Lecture 9

More Aqueous Geochemistry of Natural Waters:

Organic chemistry intro and dissolved organic carbon

This week please read

- *McSween Ch6, Ch7 (124-131)*

-or-

- *White Ch14 (589-626), Ch3 (100-end), Ch13 (555-563)*

Organic Geochemistry of Natural Waters

❶ Intro

❷ Structure, Nomenclature and Functional Groups

❸ Humic substances and other natural "OC"

❹ DOC/POC distribution

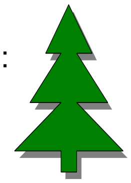
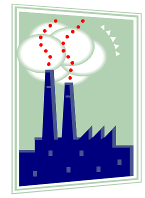
❺ Acidity

We will look briefly at natural organic molecules and summarize their behavior in the environment from the perspective of:

- functionality

- aqueous solubility and acidty.

1. Hydrospheric Organic Carbon

Organic Carbon occurs in the hydrosphere in:
natural and *contaminant* forms,
both of which can be in
dissolved and *suspended* forms:

DOC = Dissolved organic carbon, includes fulvic acids (and humic acids above pH=2).

POC = Particulate (suspended) organic carbon. Includes humin (and humic acids below pH=2).

DOC and POC concentration are variable in the hydrosphere but are generally higher in waters with high photosynthetic productivity:

e.g.,
- watershed water in forested areas,
- the outflow of high photosynthesis lakes or swamps
- sewage outfalls

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Examples of Common natural organic molecules in nature:

- simple organic molecules produced by organisms of sysnthesized naturally (i.e., methanol = CH_3-OH)
- biomolecules (i.e., chlorophyl, amino acids, proteins)
- fossilized biomolecules (i.e., petroleum components)

Common organic pollutants in nature are:

- pesticides/insecticides/herbicides/fungicides of various types (which can migrate from the application area)
- hydrocarbon components from oil spills, leaky subsurface fuel storage or transfer vessels.
- Biological waste products (untreated sewage, etc..).
- Gaseous contaminants from various sources.

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2. Structure, Nomenclature and Functional Groups:

❊ Most carbon containing molecules are known as organic molecules

❊ Organic molecules consist of a C-H backbone.

❊ sometimes organic molecules also contain other entities called "functional groups", which can take the place of either C or H, in a process know as "substitution"

❊ Organic molecules takes their structural name from the number of carbon atoms it contains and how they are bonded in the backbone.

Each carbon atom can have 4 attached bonds

❊ Organic molecules need not be associated with organisms. Many simple organic molecules are synthesized in nature by abiogenic processes

❊ A few special types of carbon bearing compounds are not considered to be organic: these are the 1 carbon oxides (including and carbonates) and *allotropic carbon (e.g., diamond and graphite). These are "inorganic carbon".*

Nomenclature

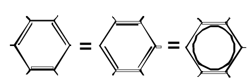
C, H - only molecules (aka hydrocarbons)

Alkane all C-C single bonds ("saturated" molecule)

Alkene at least one C=C double bond ("unsaturated" molecule, has few H atoms in structure). If more than one C=C double bond, they are said to be "conjugated" if they are arranged like this: C=C-C=C-C=C

Alkyne at least one C≡C triple bond (also "unsaturated" molecule, has few H atoms in structure)

Aryl special "unsaturated" molecule with "conjugated" C=C double bonds in a ring structure (like benzene = C_6H_6



Benzene

Nomenclature:

1 carbon:	Methane	*note: when one of these molecules is attached to another molecule, it take the names "methyl", "ethyl" or "ethylene" group for methane-like, ethane-like, and ethene like functionalities, etc..*
2 carbon:	Ethane ($H_3C\text{-}CH_3$) Ethene ($H_2C{=}CH_2$) Ethyne aka acetylene (H-C≡C-H)	
3 carbon:	Propane ($H_3C\text{-}CH_2\text{-}CH_3$) Propene ($H_2C{=}CH\text{-}CH_3$) Propyne ($HC{\equiv}C\text{-}CH_3$)	

Carbon atoms in these molecules are numbered, starting at the highest order functionality (see below), if one exists.

