Lecture #40

**Limnology (cont.): Carbon & Precursor Models I**

(Scientific Literature)

---

**Full cycle analysis**

- Dishwashing detergent causes
  - Miscarriages
  - Birth defects
  - Cancer

  $\{ \text{137,000 at risk in US} \}$

- How?

See: [Gray et al., 2001](#) [Consider the Source, Environmental Working Group report]
National Distribution

- 241,000,000 people in US are served by PWS that apply a disinfectant

High THMs are levels of at least 80 ppb over a 3 month average

Gray et al., 2001 [Consider the Source, Environmental Working Group report]

New York Water Supply System Tunnels and Aqueducts

David Reckhow
Front half of cycle

- Causal pathways for eutrophication effects on water supplies

Watershed Variables
- Land use
- Morphometry
- Watershed Mgmt.
- Climate
- Geology
- Hydrology

Reservoir Eutrophication
- Nutrients
- Algae
- Transparency
- Oxygen Depletion

Raw Water Quality
- pH
- Turb.
- Odor
- Fe
- Mn
- Ammonia
- DOC
- Color
- Precursors

Treatment & DWS Mgmt.
- Filtration
- GAC
- Disinfection
- Doses
- Dist. Sys.
- Monitoring

Treated Water Quality
- Color
- Fe/Mn
- Odor
- DBPs
- Biodegradables

User Impacts
- Plumbing
- Clothing
- Aesthetics
- Disease
- Chronic Effects

Nature of NOM in Water

- Most systems are dominated by DOC
  - 85-98% of TOC

<table>
<thead>
<tr>
<th></th>
<th>Particulate</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autochthonous</td>
<td>Algae</td>
<td>Excretion or lysis of Littoral sources (macrophytes, attached microflora) and Pelagic sources (phytoplankton)</td>
</tr>
<tr>
<td>Allochthonous</td>
<td>Soil, terrestrial plant detritus</td>
<td>Soluble components from terrestrial plants; soil organics (fulvic acids)</td>
</tr>
</tbody>
</table>

Modified from: Walker, 1983
NOM Modeling

- An important current issue
  - Affects Drinking water treatment
  - Not well studied
- Bears similarities to N&P modeling
  - Natural and human sources
  - Biologically active (consumed & produced)
  - May be closely linked to primary productivity
  - Empirical & mechanistic approaches
- Complex
  - Many types of NOM, some produce DBPs, most don’t

Empirical Models: Algae and TOC

- Walker, 1983
  - Pointed out the long held knowledge that P and primary productivity (e.g., chlorophyll) were positively correlated
  - Also pointed out that primary productivity means more TOC
  - Tied this to drinking water reservoir management
  - Presented some new data showing this correlation in 38 US lakes

Empirical Models: P and C

- From Walker's paper
- Slightly better correlation than with Chl a
- Is this causal or just autocorrelation with another parameter
- autochthonous source for TOC?

Walker, 1983, *J. AWWA*, 75(1)38-42

Other Empirical Models: DBPs

- Disinfection byproduct (DPB) precursors
- Empirical modeling hypotheses:
  - P-loading controls P concentration
  - P concentration controls algal growth
  - algal growth control TOC
  - DBP precursors are a sub-fraction of TOC
  - Therefore, P-loading controls DBP precursors
Chapra et al., 1997

- Chapra, Canale & Amy
- Added more data to Walker's correlation
  - \( \text{TOC} = 0.55 \, \text{TP}^{0.655} \)
    - Where TOC is in mg/L.
    - TP is total phosphorus in µg/L

\[ \text{TOC} (\text{mg L}^{-1}) \]

\[ \text{TP} (\text{µg L}^{-1}) \]


---

Chapra et al., 1997 (cont.)

- Related this to THM precursor content
  - \( \text{THMFP} = 43.78 \, \text{TOC}^{1.248} \)
- Used data from:
  - Amy, Edzwald, Miller, Bader
- No quantitative assessment of uncertainty

\[ \text{THMFP} (\text{µg L}^{-1}) \]

\[ \text{TOC} (\text{mg L}^{-1}) \]

Chapra et al., 1997 (cont.)

