Natural Organic Matter in Water

Formation in Watersheds and Removal in Water Treatment

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Outline

• Intro & Definitions
• NOM Generation
  • The Hydrologic Cycle
  • Land vs Water sources
  • Compounds in NOM
• Water Treatment
  • Historical
  • Types of Treatment
  • Components or Processes
• Some current issues & popular books

NOM = Natural Organic Matter

It’s one of my favorite recipes. I call it NOM
What’s in the Water?

- Natural Substances
  - Natural Organic Matter (NOM)
  - Inorganic Substances (Iron, Manganese, sodium, chloride)
- Anthropogenic Substances
  - Pesticides
  - Organic Solvents & Other Industrial Compounds
  - Carcinogens
  - Pharmaceuticals
  - Endocrine Disrupting Compounds
  - Flame Retardants
- Pathogens and other microorganisms
NOM in Natural Waters: Some definitions

Groupings Based on Origin

- **autochthonous** compounds are created within the water body
- **allochthonous** compounds can originate from either the soil or from upstream water bodies
- **aquagenic**, substances originating from any water body
- **pedogenic** for substances originating from soil
Watershed Origins

Aquifer

Lake

Sediment & Gravel in Lake Bed

Algae

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Hydrologic Cycle

- **Three levels**
  - Surface runoff, overland flow, direct runoff
  - Interflow
  - Infiltration, percolation, groundwater flow
During dry periods: base flow

http://www.ec.gc.ca/water/images/nature/grdwtr/a5f2e.htm
NOM: Which is the bigger source?

- Allochthonous
  - land plants

or

- Autochthonous
  - Aquatic plants
Aquatic sources: Algae

- From: Plummer & Edzwald, 2001
  - [ES&T:35:3661]

![](image)

- Scenedesmus quadricauda
- Cyclotella sp.

~25% from EOM

pH 7, 20-24°C, chlorine excess
Terrestrial Sources: Leaching Experiments

Darleen Bryan’s study

White Pine
White Oak
Red Maple
Leaching of leaves

- More organic matter released as the leaves remain submerged.
- Ultraviolet (UV$_{254}$) absorbance measures a certain fraction.
- The ratio of UV$_{254}$ to dissolved organic carbon (DOC) concentration is called SUVA and reflects organic matter reactivity.

$$SUVA \equiv \left( \frac{UV_{254}}{DOC} \right) \times 100$$

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Composition of an “average” leaf

- 250 g/m²/yr EABP

Highly-colored

Some color
Plant biopolymers

- Cellulose
- Lignin
  - Phenyl-propane units
  - Cross-linked
  - Radical polymerization
  - Ill defined structure
- Hemicellulose
- Terpeniods
- Proteins
Tannins, Aromatic Acids and Phenols, cont.

• Lignin monomers

p-Hydroxybenzoic Acid

Vanillic Acid
Tannins, Aromatic Acids and Phenols

- About 0.5% of Total
- Plant Products
- Likely THM Precursors
- Source of Color & DBPs

Hydrolyzable Tannin

Condensed Tannin

Gallic Acid monomers

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Carbohydrates

- **empirical formula**: $C_x(H_2O)_y$

  Glucose (monosaccharide)  
  Cellulose (polysaccharide)

  Glucosamine (amino sugar)
Fatty Acids

- maybe 4% of DOC
- other mixed acids may account for 2%

At neutral pH’s most lose $\text{H}^+$

$\text{CH}_3\text{-COO}^-$

Common Volatile Fatty Acids in Natural Waters

Formic Acid    Acetic Acid    Propionic Acid
H-COOH        CH$_3$-COOH     CH$_3$-CH$_2$-COOH

Butyric Acid    Valeric Acid
CH$_3$-CH$_2$-CH$_2$-COOH   H$_3$-CH$_2$-CH$_2$-CH$_2$-COOH
Amino Acids and Proteins

- Simple Amino Acids
- Amine and acid groups

Polypeptides & Proteins
- Comprised of many AAs

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NOM Quantification: TOC & DOC

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

\[
C_aH_bN_cO_d + (a + \frac{b}{4} - \frac{d}{2})O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2
\]

**Oxidation**
- High Temperature Pyrolysis
- UV Irradiation
- Heated Persulfate
- UV/Persulfate
Concentrations: Pedogenic

- Land Sources
  - From Woody & non-woody plants
  - Depends on vegetation, soil, hydrology
  - Most biodegradable fractions are quickly lost
- Attenuated by adsorption to clay soils
- Parallel watersheds in Australia (Cotsaris et al., 1994)
  - Clearwater Creek, high clay content: 2.5 mg/L TOC
  - Redwater Creek, sandy soil: 31.7 mg/L TOC
Concentrations: Aquagenic

- Algal & aquatic plant Sources
  - Depend on nutrient levels / trophic state
- Concentrations in Lakes (mg/L) (Thurman, 1985)

<table>
<thead>
<tr>
<th>Trophic State</th>
<th>Mean DOC</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligotrophic</td>
<td>2</td>
<td>1-3</td>
</tr>
<tr>
<td>Mesotrophic</td>
<td>3</td>
<td>2-4</td>
</tr>
<tr>
<td>Eutrophic</td>
<td>10</td>
<td>3-34</td>
</tr>
<tr>
<td>Dystrophic</td>
<td>30</td>
<td>20-50</td>
</tr>
</tbody>
</table>

- Groundwater average: 0.7 mg/L
- No algae, much soil attenuation
John #I: Dr. John Snow

1813-1858

- Characterizing “the acute problem”
- Cholera
  - First emerged in early 1800s
  - 1852-1860: The third cholera pandemic
    - Snow showed the role of water in disease transmission
    - London’s Broad Street pump (Broadwick St)
    - Miasma theory was discredited, but it took decades to fully put it to rest

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Cholera in London & Dr. John Snow

• During an outbreak of cholera in London in 1854, John Snow plotted on a map the location of all the cases he learned of. Water in that part of London was pumped from wells located in the various neighborhoods. Snow's map revealed a close association between the density of cholera cases and a single well located on Broad Street.

