Readings: Seitzinger & Mayorga (2008)
Jeandel et al. (2011)
Outline

1. Global coastal zone
2. Nutrient loading in estuaries
3. Coastal eutrophication
4. Estuarine sediments, salt marshes
5. LOICZ modeling
The Global Coastal Ocean
A Narrow, Uneven, Chemically Reactive “Ribbon”

- ~500,000 km long and averages about 50 km in width
- 5% of global ocean
- Most materials entering the ocean from land pass through this ribbon
- Most net biogeochemical reaction is thought to occur in the landward, estuarine portion
Nutrient Loading in Estuaries

- Nutrient concs naturally higher in river water than open-ocean water
- Further elevated by human activities in the watersheds (e.g., agriculture, fertilizer runoff)
- Also elevated by local inputs to the estuaries (e.g., human waste discharge, street runoff)
- Estuary systems respond to nutrient loads
Primary Production Response to N Loading

**Figure 8.14** Annual phytoplankton productivity in estuaries as a function of the new inputs of nitrogen to their waters. From Boynton et al. (1982).
Estuarine Nitrogen Budgets

• Pristine river waters generally have low levels of bioavailable N (NO\textsubscript{3} and NH\textsubscript{4})

• Bioavailable N is stripped from river water as it passes over salt marshes (discussed later)

• N-filtering by salt marshes is so efficient, rainfall can be a significant contributor to estuarine waters

• Most of the bioavailable N in estuaries is not new, but is recycled from mineralization of OM within estuarine water column and sediments

• Cessation of excess nutrient input may not have immediate effect -- because of sediment storage of N and P. Thus, bottom sediments can be a source of N and P long after pollutant input ceases.
Nutrient Loading and Coastal Eutrophication

- Increases in nutrients in rivers (usually due to high levels of N and P from agricultural fertilizer use in the watershed) result in enhanced nutrient transport to estuaries.

- Excess nutrients promote excessive primary productivity, which leads to a greater input of reactive OM to sediments.

- Summer stratification segregates bottom waters from surface waters, and bottom waters become depleted in O$_2$.

Global distribution of 400+ systems that have reported eutrophication-associated dead zones. Their distribution in the Northern Hemisphere matches the human footprint.

(Diaz & Rosenberg 2008)
Gulf of Mexico
The Original Poster-Child of Hypoxia

Areal extent of *bottom water hypoxia* (<2 mg/L)

1988 – drought
1993 – flood
Low $O_2$ has caused extreme biogeochemical shifts in the highly productive, commercially important Louisiana Shelf.
Figure S1. Cumulative increase in dead zones through time reported in the scientific literature. Systems are grouped by decade of first documented account (Table S1). The number of dead zones started to approximately double every ten years starting in the 1960s.

Diaz and Rosenberg (2008)
Sediments in Estuaries

- Big rivers (e.g., Amazon, Mississippi, Columbia, etc), and smaller rivers with little or no estuary area, discharge most of their sediment to the open continental shelf or the upper slope
  - This is the fate of most global river sediment discharge

- BUT the sediment in smaller rivers with significant estuaries is trapped in those estuaries because of slow water flow
  - This is what happens along most of the world coastlines

- Sediment reactions in estuaries and elsewhere differ from water column reactions because of low redox conditions in the sediments
**Salt Marshes**

**Definition**: A relatively flat intertidal area along the margin of an estuary where fine-grained sediment is deposited and salt-tolerant grasses grow.

Salt marshes are among the most biologically active areas on earth.
Salt Marshes - Geomorphology

Extent of channelization depends on the tidal range (more tide → more channels)
Tide-induced flushing, combined with groundwater flow from land, leads to large amounts of import & export with tidal creeks.
• Tidal flows:
  • **low tide** - low salinity flow due to flushing of marsh by freshwater runoff from land
  • **high tide** - marsh is inundated with seawater, highest salinities observed

• Salt marsh soils undergo daily cycle of changing aeration and, thus, redox state:
  • **high tide** - soils are inundated, anaerobic conditions may develop
  • **low tide** - soils drain, high redox potential re-established in surface sed

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**Figure 8.9** Schematic cross section through a salt marsh, showing the relationship between various components of the salt marsh ecosystem and the open waters of the estuary. From Wiegert et al. (1981).
Salt marsh vegetation exists in dynamic equilibrium between rate of sediment accumulation and rate of sea level rise (or coastal subsidence):

- As deposits accumulate, erosion and OM oxidation increase, slowing rate of further accumulation
- As sea level rises, marsh is inundated more frequently, and accumulation rate of sediment and peat increases

When rate of sedimentation does not kept up with sea-level rise, marshland is lost.

