Lecture 11

Organic chemistry intro and dissolved organic substances in natural waters:

please read these bits in White

first two lectures

• Ch3 (100-110), Ch13 digital (555 563)

for today

• Ch12 (12.1-12.6) -or- White digital Ch14 (589-626)

Organic Geochemistry of Natural Waters

1. Intro
2. Structure, Nomenclature and Functional Groups
3. DOC/POC, Humic substances and other natural “OC”
4. DOC/POC distribution
5. Acidity

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

- functionality
- aqueous solubility and acidity.
1. Hydrospheric Organic Carbon

Organic Carbon occurs in the hydrosphere in:
- **natural** and **contaminant** forms,
as well as in
- **dissolved** and **suspended** forms:

**DOC** = Dissolved organic carbon

**POC** = Particulate (suspended) organic carbon

**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 synthesized naturally (e.g., methanol = CH$_3$-OH)
- biomolecules (e.g., chlorophyll, amino acids, proteins)
- fossilized biomolecules (e.g., 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.
2. Structure, Nomenclature and Functional Groups:

- Organic molecules consist of a C-H backbone, sometimes plus other entities called "functional groups", which can be substituted for either C or H.

- The molecule takes its structural name from the number of carbon atoms it contains and how they are bonded.

  Each carbon atom can have 4 attached bonds

More Structure, Nomenclature and Functional Groups:

- Organic molecules need not be associated with organisms.

- Many simple organic molecules are synthesized in nature by abiotic 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 = C₆H₆)

Nomenclature:

| 1 carbon: | Methane |
| 2 carbon: | Ethane (H₃C-CH₃) | Ethene (H₂C=C:H₂) | Ethyne aka acetylene (H-C≡C-H) |
| 3 carbon: | Propane (H₃C-CH₂-CH₃) | Propene (H₂C=CH-CH₃) | Propyne (HC≡C-CH₃) |

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:

<table>
<thead>
<tr>
<th>name</th>
<th>formula</th>
<th>Alternate names:</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Ethyl Alcohol (ethanol):</td>
<td>CH₃CH₂OH (= ethane + alcohol)</td>
<td>1-hydroxy-ethane</td>
</tr>
<tr>
<td>b. Propyl Amine:</td>
<td>CH₃CH₂CH₂NH₂</td>
<td>1-amino propane</td>
</tr>
<tr>
<td>c. iso-Propyl Amine:</td>
<td>CH₃CHNH₂CH₃</td>
<td>2-amino propane</td>
</tr>
</tbody>
</table>

the "iso" prefix denotes the location of substitution at the symmetrical center of the molecule.
Common organic Functional groups:

<table>
<thead>
<tr>
<th>R-OH</th>
<th>R-O-R</th>
<th>R</th>
<th>OH</th>
<th>OR</th>
<th>H₂N OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-C=O</td>
<td>R-C=O</td>
<td>R-C=O</td>
<td>R-NH₂</td>
<td>R-C-C=O</td>
<td></td>
</tr>
</tbody>
</table>

alcohols  ethers  carbonyls  carboxylic acids  esters  amines  amino acids

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...).

One exception are halogen functional groups. “Halogenated” compounds do not act like lewis bases because these functional groups are very electronegative.

3. dissolved and particulate organic carbon

**DOC** = Dissolved organic carbon;
includes many types of molecules, such as small simple ones and more complicated ones. Generally they are highly substituted with acid-base sensitive functional groups.

**POC** = Particulate (suspended) organic carbon;
also includes many types of molecules, such as weakly substituted hydrocarbons and refractory (less reactive) resides of large molecules, solid phase biological wastes ..and *the humic substances*

*We will discuss hyperfine particulate (colloidal) POC later*
Environmental Carbon, Nitrogen and Phosphorous nomenclature

We CAN ALSO refer to dissolved CO$_2$ in any of its forms as:

**DIC** (dissolved inorganic carbon) and

**PIC** (particulate inorganic carbon).

And… we use the same convention for **N** and **P**.