Functional groups:

❊ These determine compound reactivity and water solubility.
In general, more functionality = more soluble molecule = more reactive molecule.

❊ Functional groups typically set the name of the molecule:

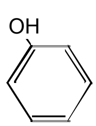
name	formula	Alternate names:
a. Ethyl Alcohol (ethanol):	CH_3CH_2OH (= ethane + alcohol)	1-hydroxy-ethane
b. Propyl Amine:	$CH_3CH_2CH_2NH_2$	1-amino propane
c. *iso*-Propyl Amine:	$CH_3CHNH_2CH_3$	2-amino propane

the "iso" prefix denotes the location of substitution at the symmetrical center of the molecule.

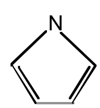
Common organic Functional groups:

("R" is an abbreviation for non-specified organic backbone)

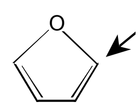
R-OH	R-O-R	R | R-C=O	OH | R-C=O	OR | R-C=O	$R\text{-}NH_2$	H_2N OH | | R-C-C=O
alcohols	ethers	carbonyls	carboxylic acids	esters	amines	amino acids



phenols



pyrroles



furans

the points of the polygons are carbon atoms, with one hydrogen atom attached

Functional groups can be acidic or basic.

Adding charge to an organic molecule generally makes it MORE water soluble and enhances Lewis acid/base interactions with metals in solution (i.e., chelation)

The more basic (electron donor) functional groups an organic molecule has, the more interaction it is likely to have with inorganic ions. These can also interact with solid surfaces (e.g., Suspended load components of a river, sediments, etc...).

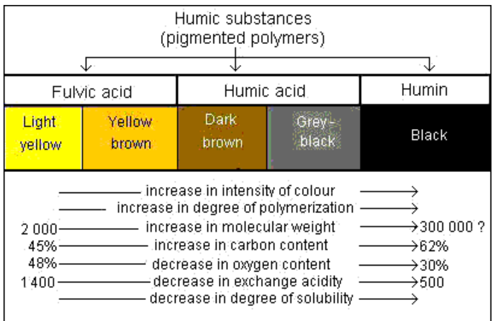
Halogen bearing functional groups are an exception. "Halogenated" compounds do not act like lewis bases because these functional groups are very electronegative.

3. Humic Substances

A special and important class of naturally occurring, highly substituted organic molecules is produced from the breakdown of natural organic matter at the interface between the biosphere/geosphere/hydrosphere.

Humic Substances are a group of compositionally complex yet related compounds that do not have a unique structure. Marine and fresh water humics are distinct, as we will discuss later in the semester.

They constitute up to 95% of the DOC in aquatic systems and are often present at equal or greater concentrations than inorganic ions



Chemical properties of humic substances. (Stevenson 1982)

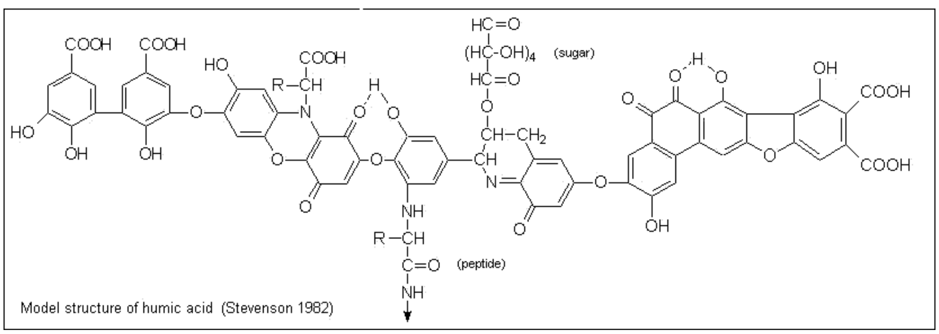
Sub-classes include:

a. humin: insoluble in H_2O at all pH (found in soils or as POC)