- The next step that they chose not to take just yet was to combine the two models
  - THMFP = 20.8 TP^{0.79}
  - Probably not a good idea because the two models were from completely different data bases
  - Uncertainty in both models probably makes this an “order of magnitude” estimate
  - Perhaps the final step in this process is to combine with a THM formation model incorporating actual chlorination conditions

- Weaknesses
  - Does not account for allochthonous sources
  - No site-specific considerations
  - No spatial or temporal resolution

DBP Precursor Case Studies

- Deer Creek Reservoir, UT
  - 1981-83
    - Cook et al., 1984, White & Adams, 1985
- Lake Rockwell, OH
  - 1985-87
    - Palmstrom et al., 1988
- Lake Youngs, WA
  - 1992
    - Canale et al., 1997
- Cannonsville Reservoir, NY
  - 1995
    - Stepczuk et al., 1998a, b, c
- San Jaoquin Delta, CA
  - 1996
    - Fuji et al., 1998
- Cambridge Reservoirs, MA
  - 1997-98
    - Waldron & Bent, 2001
- Chickahominy River, VA
  - 1998
    - Speiran, 2000
- Boston Reservoirs, MA
  - 1997-2002
    - Garvey, Takiar, Bryan et al.
Deer Creek Reservoir Study

- TOC/THM Precursor Studies
  - Adams and others
- Deer Creek
  - Supply for Salt Lake City, UT
  - Meso-Eutrophic (impounded in 1941)
    - $P_{avg} = \text{?} \mu g/L$
  - Characteristics for 1985-87
    - Hydraulics
      - $H_{mean} = 48.4 \text{ m}$
      - $V = 193.9 \times 10^6 \text{ m}^3$
      - $\tau_{mean} = 6 \text{ months}$
      - $SA = 2787 \text{ ac} = 11.28 \times 10^6 \text{ m}^2$
      - $DA = 1451 \times 10^6 \text{ m}^2$

White & Adams, 1985; UWRL Report #Q-85/01

Deer Creek Res.: Loading

- Loading
  - $\text{TOC} = \text{?} \times 10^3 \text{ kg/yr}$
  - $P = \text{?} \times 10^3 \text{ kg/yr}$

Tributary Concentrations

Approx. Reservoir Concentration
Deer Creek Res: Microcosms

- Impact of:
  - Light
  - Phosphorus
  - sediments

Deer Creek Res.: Conclusions

- Reservoir/Tributary Studies
  - No change in THMFP across reservoir (in vs. out)
  - THMFP concentrations in tributaries were greatest in June and lowest in November
  - No correlation between TOC and THMFP

- Microcosm Studies
  - Sediments had no effect on THMFP
  - Algal activity (light) resulted in higher THMFP
  - Elevated P resulted in higher THMFP
  - Algal growth products were more important than decay products
  - Application of CuSO₄ had no impact
  - No correlation between TOC and THMFP
Lake Rockwell Study

- THM Precursor Budget
  - Palmstrom, Carlson & Cooke
- Lake Rockwell
  - Supply for Akron, OH
  - Very Eutrophic (impounded in 1919)
  - \( P_{\text{avg}} = 50 \ \text{µg/L} \)
- Characteristics for 1985–87
  - Hydraulics
    - \( H_{\text{mean}} = 3.9 \ \text{m} \)
    - \( V = 10.2 \ \text{x10}^6 \ \text{m}^3 \)
    - \( \tau = 20 \ \text{d} \)
    - \( SA = 31 \ \text{ha} = 3.1 \ \text{x10}^6 \ \text{m}^2 \)
  - Loading
    - THMFP = \( 3.14 \times 10^2 \ \text{kg/yr} \)
    - \( P = 2.8 \times 10^3 \ \text{kg/yr} \)

Palmstrom et al., 1988, Lake & Res. Mgmt., 4(2)1-15

Input-output for 1985

- Low levels in winter
  - 160 µg/L average
- Increase across reservoir in early summer
  - ~ 30% increase

Palmstrom et al., 1988, Lake & Res. Mgmt., 4(2)1-15
Sometimes increase across reservoir in early summer
- ~30% increase on average
- Seen in 1985 and 1986

Sometimes no increase
- 1987

Input-output for 1986-87

Microcosm studies with
- Artificial lake water (control)
- Sediments & water
- Macrophytes, sediments & water

Macrophyte Growth
Macrophyte Degradation

- *Myriophyllum spicatum*
- Degradation in the dark
- Precursors released only under aerobic conditions

Palmstrom et al., 1988, *Lake & Res. Mgmt.*, 4(2)1-15

Release from Sediments

- Aerobic
  - High production
- Anaerobic
  - Far less production

Sediment Release (cont.)

