

# **Estuaries: Classification, Mixing, and Coastal Biogeochemistry Part II**

**OCN 623 – Chemical Oceanography  
07 Apr 2016**

# Mixing Curve

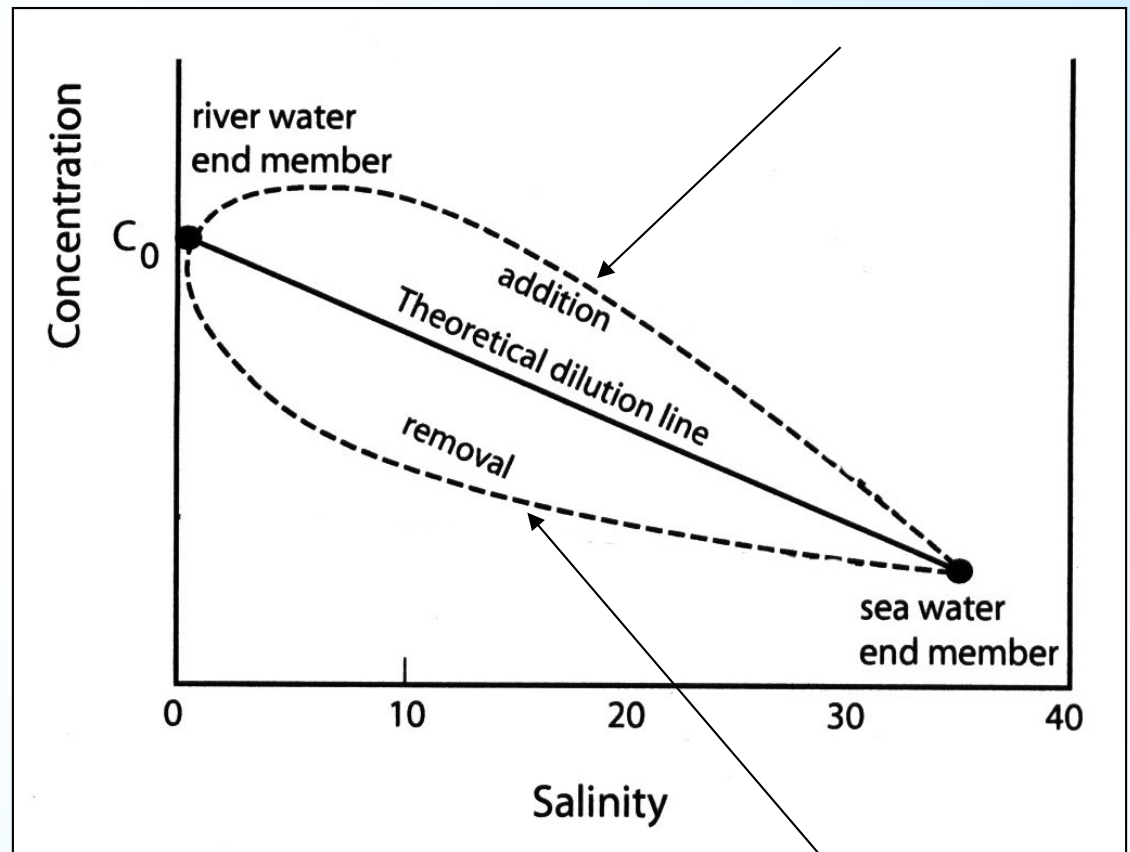
Salinity is a conservative constituent in estuaries and is a good indicator of mixing

Constituent plotted against salinity to determine if distribution is attributable to mixing processes (as opposed to non-conservative processes; nutrient uptake, flocculation, biodegradation, etc.)

If concentration vs. salinity is LINEAR, then the chemical/particle exhibits *conservative* behavior