Thus, sea-level rise due to global warming could accelerate loss of marshland
Salt Marshes as Filters and Transformers of Nutrients

• Salt marshes receive NO$_3^-$ from rivers and groundwater, and convert it to DON, PON, NH$_4^+$, and N$_2$

• Despite long-term storage of OM, most salt marshes are sources of C, N and P to estuaries
Salinity Effects on Salt Marsh Biogeochemistry

Salt marshes can exist over a wide range of salinities (and, thus, sulfate content), so there will be large variations in the biogeochemistry of different marshes:

<table>
<thead>
<tr>
<th>Organic matter oxid</th>
<th>Oxidant</th>
<th>Reductant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic oxidation</td>
<td>O₂</td>
<td>H₂O</td>
</tr>
<tr>
<td>Manganese reduction</td>
<td>MnO₂</td>
<td>Mn²⁺</td>
</tr>
<tr>
<td>Nitrate reduction</td>
<td>HNO₃</td>
<td>N₂</td>
</tr>
<tr>
<td>Iron reduction</td>
<td>Fe₂O₃</td>
<td>Fe⁺²</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>SO₄²⁻</td>
<td>S₂⁻</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>CO₂</td>
<td>CH₄</td>
</tr>
</tbody>
</table>

Figure 8.11 Annual methane lost from salt marsh soils as a function of salinity. From Bartlett et al. (1987).
Land-Ocean Interactions in the Coastal Zone (LOICZ)
Biogeochemical Budget Models

Globally applicable method of modeling estuaries

- Minimal data requirements
- Ability to work with secondary data
- Widely applicable, uniform methodology
- Informative about CNP processes and fluxes
LOICZ Budgeting Procedure

LOICZ budgeting assumes that materials are conserved.

Difference between $\sum\text{inputs}$ and $\sum\text{outputs}$ are explained by the processes within the system:

\[
[\sum (\text{sources} - \text{sinks})]
\]
Outline of the procedure

I. Define the physical boundaries of the system of interest

II. Calculate water and salt balances to determine physical dynamics

III. Estimate nutrient balances

IV. Derive the apparent net biogeochemical processes
Water, Salt and “Stoichiometrically Linked” Nutrient Budgets

- Water and salt budgets are used to estimate water exchange in coastal systems
- Departure of nutrient budgets from conservative behavior measures “system biogeochemical fluxes”
- Nonconservative DIP flux is assumed proportional to \((\text{primary production} - \text{respiration})\)
- Mismatch from “Redfield expectations” for DIP and DIN fluxes is assumed proportional to \((\text{nitrogen fixation} - \text{denitrification})\)
Schematic for a Single-box Estuary

Assume steady state
DIP Balance Illustration
Subic Bay, Philippines

\[ \Delta \text{DIP} = -2115 \]

Fluxes in $10^3$ mole yr$^{-1}$

- Residual flux = -544
- Ocean mixing = 2,367
- Rivers = 261
- Groundwater = 1
- Other fluxes = 30 (e.g., wastewater, aquaculture)

(e.g., wastewater, aquaculture)
Stoichiometric Calculations

\[(p-r) = -\Delta DIP \cdot 106(C:P)\]

\[= -(-2115) \cdot 106\]

\[= +224,190 \times 10^3 \text{ mole yr}^{-1}\]

Bay area = 306 km\(^2\)

\[= +2 \text{ mmol m}^{-2} \text{ day}^{-1}\]

\[(nfix-denit) = \Delta DIN_{\text{obs}} - \Delta DIN_{\text{exp}}\]

\[= \Delta DIN_{\text{obs}} - (\Delta DIP \cdot 16(N:P))\]

\[= 15,780 - (-2115 \cdot 16)\]

\[= +49,620 \times 10^3 \text{ mole yr}^{-1}\]

\[= +0.4 \text{ mmol m}^{-2} \text{ day}^{-1}\]

**Note:** Derived net processes are *apparent* net performance of the system. Non-biological processes may be responsible for some of the nutrient uptake or release.
Two-layer Water and Salt Budgets

- Evaporation
- Precipitation
- Surface Flow
- Runoff
- Entrainment
- Mixing
- Deep Water Flow
Latitude, Longitude of Budget Sites

Poor cover at high latitudes (N & S)
Poor cover from 10°N to 15°S
Poor cover in Africa
Net Ecosystem Metabolism

(Production – Respiration)

Rates are apparent, based on stoichiometric assumptions.

No clear overall trend; most values cluster near 0.

Extreme values (beyond ± 10) are questionable.
As Primary Production Increases, Respiration Tends to Exceed Production

Apparently reflects importance of sedimentary organic matter loading

Figure 1. Relationship between primary production ($P$) and net ecosystem metabolism ($P-R$) for the 22 estuarine and continental shelf sites listed in Table 5.
Nitrogen Fixation – Denitrification

Although values cluster near 0, clear dominance of apparent denitrification.

Apparent N fixation >5 seems too high.
Estuaries – Summary

• Water flow slows as rivers enter estuaries, and exchange via mixing with the coastal ocean becomes important

• Salinity changes occur and are accompanied by changes in chemistry (nutrients, pH, O₂, redox, etc.)

• Sediment trapping (and subsequent organic matter oxidation) occurs because of slowed flow

• Nutrient (N and P) and organic loads to estuaries are typically high and are often influenced by human sources

• Estuarine primary production is typically elevated, but estuaries may be either net autotrophic or heterotrophic