CEE 697z
Organic Compounds in Water and Wastewater

Outline

- Many ways to “slice the NOM Pie”
- Concentrations
- Characteristics
  - Size, elemental composition, functional groups
- Structures
  - Mass spectrometry with and without various levels of degradation
- General Reactivity

It’s one of my favorite recipes. I call it Fulvic Acid.
I. NOM Structure & Selected Properties

- A. Bulk Organic Matter
  - occurrence
  - simple bulk properties
    - Elemental analysis
    - absorbance
  - Know structural elements
    - bulk functionality
    - specific structures
  - General reactivity with treatment chemicals
    - THM FP, other DBP FPs

II. NOM Structure (cont.)

- B. NOM from specific source types
  1. allochthonous or pedogenic
    - lignins & non-humics
  2. autochthonous or aquogenic
    - algal (AOM)
  3. wastewater effluent organics (EfOM)
    - soluble metabolic products
  4. Major biochemical constituents
    - lignin, proteins, terpenoids, tannins, others
III. NOM Structure (cont.)

C. Subcomponents from bulk NOM

- hydrophobic acids (humics)
  - humic and fulvic acids
- Hydrophilic acids
  - meso to philic to ultra
- Neutral fractions
  - phobic, philic
- Base fractions
  - phobic, philic

In many cases we have the same characterization for these groups that we have for the bulk organic mater.

How to measure NOM

- Identify and quantify individual compounds
  - expensive and may only account for 10%
  - not practical
- Fractionate, extract and weigh
  - comprehensive, but time-consuming
  - doesn’t tell us precisely what the stuff is
- Use a collective or “gross” measurement
  - TOC, UV absorbance, DBP precursors
  - easiest method, useful for engineering purposes
TOC analysis

Principle: oxidize all organic matter to Carbon dioxide and water. Then measure the amount of carbon dioxide produced

\[ C_a H_b N_c O_d + \left( a + \frac{b}{4} - \frac{d}{2} \right) O_2 \rightarrow aCO_2 + \frac{b}{2} H_2 O + \frac{c}{2} N_2 \]

Oxidation
- High Temperature Pyrolysis
- UV Irradiation
- Heated Persulfate
- UV/Persulfate

Particulate-C vs. Dissolved-C

- Particulate organic carbon
  - larger than about 1 micron
  - determined by what is retained in laboratory filtration
  - algae, bacteria, protozoa, organics adsorbed to clays
- Dissolved organic carbon (DOC)
  - from simple molecules to large biopolymers
  - determined from the TOC of a filtered sample
  - typically comprises 90-98% of the TOC
Fractionation & Nomenclature

- Total Carbon (TC)
  - Inorganic Carbon (IC)
  - Total Organic Carbon (TOC)
    - Purgeable Organic Carbon (POC)
    - Non-purgeable Organic Carbon (NPOC)

Methods of Fractionation

- Resin-based
  - Usually XAD resins
  - May combine with ion exchange resins
- Evaporative or RO
- RO & ED
  - Drewes et al., 2002 WQTC
  - Perdue
Simple Hydrophobicity Test

- **Hydrophobic NOM**
  - Retained on XAD-8
  - TOC#1-TOC#2

- **Mesophilic NOM**
  - Retained on XAD-4, but not on XAD-8
  - TOC#2-TOC#3

- **Hydrophilic NOM**
  - Not retained
  - TOC#3

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Mini-XAD Lab setup
Simple Hydrophobicity Test

- Hydrophobic NOM
  - Retained on XAD-8
  - TOC#1-TOC#2
- Mesophilic NOM
  - Retained on XAD-4, but not on XAD-8
  - TOC#2-TOC#3
- Hydrophilic NOM
  - Not retained
  - TOC#3

Simple Hydrophobicity Test #2

- Back elution with NaOH
- Allows recovery of fractions and check of direct fractionation
- Desorbable hydrophobics = TOC#4
- Desorbable mesophilics = DOC #5
Analysis of Hydrophobicity

A. Water Sample → Humic Substances
   - XAD-8
   - Eluent
   - XAD-8
   - Eluent
   - XAD-4
   - Eluent
   - XAD-4
   - Eluent
   - RO
   - Permeate
   - Hydrophilic NOM (Retentate)

B. Rotary Evaporator → Condensate
   - Test Water
   - XAD-8
   - Humics
   - NaOH
   - APS from UF
   - SPP is not retained