*for example*

- DIP = dissolved inorganic phosphorous
- DIN = dissolved inorganic nitrogen
- POP = particulate organic phosphorous

etc…

In general:

- **D** = “dissolved”
- **P** = “particulate” or “phosphorous” (depending on where it is in the acronym)
- **O** = “organic”
- **I** = “Inorganic”
- **N** = “Nitrogen”
- **C** = “carbon”

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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.

Sub-classes include:

- a. humin: insoluble in H$_2$O 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](http://www.ar.wroc.pl/~weber/humic.htm)*

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
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.

They affect the abundance in natural waters of:
- micronutrients
- toxic metals
- radionuclides
- halogens

Humic substances contain long-lived free radicals which can reduce inorganic species such as Hg, Cr, and Pu.

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

Notice the large number of acidic functional groups.

With dissolved CO₂, they act as a primary acidity buffering and can dramatically affect lake and river pH.

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 particularly when the O, N or S can gain or lose a H⁺ (and thereby give charge to the molecule).

Halogen functional groups do much less to change solubility.

5. Distribution of Organic Carbon in natural water

Total Organic Carbon (TOC) in Rivers and Lakes

- In the fresh water hydrosphere organic carbon is in both dissolved (DOC) and Particulate/suspended (POC) forms.
- DOC & POC are highest in regions of high biological productivity (natural and polluted).

TOC contains simple molecules and complex biomolecules

<table>
<thead>
<tr>
<th>natural sources</th>
<th>Pollutant sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>All organisms produce liquid and solid wastes</td>
<td>numerous sources of soluble and particulate forms</td>
</tr>
</tbody>
</table>

Solids: the POC:suspended ratio load is variable in rivers

- "normal" rivers ~1:100 in. (1%)
- It can be higher in very clear (e.g., non-turbid) rivers or in some very polluted rivers.

Solutes: DOC:TDS ~ 1:20 for most rivers. (5%)
More 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 (e.g., 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).

Both POC and DOC interact with inorganic materials in natural environments:

**TABLE 6.3** DISOLUTION OF SELECTED MINERALS AFTER 24 HOURS AT 25°C*

<table>
<thead>
<tr>
<th>Mineral</th>
<th>ION</th>
<th>ionic/CO₂</th>
<th>Humic acid</th>
<th>H₂O/CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>Ca</td>
<td>0.45</td>
<td>17.40</td>
<td>2.73</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Ca</td>
<td>0.31</td>
<td>7.39</td>
<td>0.43</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Mg</td>
<td>0.11</td>
<td>3.45</td>
<td>0.33</td>
</tr>
<tr>
<td>Hornblende</td>
<td>Fe</td>
<td>0.09</td>
<td>1.81</td>
<td>0.28</td>
</tr>
<tr>
<td>Mica</td>
<td>Fe</td>
<td>0.06</td>
<td>0.78</td>
<td>0.13</td>
</tr>
<tr>
<td>Glaucophane</td>
<td>Fe</td>
<td>0.04</td>
<td>0.32</td>
<td>0.06</td>
</tr>
<tr>
<td>Glaucophane</td>
<td>Al</td>
<td>0.04</td>
<td>0.24</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*All solution concentrations are in mg l⁻¹ except as noted. Based on data selected from Baker (1988).

- They increase solubility of many minerals
- They bind ions in water by chelation
- They attach to mineral surfaces

Chelation

Attachment of organic acid to inorganic materials

where 3Al(OH) represents the surface of a hydrated aluminum
**Chelates**: Both POC and DOC bind ions in natural waters.

- The abilities of organic ligands in the hydrosphere to chelate ions are functional-group and pH dependent.
- DOC complexed ions are dissolved.
- POC-complexed ions are bound to particle surfaces, which can settle-out of river water if conditions of flow in the river change.
- Colloidal POC complexed ions are sort of both dissolved and not
- Major and trace elements compete with each for DOC complexation sites.

Because DOC:TDS ~ 1:20 for most rivers, there are 20 times as many major ions in river water as there are DOC complexing agents. So,

- DOC chelation of major ions has a relatively small effect on their solubility.
- DOC chelation of the lower concentration trace ions can significantly affect their absolute solubility.

