Biogeochemistry of C

NREM 665

- CO$_2$ diffusion
- CH$_4$ ebullition
- DOC methanogenesis
- Organic-C accretion
- CO$_2$ photosynthesis
- CO$_2$ respiration
- CH$_4$ methane-oxidation
# C Biogeochemistry

## I. Forms of C in WTLs & Coastal Ecosystems

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Oxidation State</th>
<th>Form/Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide, CO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane, CH$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate, CO$_3^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bicarbonate, HCO$_3^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonic Acid, H$_2$CO$_3$</td>
<td></td>
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</tr>
</tbody>
</table>

Operationally-defined forms of C:

- Dissolved org. C (DOC) <0.7 µm
- Particulate org. C (POC) >0.7 µm

- Plant biomass, microbial biomass, litter, soil C
Carbonate Buffer System

\[ \text{CO}_2 + \text{H}_2\text{O} \overset{\text{H}_2\text{CO}_3}{\rightleftharpoons} \text{H}^+ + \text{HCO}_3^- \overset{\text{2H}^+ + \text{CO}_3^{2-}}{\rightleftharpoons} \]

Figure 1. Percentage of total carbon dioxide in each of its three forms in water as a function of pH. The vertical broken lines indicate the approximate pH range of seawater.
II. **Aerobic** conditions: PSN & Resp. **dominant** rxns

A. \(6\text{CO}_2 + 12\text{H}_2\text{O} + \text{light} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 + 6\text{H}_2\text{O}\)

B. \(\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy}\)

C. **C storage = Production– Decomposition**
Ratio of aboveground to belowground biomass can range from 0.2 to 3.9 (Gopal & Massing 1990)
1. Decomp inhibited in flooded soils → high C storage in WTLs, SGBs

2. NPP, Decomp, C storage vary across WTL types
   
a. due to climate, hydrology, veg type, soil type, nutrient availability, microbial community/activity, etc.

   b. lability of FW marsh litter    TSM litter

3. Litter/detritus processing in WTLs/SGBs is complex: involves microbes, shredders, deposit feeders, filter feeders, release of DOC & POC
Decomposition of Freshwater Marsh Vegetation

Figure 9–5. The rate of decay of leaves of Zizania aquatica, Pontederia cordata, Sagittaria latifolia, and Nuphar luteum as shown by the amount of material (ash free dry weight) remaining with time in submerged litterbags. Each data point represents four replicates. (From W. E. Odum and Heywood, 1978; copyright © 1978 by Academic Press, reprinted with permission)
Sagittaria latifolia
(arrowhead, duck potato)

Pontederia cordata
(pickerelweed)
Nuphar advena  (yellow pond lilly)
http://plants.ifas.ufl.edu/nulupic.html

Zizania aquatica
Wild-rice
Photo by Ann Murray
Copyright 1999 University of Florida

http://aquat1.ifas.ufl.edu/zizaqu1m.jpg
Decomposition of Salt Marsh Vegetation

![Graph showing decomposition rates of different species of Spartina over time.](image)

- **Juncus**
- **S. Spartina**
- **M. Spartina**
- **T. Spartina**

**LSD**.05 = 14.60

(McKee & Seneca 1982)
**Spartina alterniflora**
(saltmarsh cordgrass)

**Juncus roemerianus**
(black needlerush)
Regulators of Decomposition (Reddy & DeLaune 2008)
Figure 13: Decomposition & burial of OM (Reddy & DeLaune 2008)

- Detrital plant biomass
- Detritus
- Peat
- Decomposition & burial of OM
  - Decomposition
  - Burial
  - Compaction

Water table

III. **Anaerobic** conditions: Fermentation (Ferm) & Methanogenesis (MTG) dominant

A. Ferm occurs when organic matter is TEA in **anaerobic respiration**

1. \( \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{CH}_3\text{CH}_2\text{OCOOH} \) (Ferm) \( \Delta G^o = 239 \text{ kJ mol}^{-1} \)

