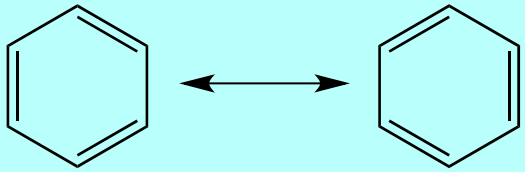
Steric Arrangement



Schwarzenbach, Gschwend, Imboden, 2003

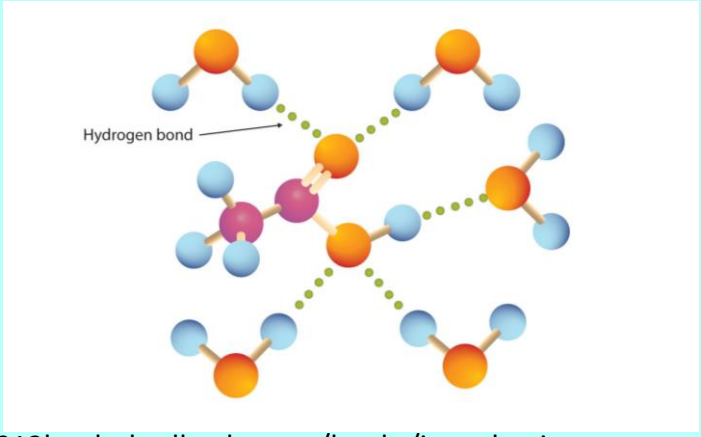
Delocalized Electrons



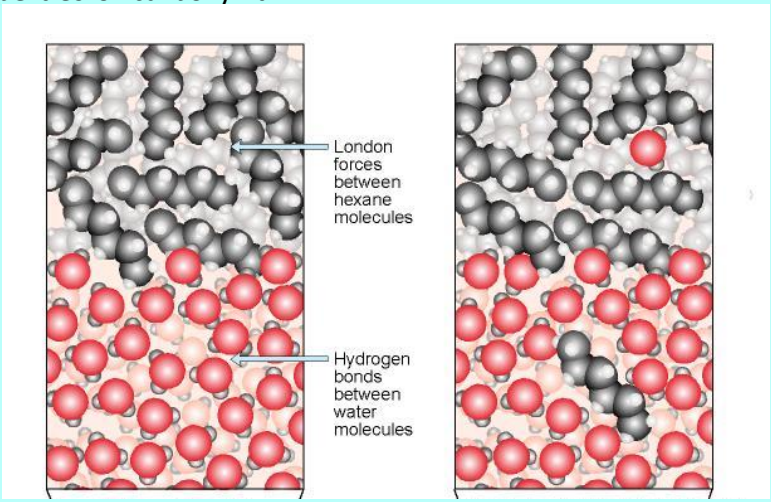


Types of Interactions

- Dipole-induced dipole forces
- Dipole-dipole forces
- H-bonding (electron donor-acceptor interaction)



http://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/s18-04-physical-properties-of-carboxy.html



http://www.chem.fsu.edu/chemlab/chm1046course/solnprocess.html

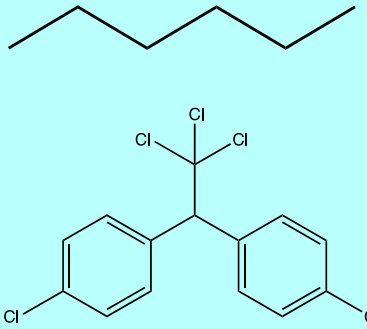
Partitioning

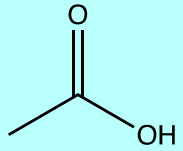
- air-water
- octanol-water
- organic matter-water
- lipid-water