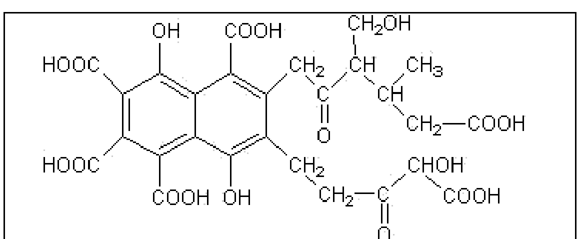
b. humic acid: insoluble at pH <2 but soluble at higher pH

c. fulvic acid: soluble at all pH

This image and next two from: http://www.ar.wroc.pl/~weber/humic.htm



Model structure of humic acid (Stevenson 1982)

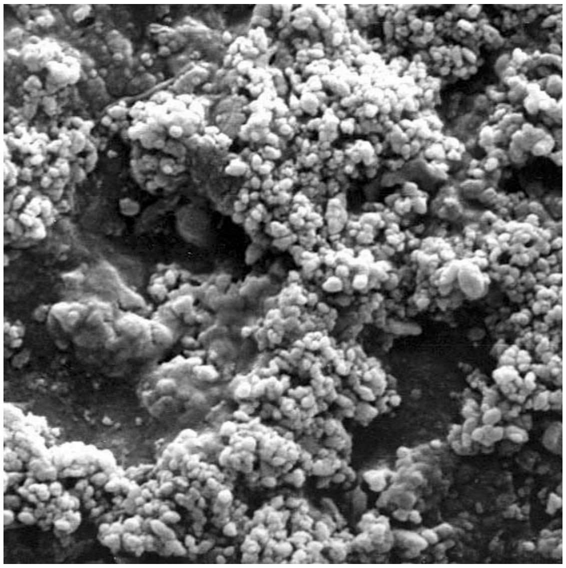

Model structure of fulvic acid by Buffle

HA contains an aromatic backbone linked by sugar, protein, amino acid, and other biomolecule residues. FA are more simple.

Notice the large number of acidic functional groups (e.g., COOH).

With dissolved CO_2, they act as a primary acidity buffer and can dramatically affect lake and river pH.

Humic Substances interact with other elements and compounds in nature. For instance, they act as chelating agents for many metals in the hydrosphere and food sources for many aquatic microbes



Humics in natural waters affect the abundance of

- **micronutrients**
- **toxic metals**
- **radionuclides**
- **halogens**

humic substances contain long-lived free radicals which can reduce the oxidation state of inorganic species such as Hg, Cr, and Pu.

SEM image at 2000x magnification from www.hagroup.neu.edu/

4. Solubility of Organic Molecules in water

✹ pure hydrocarbons have very low aqueous solubility

✹ substituted hydrocarbons increase in solubility by the number and type of functional groups it has.

O, N and S bearing functional groups increase solubility more than halogens, particularly when the O, N or S can gain or lose a H^+ (and thereby give charge to the molecule)

5. Distribution of Organic Carbon in natural water

Abundance variations of DOC and POC are similar but POC is typically lower than DOC in most of the hydrosphere.

- ♦ Very clear (i.e., non-turbid) waters can have relatively high DOC and POC compared to inorganic solutes due to photosynthesis.
- ♦ Very polluted waters can also have high DOC and POC from the pollutants or from enhanced photosynthesis/ respiration (wastes from organisms)

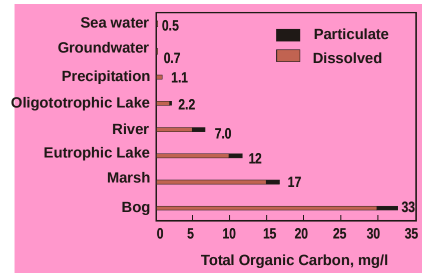


Figure 14.19. Average concentration of dissolved, particulate and total organic carbon in various natural waters. From Thurman (1985). *From White "Geochemistry"*

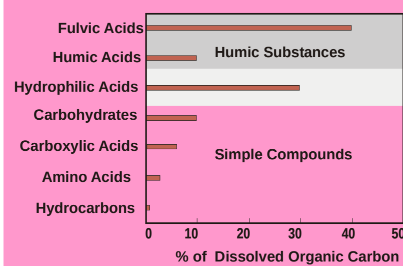


Figure 14.20. Components of dissolved organic carbon in typical river water. After Thurman (1985). *From White "Geochemistry"*

Both POC and DOC bind ions in water.