2. \( \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{CH}_3\text{CH}_2\text{OH} + 2\text{CO}_2 \) (Ferm) \( \Delta G^o = 122 \text{ kJ mol}^{-1} \)
B. MTG occurs when methanogens use $\text{CO}_2$ (or other simple C compounds) as TEA in respiration & produce $\text{CH}_4$

1. $\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \Rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

2. $\text{CH}_3\text{COO} + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_4 + 2\text{H}_2\text{O}$

3. MTG rates:

   a. summer $\gg$ winter in temperate zones, less seasonal var. in tropics

   b. $f$(flood freq. & duration, pres/abs of veg)

   c. permanently flooded $\gg$ intermittently flooded

Figure 5.14: Comparison of methane emission rates from Florida (subtropical) and Minnesota (temperate with cold winters), and model results that attempted to simulate both conditions. (After Cui et al., 2005.)
4. MTG in FW WTLs >> MTG in tidal WTLs?

a. 

b. C flux in GA salt marsh vs WI lake sed (M&G 2000)

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Salt Marsh gC m(^{-2}) yr(^{-1})</th>
<th>Lake Sediment gC m(^{-2}) yr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic Respiration</td>
<td>361</td>
<td>—</td>
</tr>
<tr>
<td>Nitrate Reduction</td>
<td>5</td>
<td>8(^a)</td>
</tr>
<tr>
<td>Fermentation-Sulfate Reduction</td>
<td>432</td>
<td>61</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>6</td>
<td>254</td>
</tr>
<tr>
<td>Total</td>
<td>804</td>
<td>—</td>
</tr>
</tbody>
</table>
IV. CH$_4$ oxidation: Methanotrophs convert CH$_4$ to methanol, formaldehyde, & CO$_2$

\[ \text{CH}_4 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{HCHO}^- \rightarrow \text{HCOOH} \rightarrow \text{CO}_2 \]

1. CH$_4$ produced @ depth oxidized by methanotrophs @ surface (↓CH$_4$ flux)
2. Net CH$_4$ emission = $f$(methanogenesis – methane oxidation)

a. rates of CH$_4$ emission for different wetland types

<table>
<thead>
<tr>
<th>Wetland Type</th>
<th>Boreal</th>
<th>Temperate</th>
<th>Subtropical/Tropical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tundra</td>
<td>3.7–1,500 (12)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bog</td>
<td>0.7–17 (5)</td>
<td>20–221 (7)</td>
<td>—</td>
</tr>
<tr>
<td>Fen</td>
<td>14–325 (11)</td>
<td>3–314 (8)</td>
<td>—</td>
</tr>
<tr>
<td>Freshwater marsh</td>
<td>23–80 (2)</td>
<td>0.1–498 (17)</td>
<td>29–443 (7)</td>
</tr>
<tr>
<td>Forest swamp</td>
<td>5–66 (2)</td>
<td>7.4–106 (6)</td>
<td>44–144 (7)</td>
</tr>
<tr>
<td>Rice paddy</td>
<td>—</td>
<td>10–880 (34)</td>
<td>47–486 (9)</td>
</tr>
<tr>
<td>Salt marsh</td>
<td>—</td>
<td>0–109 (17)</td>
<td>2.5 (1)</td>
</tr>
<tr>
<td>Mangrove</td>
<td>—</td>
<td>—</td>
<td>3–61 (3)</td>
</tr>
</tbody>
</table>

Figure 5.12 The carbon cycle in wetlands. Major pathways illustrated are photosynthesis, respiration, fermentation, methanogenesis, and methane oxidation (anaerobic and aerobic). Also indicated are the roles of sulfate and nitrate reduction in the carbon cycle.
### Long-term Accumulation of Organic Matter in Selected Wetlands