Octanol-Water Partitioning

$$K_{ow} = C_{io} / C_{iw}$$

Set of Compounds	log K_{iow} range [c]
Alkanes	3.0 to 6.3
Alkylbenzenes	2.1 to 5.5
Polycyclic aromatic hydrocarbons	3.3 to 6.3
Chlorobenzenes	2.9 to 5.8
Polychlorinated biphenyls	4.0 to 8.0
Polychlorinated dibenzodioxins	4.3 to 8.0
Phthalates	1.5 to 7.5
Aliphatic esters (RCOOR')	–0.3 to 2.8
Aliphatic ethers (R–O–R')	0.9 to 3.2
Aliphatic ketones (RCOR')	–0.2 to 3.1
Aliphatic amines (R—NH_2, R–NHR')	–0.4 to 2.8
Aliphatic alcohols (R–OH)	–0.7 to 3.7
Aliphatic carboxylic acids (R–COOH)	–0.2 to 1.9





Schwarzenbach, Gschwend, Imboden, 2003

Estimating K_{ow}

$$\log K_{ow} = \underbrace{\Sigma n_k * f_k}_{\text{fragments}} + \underbrace{\Sigma n_j * c_j}_{\text{corrections}} + 0.23$$

$$\log K_{ow} = \log K_{ow}\,(\text{related compound}) \underbrace{- \Sigma n_k * f_k + \Sigma n_k * f_k}_{\text{fragments}} \underbrace{- \Sigma n_j * c_j + \Sigma n_j * c_j}_{\text{corrections}}$$

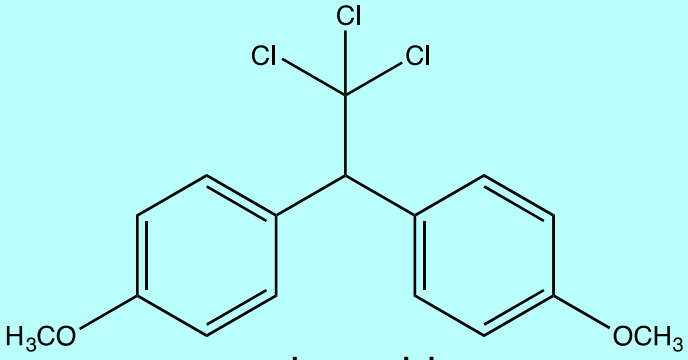
removed added removed added

Atom/Fragment	f_k
Carbon	
$-CH_3$	0.55
$-CH_2-$	0.49
$-CH<$	0.36
$>C<$	0.27
$=CH_2$	0.52
$=CH-$ or $=C<$	0.38
C_{ar}	0.29

Aliphatic Oxygen	
al–O–al	–1.26
al–O–ar	–0.47
ar–O–ar	0.29
al–OH	–1.41
ol–OH	–0.89
ar–OH	–0.48
al–O–(P)	–0.02
ar–O–(P)	0.53

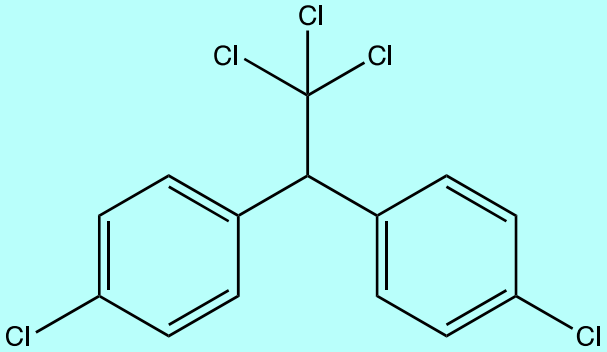
Schwarzenbach, Gschwend, Imboden, 2003

Estimating K_{ow} Example



methoxychlor

K_{ow} = 5.08



DDT

	Fragment	f_k	x	n_k	=	Value
Starting	K_{ow}					5.08
Remove	$-CH_3$	0.55		2		-1.10
	al-O-ar	-0.47		2		0.94
Add	ar-Cl	0.64		2		1.28
					log K_{ow} (est.)	6.20
					(exp.)	6.20

