Carbonate Buffer System

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

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 sea water.
Major Components of the C Cycle

**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

\[
C_6H_{12}O_6 \rightarrow 2CH_3CH_2OCOOH \quad \text{Or} \quad C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2
\]

**Methanogenesis:**
Bacteria use CO\(_2\) as TEA in anaerobic respiration

\[
CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O
\]

**CH\(_4\) Oxidation:**
Methanotrophs convert CH\(_4\) to methanol, formaldehyde, & CO\(_2\) in aerobic surface soil zones
Ratio of aboveground to belowground biomass can range from 0.2 to 3.9 (Gopal & Massing 1990)
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

http://plants.usda.gov/
Nuphar advena
(Nuphar lutea ssp. advena)
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

(McKee & Seneca 1982)
Spartina alterniflora, saltmarsh cordgrass

Juncus roemerianus, black needlerush
Regulators of Decomposition (Reddy & DeLaune 2008)
Decomposition & burial of OM (Reddy & DeLaune 2008)

- Detrital plant biomass

- Water table

- Detritus

- Peat

- Decomposition

- Burial

- Compaction
## 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</td>
<td>Florida</td>
<td>163-387</td>
<td>Reddy et al. 1993</td>
</tr>
<tr>
<td>Typha sp.</td>
<td></td>
<td>86-140</td>
<td></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>
Methanogenesis

- Bacterially-mediated utilization of C as TEA in anaerobic respiration

<table>
<thead>
<tr>
<th>Table 6-4 Ranges of mean methane emission rates (number of sites/treatments) for major wetland types</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ Emission Rates (mg C m⁻² day⁻¹)</td>
</tr>
<tr>
<td>Boreal</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td><strong>FRESHWATER WETLANDS</strong></td>
</tr>
<tr>
<td>Tundra</td>
</tr>
<tr>
<td>Bog</td>
</tr>
<tr>
<td>Fen</td>
</tr>
<tr>
<td>Freshwater marsh</td>
</tr>
<tr>
<td>Forest swamp</td>
</tr>
<tr>
<td>Rice paddy</td>
</tr>
<tr>
<td><strong>SALTWATER WETLANDS</strong></td>
</tr>
<tr>
<td>Salt marsh</td>
</tr>
<tr>
<td>Mangrove</td>
</tr>
</tbody>
</table>

*Source: Mitsch and Wu (1995).*
Table 5–5. Carbon Dioxide Release, gC m⁻² yr⁻¹ from Mineralization of Organic Matter in a New England Salt Marsh and Wisconsin Freshwater Lake Sediments

<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>8ᵃ</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>

ᵃEstimated from previous study

Sources: Ingvorsen and Brock, 1982; Howes et al., 1984, 1985
Global Warming Potential (GWP)

<table>
<thead>
<tr>
<th>Greenhouse gas</th>
<th>Time Horizon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 years</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>1</td>
</tr>
<tr>
<td>Methane</td>
<td>62</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>275</td>
</tr>
<tr>
<td>CFC-12</td>
<td>7900</td>
</tr>
<tr>
<td>HCH-22</td>
<td>4300</td>
</tr>
</tbody>
</table>

http://www.ace.mmu.ac.uk/eae/Global_Warming/Older/GWPs.html
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.
Case Study: Are *Phragmites*-dominated wetlands a net source or a net sink for greenhouse gases?

(Brix et al. 2001)
Carbon cycling in wetlands

- Photosynthesis: CO$_2$ to CH$_4$
- Diffusion & ebullition: CO$_2$ to CH$_4$
- Methane-oxidation: CH$_4$ to CO$_2$
- Methanogenesis: CO$_2$ to CH$_4$
- Respiration: DOC to CO$_2$
- Organic-C accretion
CO\textsubscript{2} & CH\textsubscript{4} dynamics in a \textit{Phragmites}-wetland

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

- Photosynthesis: 98 mol m$^{-2}$ year$^{-1}$
- Diffusion & ebullition: 4 mol m$^{-2}$ year$^{-1}$
- Methane-oxidation: 14 mol m$^{-2}$ year$^{-1}$
- Methanogenesis: 18 mol m$^{-2}$ year$^{-1}$

Organic-C accretion: 49 mol m$^{-2}$ year$^{-1}$

(Brix et al. 2001)
Phragmites Carbon budget:

- Net CO$_2$ Assimilation: 98 mol m$^{-2}$ yr$^{-1}$
- CO$_2$ Emission: 45 mol m$^{-2}$ yr$^{-1}$
- CH$_4$ Emission: 4 mol m$^{-2}$ yr$^{-1}$

- Net C Fixation: 98 - 45 - 4 = 49 mol m$^{-2}$ yr$^{-1}$

- Ratio CH$_4$ 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

- **Net Global Warming Effect (relative unit)**
  - Y-axis range: 0 to 4
  - Key points: 0.20, 0.05

- **Number of years**
  - X-axis range: 0 to 100
  - Key points: 0, 10, 20, ..., 100

- **Ratio between CH₄ emitted and net C fixed**
  - 0.20

- **Graph Description**
  - 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).

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