**Reinforcing…**

When DOC chelates ions they are in solution, whereas POC chelated have ions are bound to particle 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 will have different reactivities for specific ions in water.

There are also many pollutive ligands that are introduced in the hydrosphere (natural ligands in non-natural concentration and non-natural ligands in any concentration).

6. 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.

\[
\text{Remember,} \quad \text{R-C}=\text{O} \leftrightarrow \text{R-C}=\text{O} \\
| \quad \text{OH} \quad | \quad \text{O}^- + \text{H}^+ \\
\]

\[
K_a = \frac{[A^-][H^+][HA]}{[HA]} \quad \text{pK}_a = -\log([A^-]/[HA]) + \text{pH} \\
\]

When \( pK_a = \text{pH} \), 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.

<table>
<thead>
<tr>
<th>pH</th>
<th>[A^-]/[HA]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Even if we don’t know the exact \( pK_a \) of a specific acid functionality on an organic molecule, we can estimate it’s \( pK_a \) from ones we do know and some simple concepts regarding electron distribution.
I usually think of pK$_a$ of carboxylic acids relative to the common organic acid acetic acid (CH$_3$COOH) = 4.8.

The pK$_a$ of an organic acid will be < or > than that of acetic acid depending on its structure

(e.g., other electronegative atoms or functional groups in the molecule, conjugating systems, etc.).

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$_2$CO$_3$ (= 4.3)
A carboxylic acid will be more acidic than acetic acid if the remaining conjugate base has a way of stabilizing the negative charge after the H⁺ has been removed.

- Electronegative or electron-deficient functional groups in an organic acid decrease pKₐ (increase acidity).
- If the resulting minus charge on the conjugate base is stabilized by conjugation, this will also lower pKₐ (e.g., benzoic acid).
- Non-electronegative, electron-excessive functional groups do the opposite (increase pKₐ).