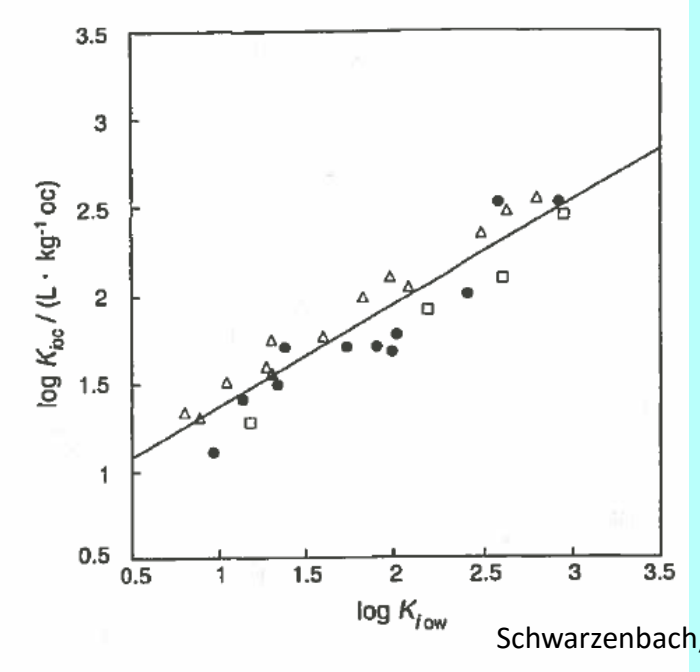
Schwarzenbach, Gschwend, Imboden, 2003

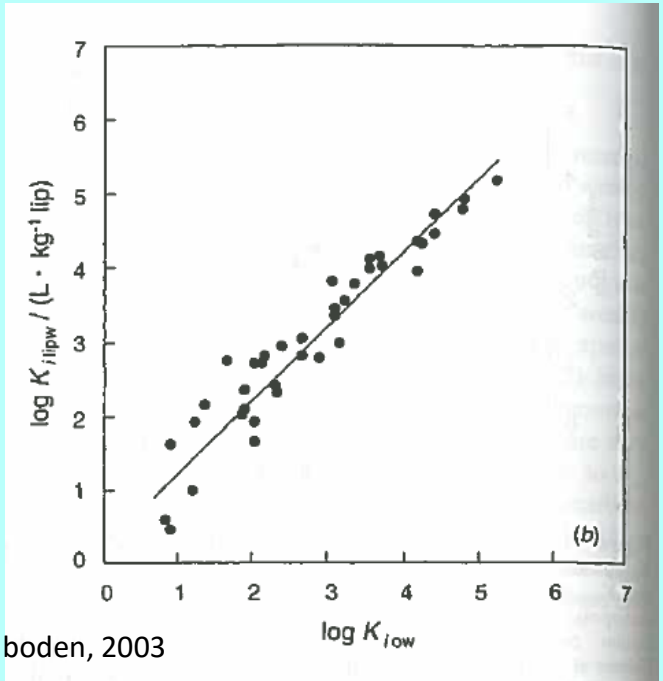
Predict Other Phase Partitioning from K_{ow}

$\log K_{ow}$

$\log K_{oc} = a*\log K_{ow} + b$

$\log K_{lipw} = 0.91*\log K_{ow} + 0.50$





Schwarzenbach, Gschwend, Imboden, 2003

Oil Partitioning is Complex

Analyte	MW-1 content
Gas[†]	
Methane	82.5% ($\delta^{13}C = -57.5‰$; $\delta D = -187‰$)
Ethane	8.3% ($\delta^{13}C = -31.5‰$; $\delta D = -147‰$)
Propane	5.3% ($\delta^{13}C = -29.2‰$; $\delta D = -123‰$)
Isobutane	0.97% ($\delta^{13}C = -29.9‰$)
n-butane	1.9% ($\delta^{13}C = -27.9‰$; $\delta D = -119‰$)
Isopentane	0.52%
n-pentane	0.52%
Methane/ethane	9.9
Methane/propane	15.5
GOR (measured)	1,600 standard cubic feet per barrel
GOR (estimated)	1,730 standard cubic feet per barrel [§]
GOR	
Oil (select properties) [‖]	
Density	820 g L^{-1}
Gravity	40° API
Carbon	86.6%
Hydrogen	12.6%
Nitrogen	0.38%
Sulfur	0.39%
Saturated hydrocarbons	74% ($\delta^{13}C = -27.9‰$)
Aromatic hydrocarbons	16% ($\delta^{13}C = -26.5‰$)
Polar hydrocarbons	10%