DOC chelates ions in solution whereas POC can have ions bound to their surfaces.

⁎ For DOC, the complexed ion itself stays dissolved.

⁎ For POC the complexed ion is only suspended in the water on the POC substrate. POC-complexed ions can settle-out of water if conditions of flow change

There are many natural organic ligands in the hydrosphere.

- Their abilities to chelate ions are pH dependent.
- Different ligands or functional groups on complex molecules such as fulvic acids have different reactivities for specific ions in water.

5. Acidity of Organic Acids

Depending on pH, DOC (and POC) can be significantly ionized in the hydrosphere. Most carboxylic acids, for instance, have significant amounts of the deprotonated form present at all but very low (<2) pH.

Remember, R-C=O ↔ R-C=O
| |
OH O^- + H^+

$K_a = [A^-][H^+]/[HA]$ ➜ $pK_a = -\log([A^-]/[HA]) + pH$
when $pK_a = pH$, then $-\log([A^-]/[HA]) = 0$ and $[A^-]/[HA] = 1$

pK_a of an acid gives us a quick method of estimating the ratio of acid to conjugate base for a given pH. For instance, take an acid with a pK_a of 8.

pH	$[A^-]/[HA]$
8	1
7	0.1
6	0.01

Even if we don't know the exact pK_a of a specific acid funcitionality on an organic molecule, we can estimate it's pK_a from ones we do know and some simple concepts regarding electron distribution.

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I usually think of pK_a of carboxylic acids relative to the common organic acid acetic acid (CH_3COOH) = 4.8.

You can understand if the pK_a of your acid is < or > that of acetic acid from their structure (presence or absence of other electronegative atoms or functional groups, conjugating systems, etc..).

A carboxylic acid will be more acidic if the remaining conjugate base ($R\text{-}COO^-$) has a way of stabilizing the negative charge in the R group after the H^+ has been removed.

✷ Electronegative or electron-deficient functional groups in an organic acid decrease pK_a (increase acidity).

✷ If the resulting minus charge on the conjugate base is stabilized by conjugation, this will also lower pK_a (e.g., benzoic acid).

✷ Non-electronegative, electron-excessive functional groups do the opposite (increase pK_a).

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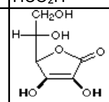
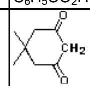
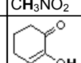
http://www.cem.msu.edu/~reusch/OrgPage/

Common Name	**Formula**	**Ka**	**pKa**	**Comments**
acetic acid	CH_3CO_2H	$1.77x10^{-5}$	4.75	"Baseline" organic acid
trifluoroacetic acid	CF_3CO_2H	1.0	0.0	Effect of F, which is highly electronegative
picric acid	$(O_2N)_3C_6H_2OH$	0.5	0.3	
trichloroacetic acid	CCl_3CO_2H	0.23	0.77	
oxalic acid	$(CO_2H)_2$	$K_1 = 6.5x10^{-2}$ $K_2 = 6.1x10^{-5}$	1.2 4.2	
dichloroacetic acid	$CHCl_2CO_2H$	$5.5x10^{-2}$	1.25	
fluoroacetic acid	FCH_2CO_2H	$2.5x10^{-3}$	2.6	Even one halogen makes this acid much stronger than acetic
chloroacetic acid	$ClCH_2CO_2H$	$1.36x10^{-3}$	2.87	
citric acid	$C(OH)(CH_2CO_2H)_2CO_2H$	$K_1 = 7.4x10^{-4}$ $K_2 = 1.7x10^{-5}$ $K_3 = 4.0x10^{-7}$	3.13 4.76 6.40	Think lemons...
formic acid	HCO_2H	$1.77x10^{-4}$	3.75	Ant-trail chemical
ascorbic acid		$K_1 = 6.7x10^{-5}$ $K_2 = 2.5x10^{-12}$	4.17 11.6	Vitamin C
benzoic acid	$C_6H_5CO_2H$	$6.3x10^{-5}$	4.20	
5,5-dimethyl-1,3-cyclohexadione		$1.6x10^{-5}$	4.8	An acidic H bonded to a C atom because of the stability of the ensuing anion
propionic acid	$CH_3CH_2CO_2H$		4.9	Like the baseline (no conjugated C, no more electroneg. gps.)