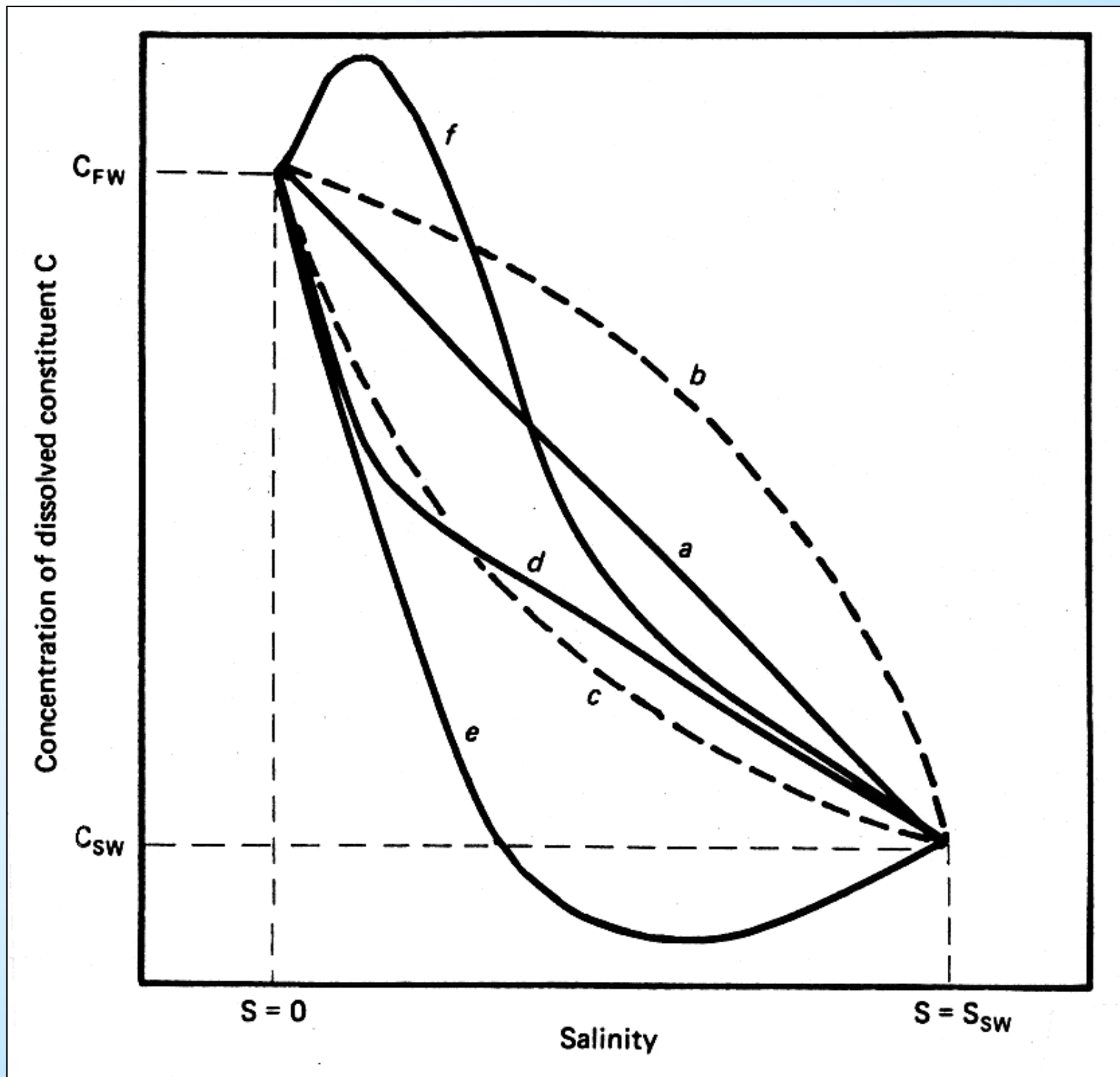
If plot of concentration vs. salinity is NOT LINEAR, then the chemical/particle exhibits *NON-conservative* behavior

*Non-conservative mixing (source)*



*Non-conservative mixing (sink)*

Assumes end-members are constant over the flushing time of the estuary



Elegantly laid out by Morris (1985):

“estuaries are classical examples of complex thermodynamically open systems, subject to constantly changing input and output fluxes and to continuous internal chemical reactions...” which do not usually reach a steady-state equilibrium

Many important reactions & processes are identified

BUT, still difficult to predict process rates & fluxes because of a lack of information on speciation of trace metals, kinetics of reactions, microbial activity, and heterogeneous nature of dissolved and solid phases

This leads to a heavy reliance on salinity as a conservative index for mixing & comparison

Pitfalls can include defining end-members, role of tributaries, and mixing of different water masses along the estuary