NOM Pool Fractionation

- Back elution with NaOH
- Allows recovery of fractions and check of direct fractionation
- Humics elute from XAD-8
- APS from UF
- SPP is not retained
Polarity Rapid Assessment Method (PRAM)

Figure 1 Experimental setup for PRAM. SPE cartridges contained 100 mg of sorbent with a total volume of 1.5 mL and average pore size of 60 Å. The retention coefficient (RC) is calculated based on the maximum breakthrough concentration and the initial concentration. C-18, C-8, and C-2 are nonpolar sorbents; Silica, Diol, and Cyanide (CN) are polar sorbents; Amino (NH-2) is a weak anion exchanger and SAX is the strong anion exchanger.

Differences between UMass method and the Rosario-Ortiz method are in red.

Published in: Fernando L. Rosario-Ortiz; Shane Snyder; I. H. (Mel) Suffet; Environ. Sci. Technol. 2007, 41, 4895-4900. DOI: 10.1021/es062151t

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The Humics and Non-humics: Comprehensive NOM Fractionation

Water Sample

Filter

Hydrophobic Resin
Amberlite XAD-8

Cation Exchange Resin
MSC-1

Anion Exchange Resin
Duolite A-7

Hydrophobic Bases
Weak Hydrophobic Acids
Hydrophobic Neutrals

Hydrophilic Bases

Humic Acid
Fulvic Acid

Hydrophilic Neutrals

Hydrophilic Acids

Leenheer & Noyes, 1984

MSC-1
## Proposed Assignments for Organic Fractions

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colloidal</strong></td>
<td>Bacterial peptidoglycan cell wall components (hydrophilic neutral)</td>
</tr>
<tr>
<td><strong>Hydrophobic</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Acids</strong></td>
<td></td>
</tr>
<tr>
<td>Weak</td>
<td>tannins; phenols; intermediate MW alkyl monocarboxylic acids (C5-C8), dicarboxylic acids (C8-C11)</td>
</tr>
<tr>
<td>Strong</td>
<td>fulvic acids; humic acids; high MW alkyl monocarboxylic acids (≥C9), and dicarboxylic acids (≥C12); aromatic acids</td>
</tr>
<tr>
<td><strong>Bases</strong></td>
<td>amphoteric proteinaceous materials; high MW (JC12) alkyl amines; alkyl pyridines; aromatic amines</td>
</tr>
<tr>
<td><strong>Neutrals</strong></td>
<td>hydrocarbons; high MW (≥C6) methyl ketones; furans; most ethers; high MW (≥C5) alkyl alcohols, and aldehydes; lactones; pyrrole, alkyl aromatic sulfonates</td>
</tr>
<tr>
<td><strong>Hydrophilic</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Acids</strong></td>
<td>hydroxy acids; sugar acids; sulfonic acids; low MW alkyl monocarboxylic acids (C1-C4), and dicarboxylic acids (C2-C7)</td>
</tr>
<tr>
<td><strong>Bases</strong></td>
<td>low MW (C1-C11) alkyl amines; amino acids; purines; pyrimidines; pyridine; hydroxy pyridines</td>
</tr>
<tr>
<td><strong>Neutrals</strong></td>
<td>polysaccharides; Low MW (C1-C4) alkyl alcohols, aldehydes, and ketones; polyketones; amides, N-acetyl amino sugars, non-carbohydrate alcohols</td>
</tr>
</tbody>
</table>

+Based on: Leenheer and Noyes, 1984; Leenheer et al., 1982; and Reckhow et al., 1992

## The Humic Substances

- Analytically defined
  - Humic & fulvic acids
- True structure is unknown
  - Many ideas
- Chemical Characterization
  - Elemental Composition
  - Aromaticity: High
  - Functional Groups: Moderate acidity
  - Molecular Size: Moderate
  - Absorbance: High
Elemental Composition: Humics

**Elemental Composition of Aquatic Humic Substances**
(average of 15 riverine samples, after Thurman, 1985)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulvic</td>
<td>51.9</td>
<td>5.0</td>
<td>40.3</td>
<td>1.1</td>
<td>0.2</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Humic</td>
<td>50.0</td>
<td>4.7</td>
<td>39.6</td>
<td>2.0</td>
<td>5.0</td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