- Summary of rate experiments
  - µg THMFP/m²/day

![Graph](image)


Model

- No mention of biodegradation of THM precursors
- Used site-specific macrophyte data

![Diagram](image)

Palmstrom et al., 1988, *Lake & Res. Mgmt.*, 4(2)1-15
Estimated Loadings

<table>
<thead>
<tr>
<th></th>
<th>Palmström et al., 1988</th>
<th>Martin et al., 1993</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modeling results</td>
<td></td>
<td>Re-evaluated some of the earlier data</td>
</tr>
<tr>
<td>Riverine</td>
<td>47</td>
<td>63-204</td>
</tr>
<tr>
<td>Macrophyte</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Degradation</td>
<td>22</td>
<td>0.08-2.1</td>
</tr>
<tr>
<td>Active growth</td>
<td>0.85</td>
<td>0.82</td>
</tr>
<tr>
<td>Sediments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Littoral</td>
<td>0.014</td>
<td>0.26</td>
</tr>
<tr>
<td>Profundal</td>
<td></td>
<td>0.23</td>
</tr>
<tr>
<td>Algae</td>
<td>0.1-100</td>
<td>21-103</td>
</tr>
</tbody>
</table>

Palmström’s algae loading based on a single net algal carbon production rate (0.33 g/m²/d) and a fixed THM/TOC ratio from the literature (Hoehn et al., 1980)

Lake Youngs Study

- Mechanistic Carbon Model
- Canale, Chapra, Amy & Edwards
- Lake Youngs
  - Supply for Seattle, WA
  - Oligotrophic (impounded in 1923)
  - Characteristics for 1992
    - Hydraulics
      - $H_{\text{mean}} = 14.7$ m
      - $H_{\text{max}} = 30.5$ m
      - $V = 41.6 \times 10^6$ m³
      - $\tau = 125$ d
      - $SA = 2.83 \times 10^6$ m²
    - Loading
      - Total C = $2.38 \times 10^3$ kg/yr
      - P = $1.12 \times 10$ kg/yr

Mechanistic Development

- 3 Carbon types
  - DOC (decays)
  - Allochthonous
  - Autochthonous
  - PrOC (settles)
- Processes excluded
  - based on Lake Rockwell papers
  - Macrophyte release of DOC
  - Sediment DOC release set to zero

Parameter Estimation

- Site-specific measurements (2)
  - Settling rate
  - Sediment traps used
  - THMFP yield
- Other parameters (14)
  - Literature values
  - With "model calibration"
  - Included some use of in-situ algal data

---

**TABLE 1. Kinetic Coefficient Values for Lake Youngs THMFP Model**

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value (2)</th>
<th>Basis (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setting velocity</td>
<td>46 m/hr</td>
<td>Experiments (1991, 1994)</td>
</tr>
<tr>
<td>Algal maximum growth rate</td>
<td>1.5 d^{-1}</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Algal respiration</td>
<td>0.25 d^{-1}</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Light half-reaction</td>
<td>200 μgO₂/m²/day</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Phosphorus half-reaction</td>
<td>0.1 mgP/m³</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Zooplankton grazing</td>
<td>1.51 mg/100 C with 0.075 N</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Zooplankton respiration</td>
<td>0.5</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Grazing efficiency</td>
<td>0.2 mg/TOC</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Algal carbon half-reaction</td>
<td>1 mg/TOC</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Sediment P release</td>
<td>0.3 g/TOC</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Sediment oxygen demand</td>
<td>0.3 g/TOC</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>TOC oxidation</td>
<td>0.052 mg/L</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Resistant TOC</td>
<td>0.5 mg/L</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>0.025 mg/L</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
<tr>
<td>Respiration</td>
<td>0.2 mg/L</td>
<td>Bowie et al., 1985, model calibration</td>
</tr>
</tbody>
</table>

Used the same fixed
THMFP:TOC relationship as in Chapra et al., 1997
Resolution

- **Spatial**
  - 2 vertical layers

- **Temporal**
  - Time variable for
    - Temperature
      - Determines vertical exchange coefficient
    - Light
    - Flow
    - loading

---

Algae


David Reckhow  CEE 577 #40
TOC & FP

- TOC and D.O. models

- THMFP = 0.25*TOC


Sources

- Based on existing loading & P levels

- Based on hypothetical elevated P and low TOC loading

Dissolved Autochthonous/Allochthonous = 0.1-0.5

Implications

<table>
<thead>
<tr>
<th>Total P</th>
<th>Loading conditions</th>
<th>Days of Violations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>TOC (2)</td>
<td>Surface waters (3)</td>
</tr>
<tr>
<td>Current</td>
<td>Current</td>
<td>79</td>
</tr>
<tr>
<td>Decrease (90% reduction)</td>
<td>Current</td>
<td>66</td>
</tr>
<tr>
<td>Current</td>
<td>Decrease (25% reduction)</td>
<td>0</td>
</tr>
<tr>
<td>Increase (double)</td>
<td>Current</td>
<td>91</td>
</tr>
<tr>
<td>Current</td>
<td>Increase (25% increase)</td>
<td>114</td>
</tr>
<tr>
<td>Increase (double)</td>
<td>Decrease (25% reduction)</td>
<td>34</td>
</tr>
</tbody>
</table>


- Leaching of NOM from litterfall, soils etc.
• To next lecture