• Removing the pump handle of the Broad Street well put an end to the epidemic. This despite the fact that the infectious agent that causes cholera was not clearly recognized until 1905.

• John Snow's map showing cholera deaths in London in 1854 (courtesy of The Geographical Journal). The Broad Street well is marked with an X (within the red circle).

http://www.ph.ucla.edu/epi/snow.html
Cluster Map of Fatal Cholera Cases in London, 1854

John #2: Dr. John L. Leal

- Solutions to “the acute problem”
  - Jersey City’s Boonton Reservoir
  - Leal experimented with chlorine, its effectiveness and production
    - George Johnson & George Fuller worked with Leal and designed the system (1908)

“Full-scale and continuous implementation of disinfection for the first time in Jersey City, NJ ignited a disinfection revolution in the United States that reverberated around the world”

M.J. McGuire, JAWWA 98(3)123
Chlorination

- 1-2 punch of filtration & chlorination

US Death Rates for Typhoid Fever


Today’s Conventional Treatment

- Coagulation & solids separation
  - Use of alum or another chemical coagulant
  - rapid mix, flocculation, settling, filtration
- Disinfection
  - including clearwell for contact time
- Most common sequence for surface water

Removes some of the NOM & suspended particles

Kills or inactivates pathogenic organisms

Diagram:
- raw water
- rapid mix
- flocculation
- settling
- filtration
- clearwell
- dist. sys.
Coagulation chemistry

Ferric Sulfate

\[ Fe_2(SO_4)_3 + 6\, OH^- \rightarrow 2Fe(OH)_3 \downarrow + 3\, SO_4^{2-} \]

Alum

\[ Al_2(SO_4)_3 \cdot 18H_2O \rightarrow 2\, Al(OH)_3 \downarrow + 3SO_4^{-2} + 6H^+ + 12H_2O \]

Mechanisms

• Precipitation of metal hydroxide, then:
  • Adsorption of contaminants
  • Enmeshment of particles
NOM removal by alum coagulation

- Impacts of pH and dose

Rennes IV Raw Water (France) 11/19/84
Reckhow & Bourbigot (unpublished data)
Flocculation

- An Empty full-scale rectangular flocculation tank in Southern CA

Can be done in the lab by slowly mixing your sample with a stirrer or on a shaking table.
Settling

- Circular and rectangular designs

Can be done in the lab by letting your sample sit in a jar quiescently.
Filtration

- Sand media
  - Empty filter, not in service (Cincinnati)
Chlorination

- Chlorine tanks
- Left side is currently feeding
- Right side is on reserve
Other Types: Ozone Plants

- Many types
  - Simplest type: ozone, non-filtration shown below
    - examples: MWRA (Boston), Portland ME
  - More complex: including coagulation & Filtration
    - examples: Andover MA, Amherst MA
  - Always includes final disinfection with chlorine or chloramines
Ozone

- Generator
- Diffusers

Can be done in the lab with a $70 fish tank sized ozone generator
Ultraviolet Light

- Waterloo, Ont
Membrane Treatment

- National City, CA
John #III: John Rook

- Chlorine: “the chronic problem”
  - Brought headspace analysis from the beer industry to drinking water
  - Found trihalomethanes (THMs) in finished water
    - Carcinogens !?!
  - Published in Dutch journal H2O, Aug 19, 1972 issue
  - Deduced that they were formed as byproducts of chlorination
  - Proposed chemical pathways

Reactions with Disinfectants: Chlorine

**HOCl**

+ **natural organics**

(NOM)

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**The Precursors!**

**Oxidized NOM**

and inorganic chloride

• Aldehydes

**Chlorinated Organics**

• TOX

• THMs

• HAAs

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**The THMs**

- Chloroform
- Bromodichloromethane
- Chlorodibromomethane
- Bromoform
Hours of transit time from the water filtration plant to your house.
Multiple Routes of Exposure

- Inhalation in the shower produces highest blood level and response is fast

Gordon et al., 2006 [Env. Health Persp.114:514-521]
Epidemiology

- Bladder Cancer
  - DBPs linked to 9,300 US cases every year
- Other Cancers
  - Rectal, colon
- Reproductive & developmental effects
  - Neural tube defects
  - Miscarriages & Low birth weight
  - Cleft palate
- Other
  - Kidney & spleen disorders
  - Immune system problems, neurotoxic effects

“I think you should be more explicit here in step two”
Observational: The DBP Iceberg

Halogenated Compounds

Non-halogenated Compounds

ICR Compounds

50 MWDSC DBPs

~700 Known DBPs

THMs, THAAs

DHAAs

Susan Richardson

Stuart Krasner

Halogenated Compounds

Non-halogenated Compounds

50 MWDSC DBPs

~700 Known DBPs

THMs, THAAs

DHAAs

Halogenated Compounds

Non-halogenated Compounds

ICR Compounds
Another

• Sandra Hempel
  • Journalist
• 2007 publication date
• Similar in many ways to Johnson’s book
Biography

- A serious biography
- 2003 publication
- Primarily written by MDs
Cholera & beyond

• Robert Morris
  • Environmental epidemiologist
  • 2007 publication date
• More comprehensive
  • Cholera to DBPs to Crypto
Lead Hazards

- 2006 publication date
- Werner Troesken
  - Professor of History
- Presents many historical lessons on society’s failure to balance public health with profit
The End