High oxygen content
FA and HA Similar, except:
• humics tend to have more N

Elemental Analysis

From: Perdue & Ritchie, 2004
Elemental Ratios

- Van Krevelen Plot

From: Perdue & Ritchie, 2004

Size of NOM

0.45 µm

Particulate

Relative Size of Natural Organic Carbon

FA=fatty acids; CHO=carbohydrates; AA=amino acids; HC=hydrocarbons
(Modified from: Thurman, 1985)
Molecular Size

- **Ultrafiltration**
  - series vs parallel
  - membrane calibration
- **Size Exclusion Chromatography**
  - HPSEC vs LC
- **Others**
  - Vapor Pressure Osmometry

Molecular Size: Ultrafiltration

- **Humic Acid**
  - Polydisperse
  - Moderate to large

- **Fulvic Acid**
  - Polydisperse
  - Moderate to large
Molecular size: non-humics

Abundance of high-molecular size compounds in Seven Organic Fractions
(from Reckhow et al., 1993)

From: Perdue & Ritchie, 2004
HPSEC

- Effective size
- UV abs or DOC detection

- Requires size calibration

```
<table>
<thead>
<tr>
<th>Effective Molecule Weight (Da)</th>
<th>Normalized Absorbance at 254 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1e+2</td>
<td>0.000</td>
</tr>
<tr>
<td>1e+3</td>
<td>0.002</td>
</tr>
<tr>
<td>1e+4</td>
<td>0.004</td>
</tr>
<tr>
<td>1e+5</td>
<td>0.006</td>
</tr>
<tr>
<td>1e+6</td>
<td>0.008</td>
</tr>
<tr>
<td>1e+8</td>
<td>0.010</td>
</tr>
<tr>
<td>1e+10</td>
<td>0.012</td>
</tr>
</tbody>
</table>
```

- Comparison of HPSEC with FFFF
  - be careful of solute: gel interactions
  - Pelekani et al., 1999 [ES&T, 2807]
Aromaticity: $^{13}$C-NMR

![Aromatic and Aliphatic Content of Aquatic Humic Substances](from Reckhow et al., 1990)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Percent Aromatic</th>
<th>Percent Aliphatic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Range</td>
</tr>
<tr>
<td>Fulvic</td>
<td>17</td>
<td>14-19</td>
</tr>
<tr>
<td>Humic</td>
<td>32</td>
<td>30-35</td>
</tr>
</tbody>
</table>
Carbon type: $^{13}$C-NMR

Westerhoff et al., 1996

Impact of Origin

More allochthonous
Higher MW

C/N Ratio

Aromatic/Aliphatic Ratio

Lignin origin

Algal origin
Showing “end-members” from McKnight

![Graph showing C:N vs. AR/AL-1 ratio for various aquatic environments.]

**Functional Groups: Humics**

- **Phenolic Group**
- **Carboxyl Groups**

**Functional Group Content of Aquatic Humic Substances** (meq/g, After Thurman, 1985)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Carboxyl</th>
<th>Phenolic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulvic</td>
<td>5.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Humic</td>
<td>4.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Source of electrical charge; responsible for coagulant demand
Functional Groups: non-humics

Net Organic Charge on Seven Aquatic Organic Fractions from Forge Pond
(After Reckhow et al., 1993)

From: Perdue & Ritchie, 2004
Size and Charge Relationships for NOM Fractions
from: Bezbarua and Reckhow, 1995

Functional Groups and Complexation

- Complexation with Coagulants, Major Cations and Heavy Metals
  - soluble complexes
  - surface complexes (insoluble)

- Role of organic structure
  - Enolate > Amine > Azo Compounds > Carboxyl > Ether > Ketone
  - bidentate > monodentate
  - geometry

- Role of metal: the Irving-Williams series:
  - Fe^{3+}>Al^{3+}>Pb^{2+}>Hg^{2+}>Cu^{2+}>Ni^{2+}>Zn^{2+}>Co^{2+}>Fe^{2+}>Mn^{2+}>Cd^{2+}>Ca^{2+}>Mg^{2+}
An Aquatic Humic “Structure”

- Features
  - Aromatic rings
  - Reactive with oxidants
  - Aliphatic carbon chains
  - Many oxygenated groups that can bind with coagulants
    - Phenolic -OH
    - Aliphatic -OH
    - Carboxylic (COOH)

Other Concepts

- From Suwanee River FA characterization
  - A. Simple view
  - B. With an N (anthranillic acid – type)
  - C. Containing a semiquinone free radical

Averett et al., 1988

Dave Reckhow - Organics
To next lecture