Reddy et al., 2011

Chemical Transformations

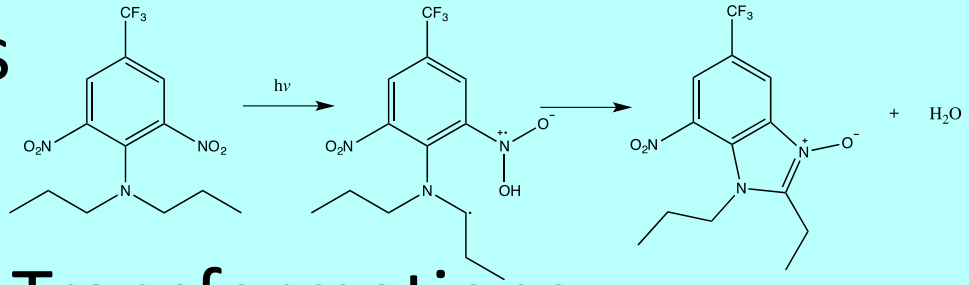
- Hydrolysis

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COO^- + HOCH_2CH_3 + H^+$$

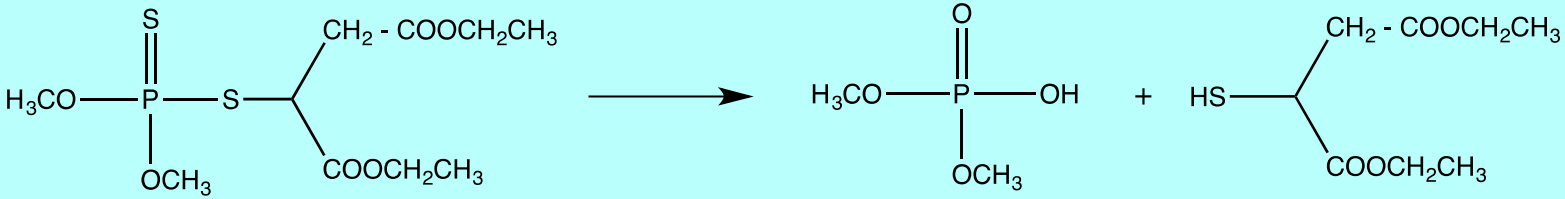
- Redox Reactions

$$R\text{-}COOH + 2\ H^+ + 2\ e^- \leftrightarrow R\text{-}CHO + H_2O$$

- Photolysis



- Biological Transformations

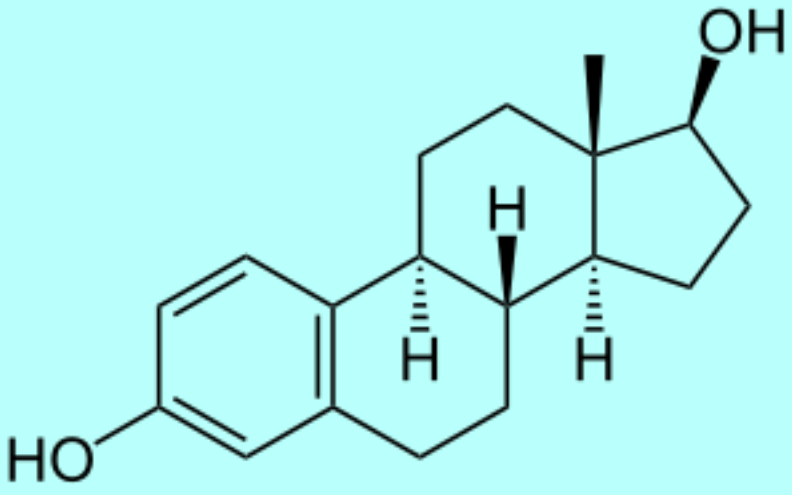


Malathion (insecticide)