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

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Formula</th>
<th>Ka</th>
<th>pKa</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>C₂H₃CO₂H</td>
<td>1.77x10⁻⁵</td>
<td>4.75</td>
<td>The “Baseline” organic acid</td>
</tr>
<tr>
<td>trifluoroacetic</td>
<td>CF₃CO₂H</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>picric acid</td>
<td>C₆H₅(NO₂)₃</td>
<td>0.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>trichloroacetic</td>
<td>CCl₃CO₂H</td>
<td>0.23</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>oxalic acid</td>
<td>CO₂H₂</td>
<td>K₁ = 6.5x10⁻⁴</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>dichloroacetic</td>
<td>CHCl₂CO₂H</td>
<td>5.9x10⁻⁵</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>fluoroacetic</td>
<td>CHF₂CO₂H</td>
<td>2.5x10⁻⁵</td>
<td>2.8</td>
<td>Even one halogen makes this acid much stronger than acetic acid</td>
</tr>
<tr>
<td>chloroacetic</td>
<td>CCl₃CO₂H</td>
<td>1.38x10⁻⁵</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>citric acid</td>
<td>C₆H₈(OH)₂(C₂H₃CO₂H)₂</td>
<td>K₁ = 7.4x10⁻³</td>
<td>3.13</td>
<td></td>
</tr>
<tr>
<td>formic acid</td>
<td>HCO₂H</td>
<td>1.77x10⁻⁵</td>
<td>3.75</td>
<td>Ant trail chemical</td>
</tr>
<tr>
<td>ascorbic acid</td>
<td>H₂C₅O₄</td>
<td>K₁ = 6.7x10⁻⁵</td>
<td>4.17</td>
<td>Vitamin C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K₂ = 2.5x10⁻¹⁰</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>benzoic acid</td>
<td>C₆H₅CO₂H</td>
<td>6.3x10⁻⁵</td>
<td>4.20</td>
<td></td>
</tr>
<tr>
<td>5,5-dimethyl-1,3-</td>
<td></td>
<td>1.6x10⁻⁵</td>
<td>4.8</td>
<td>An acidic H bonded to a C atom because of the stability of the ensuing anion</td>
</tr>
<tr>
<td>cyclohexadione</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propionic acid</td>
<td>CH₃CH₂CO₂H</td>
<td>4.9</td>
<td></td>
<td>Like the baseline</td>
</tr>
<tr>
<td>Common Name</td>
<td>Formula</td>
<td>Ka</td>
<td>pKa</td>
<td>Comments</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------------------------</td>
<td>-----</td>
<td>------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Butyric Acid</td>
<td>CH₃CH₂CH₂CO₂H</td>
<td>4.9</td>
<td>6.1</td>
<td>Like the baseline</td>
</tr>
<tr>
<td>α-Butyric Acid</td>
<td>CH₃CH₂CClHCO₂H</td>
<td>3.8</td>
<td>6.8</td>
<td>Add in a Cl near the acid group, acidity goes up by 13x</td>
</tr>
<tr>
<td>β-Butyric Acid</td>
<td>CH₃CHClCH₂CO₂H</td>
<td>4.1</td>
<td>5.9</td>
<td>Add the Cl one carbon away and acidity goes up 5x</td>
</tr>
<tr>
<td>γ-Butyric Acid</td>
<td>CClH₂CH₂CH₂CO₂H</td>
<td>4.5</td>
<td>5.5</td>
<td>Add the Cl two carbons away and acidity goes up 2.5x</td>
</tr>
<tr>
<td>Thiophenol</td>
<td>C₆H₅SH</td>
<td></td>
<td>2.5x10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>O₂NC₆H₄OH</td>
<td>5.7x10⁻⁸</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Peracetic acid</td>
<td>CH₃COO₂H</td>
<td>5.7x10⁻⁹</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>HCN</td>
<td>6.3x10⁻¹⁰</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>Succinimide</td>
<td>(CH₂COO₂H)NH</td>
<td>2.5x10⁻¹⁰</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>C₆H₅OH</td>
<td>10⁻¹⁵</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Nitromethane</td>
<td>CH₃NO₂</td>
<td>6.3x10⁻¹¹</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxy-2-cyclohexenone</td>
<td>CH₃O</td>
<td>5.0x10⁻¹¹</td>
<td>10.3</td>
<td>Not an acidic H because the resultant anion is not very stable</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>C₄H₄NH</td>
<td>10⁻¹⁵</td>
<td>15</td>
<td>Everything below here never ionizes under natural conditions</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>10⁻¹⁴</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Methyl ketones</td>
<td>RCOCH₃</td>
<td>10⁻²⁵</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Alkyl esters</td>
<td>RCH₂CO₂C₂H₅</td>
<td>10⁻²⁵</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Nitrites</td>
<td>RCH₃CN</td>
<td>10⁻²⁵</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
<td>HC≡CH</td>
<td>10⁻⁷</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₅</td>
<td>10⁻¹²</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>10⁻¹⁴</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>C₃H₆</td>
<td>10⁻¹⁶</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>10⁻¹⁶</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

**Aqueous ionic balance and organic acid dissociation:**

The amount of DOC affects ionic balance in a natural water, especially 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 ...

\[ \sum (\text{inorganic cations}) = \sum (\text{inorganic anions}), \text{ e.g., } \text{HCO}_3^-, \text{Cl}^-, \text{SO}_4^{2-}. \]

🧬 However, if the low pH is due mostly to organic acids ... then

\[ \sum (\text{inorganic cations}) > \sum (\text{inorganic anions}) \text{ because } \sum (\text{inorganic cations}) \sim \sum (\text{inorganic anions}) + \sum (\text{organic anions}) \]

In general, **the lower the ratio** \[ \frac{\sum (\text{inorganic anions})}{\sum (\text{inorganic cations})} \]

**... the higher the DOC concentration**

Also, high DOC waters have low [\text{HCO}_3^-] due to

\[ \text{RCOOH} + \text{HCO}_3^- \rightleftharpoons \text{RCOO}^- + \text{H}_2\text{O} + \text{CO}_2 \]