Common Name	**Formula**	**Ka**	**pKa**	**Comments**
butyric Acid	$CH_3CH_2CH_2CO_2H$		4.9	Like the baseline
α-butyric Acid	$CH_3CH_2CClHCO_2H$		3.8	Add a Cl near the acid group and acidity goes up by 13x
β-butyric Acid	$CH_3CClHCH_2CO_2H$		4.1	Add the Cl one carbon away and acidity goes up 6.3x
γ-butyric Acid	$CClH_2CH_2CH_2CO_2H$		4.5	Add the Cl two carbons away and acidity goes up 2.5x
thiophenol	C_6H_5SH	$2.5x10^{-7}$	6.6	
p-nitrophenol	$O_2NC_6H_4OH$	$5.7x10^{-8}$	7.2	
peracetic acid	CH_3COO_2H	$5.7x10^{-9}$	8.2	
hydrocyanic acid	$\mathbf{H}CN$	$6.3x10^{-10}$	9.2	
succinimide	$(CH_2CO)_2NH$	$2.5x10^{-10}$	9.6	
phenol	C_6H_5OH	10^{-10}	10.0	
nitromethane	$\mathbf{CH_3}NO_2$	$6.3x10^{-11}$	10.2	
2-hydroxy-2-cyclohexenone		$5.0x10^{-11}$	10.3	Not an acidic H because the resultant anion is not very stable
pyrrole	C_4H_4NH	10^{-15}	15	*Everything below here never ionizes under natural conditions*
ethanol	C_2H_5OH	10^{-16}	16	
methyl ketones	$RCOC\mathbf{H}_3$	10^{-25}	25	
alkyl esters	$RC\mathbf{H}_2CO_2C_2H_5$	10^{-25}	25	
nitriles	$RC\mathbf{H}_2CN$	10^{-25}	25	
acetylene	$HC/C\mathbf{H}$	10^{-25}	25	
benzene	$C_6\mathbf{H}_6$	10^{-43}	43	
ethylene, ethane	$C_2\mathbf{H}_4$	10^{-44}	44	
cyclopropane	$C_3\mathbf{H}_6$	10^{-46}	46	
ethane	$C_2\mathbf{H}_6$	10^{-48}	48	

Many biological carboxylic acids have $pK_a < pK_a$acetic acid.

Thus, acid groups in DOC are **significantly ionized** in most natural waters, even at pH < lower endpoint of H_2CO_3 (= 4.3)

One can determine the amount of DOC in natural waters by looking at the relative proportion of inorganic cations and anions. If the low pH of a natural water is due mostly to mineral acid constituents, the organic acid content should be low.

Then, because of charge balance requirements ...
Σ(inorganic cations) = Σ(inorganic anions), e.g., HCO_3^-, Cl^-, SO_4^{2-}.

However, it the low pH is due mostly to organic acids ...
Σ(inorganic cations) > Σ(inorganic anions) because
Σ(inorganic cations) ~ Σ(inorganic anions) +Σ(organic anions)

In general, **the lower the ratio** $\frac{\Sigma(\text{inorganic anions})}{\Sigma(\text{inorganic cations})}$

… the higher the DOC concentration

Also, high DOC waters have low $[HCO_3^-]$ because

$$RCOOH + HCO_3^- \leftrightarrow RCOO^- + H_2O + CO_2$$