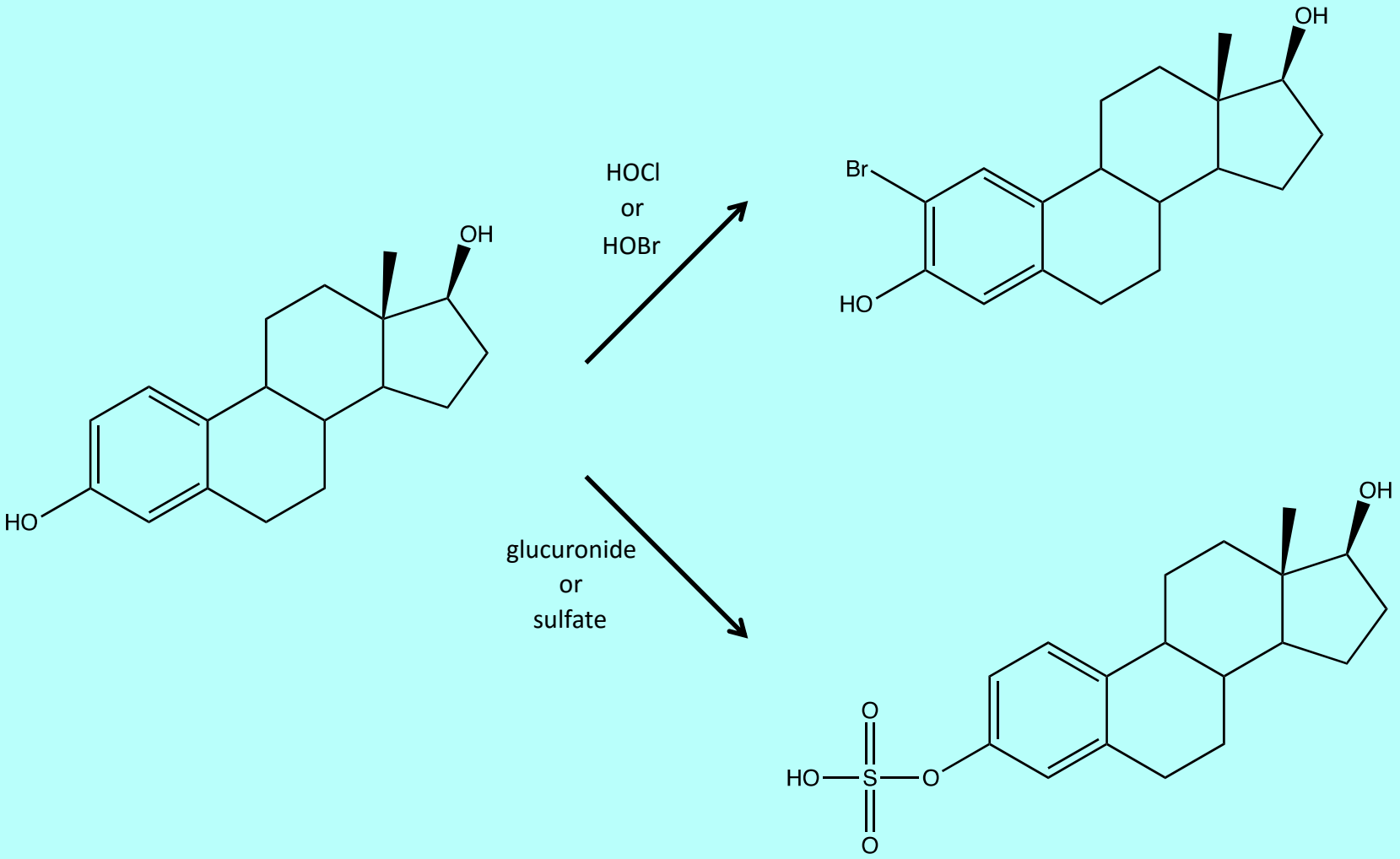
Reactivity: Estrogens

- Elevated levels of estrogens can disrupt reproductive function in vertebrates (fish)