<table>
<thead>
<tr>
<th>Wetland</th>
<th>Location</th>
<th>C Accumulation (g m⁻² yr⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everglades Typha sp.</td>
<td>Florida</td>
<td>163-387 86-140</td>
<td>Reddy et al. 1993</td>
</tr>
<tr>
<td>Cladium sp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt Marsh</td>
<td>Louisiana</td>
<td>200-300</td>
<td>Hatton et al. 1993</td>
</tr>
<tr>
<td>Mangrove</td>
<td>Mexico</td>
<td>100</td>
<td>Twilley 1992</td>
</tr>
<tr>
<td>Cypress Swamp</td>
<td>Georgia</td>
<td>45</td>
<td>Cohen 1974</td>
</tr>
<tr>
<td>Peatland</td>
<td>Alaska</td>
<td>22-122</td>
<td>Billings 1987</td>
</tr>
<tr>
<td>Bog</td>
<td>Wisconsin</td>
<td>34-75</td>
<td>Kratz &amp; Dewitt 1986</td>
</tr>
</tbody>
</table>
3. C sinks in WTLs

   a. **Short-term**: immob, herb. plant & algal production

   b. **Long-term**: woody production, C seq. in soil/sediment

V. C Cycling in Tidal WTLs vs FW WTLs

   A. Tidal WTLs have high prod & frequent tidal exchange → export higher amounts of C than FW WTLs
VI. Case Study: Are *Phragmites*-dominated wetlands a net source or net sink for greenhouse gases?

(Brix et al. 2001)
C cycling in wetlands

- Photosynthesis: CO$_2$ (photosynthesis)
- Respiration: CO$_2$ (respiration)
- Methane-oxidation: CH$_4$ (methane-oxidation)
- Methanogenesis: DOC (methanogenesis)
- Diffusion & ebullition: CO$_2$ (diffusion & ebullition)
- Diffusion & ebullition: CH$_4$ (diffusion & ebullition)

Organic-C accretion
CO$_2$ & CH$_4$ dynamics in a *Phragmites*-wetland

(Brix et al. 2001)
Phragmites wetland:
Units: mol m\(^{-2}\) year\(^{-1}\)

CO\(_2\) photosynthesis

45 CO\(_2\)

4 CH\(_4\)

98 CO\(_2\) diffusion & ebullition

49 Organic-C accretion

14 methane-oxidation

18 methanogenesis

DOC methanogenesis

(Brix et al. 2001)
Phragmites C budget:

- Net CO₂ Assimilation: 98 mol m⁻² yr⁻¹
- CO₂ Emission: 45 mol m⁻² yr⁻¹
- CH₄ Emission: 4 mol m⁻² yr⁻¹

- Net C Fixation: 98 - 45 - 4 = 49 mol m⁻² yr⁻¹

- Ratio CH₄ Emission:Net C Fixation: 0.08
The ratio of CH$_4$ released to annual net C fixed varies generally from 0.05 to 0.13 (Whiting & Chanton 1997)
Question:

Are wetlands a net source or a net sink for greenhouse gases?

Answer:

Depends on the ratio of CH$_4$ emitted to annual net C fixed & time scale evaluated.
Greenhouse effect as a function of time scale

- Wetlands may be sources of GHGs on short time scales (<10 yr) but sinks over longer time scales (>100 yrs). Lower the ratio, sooner a site becomes a sink (Brix et al. 2001).
VII. C Biogeochemistry Conclusions

A. **Major processes**

**Production:** Fixation of C from atmosphere via PSN

**Decomposition:** Conversion of complex molecules into simpler molecules via activities of aerobes & anaerobes

**Fermentation:** Use of organic matter as TEA in anaerobic respiration

**Methanogenesis:** Bacteria use CO$_2$ as TEA in anaerobic respiration

**CH$_4$ Oxidation:** Methanotrophs convert CH$_4$ to methanol, formaldehyde, & CO$_2$ in aerobic surface soil zones

B. **Although WTLs cover ~ 7% of Earth’s land area, they have a disproportionate effect on global C cycle**