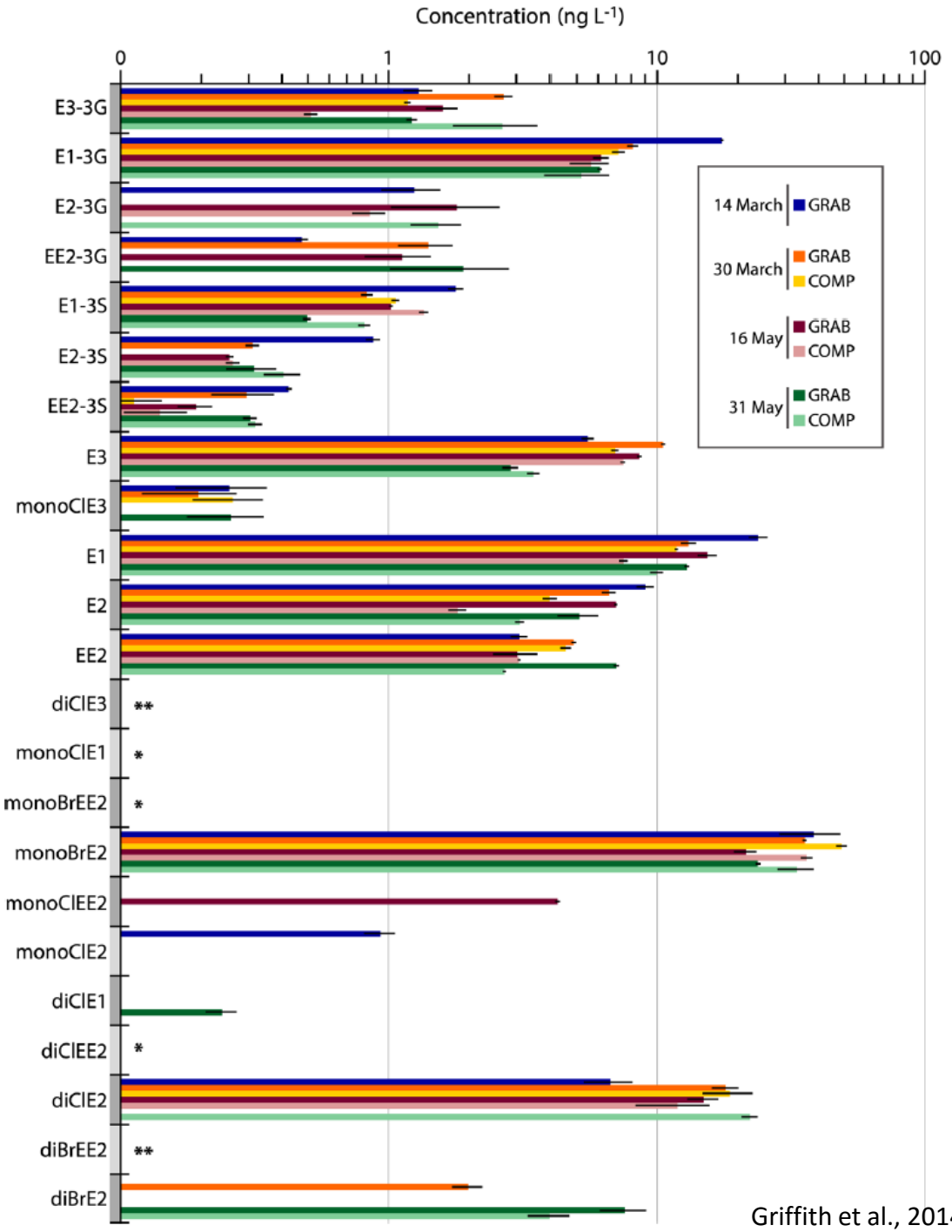
- Sources:
  - Wastewater (human hormone, contraceptive drug)
  - Livestock Waste (growth promoter)



Transformations of Estrogens



Estrogen Measurements



Griffith et al., 2014

Findings

- Measured free, conjugated, and halogenated estrogens in treated wastewater

- Free estrogens were only 30-40% of total

- Implications for bioaccumulation
  - log K_{ow} = 5.40 (halogenated)
  - log K_{ow} = 4.16 (free)

Griffith et al., 2014

Conclusions

- Structure of organic molecules dictates where they will partition

- Transformations of organic contaminants are essential to account for to fully understand their impact

Questions?