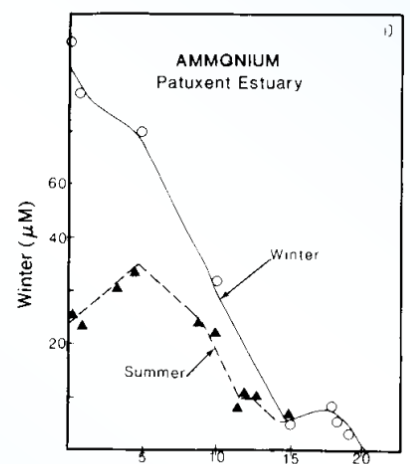
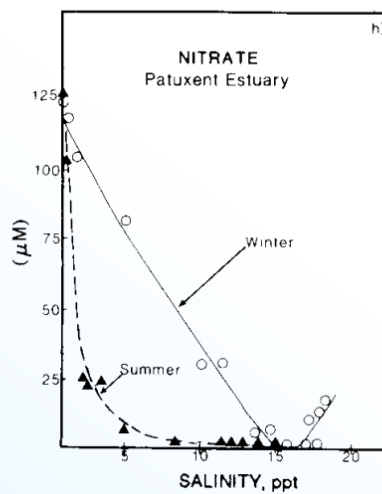
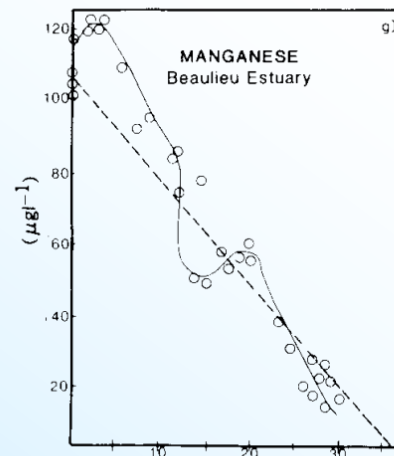
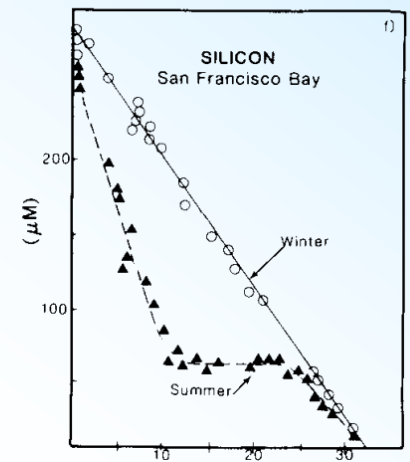
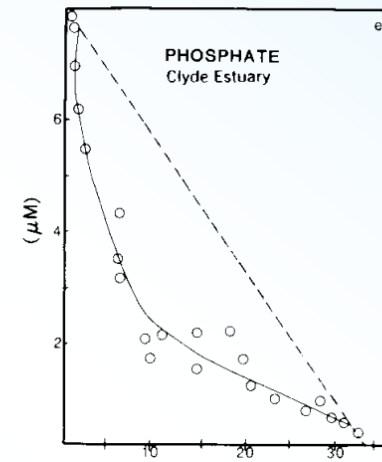
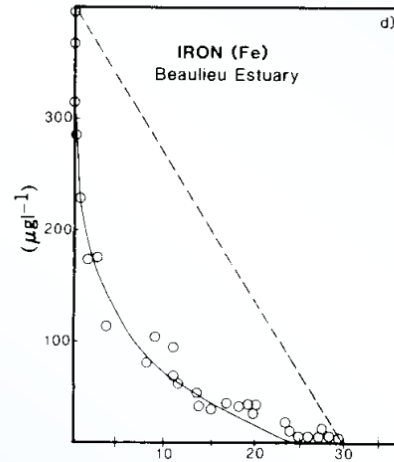
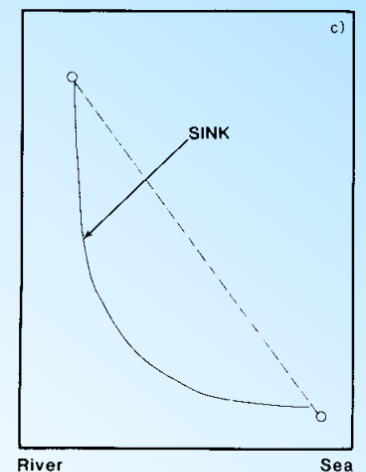
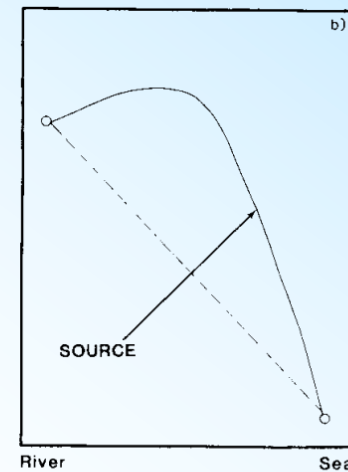
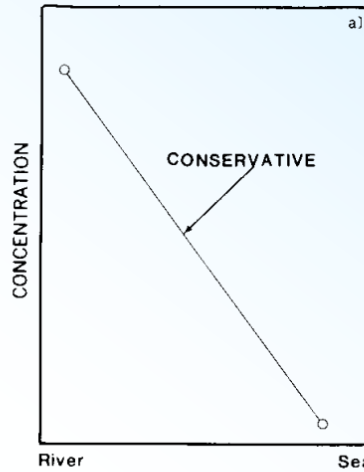
# Mixing Diagram Examples

Mixing line  
assumptions:

Concentration & flux  
are constant

Only 2 significant end-  
members

(from Day et al. 1989)





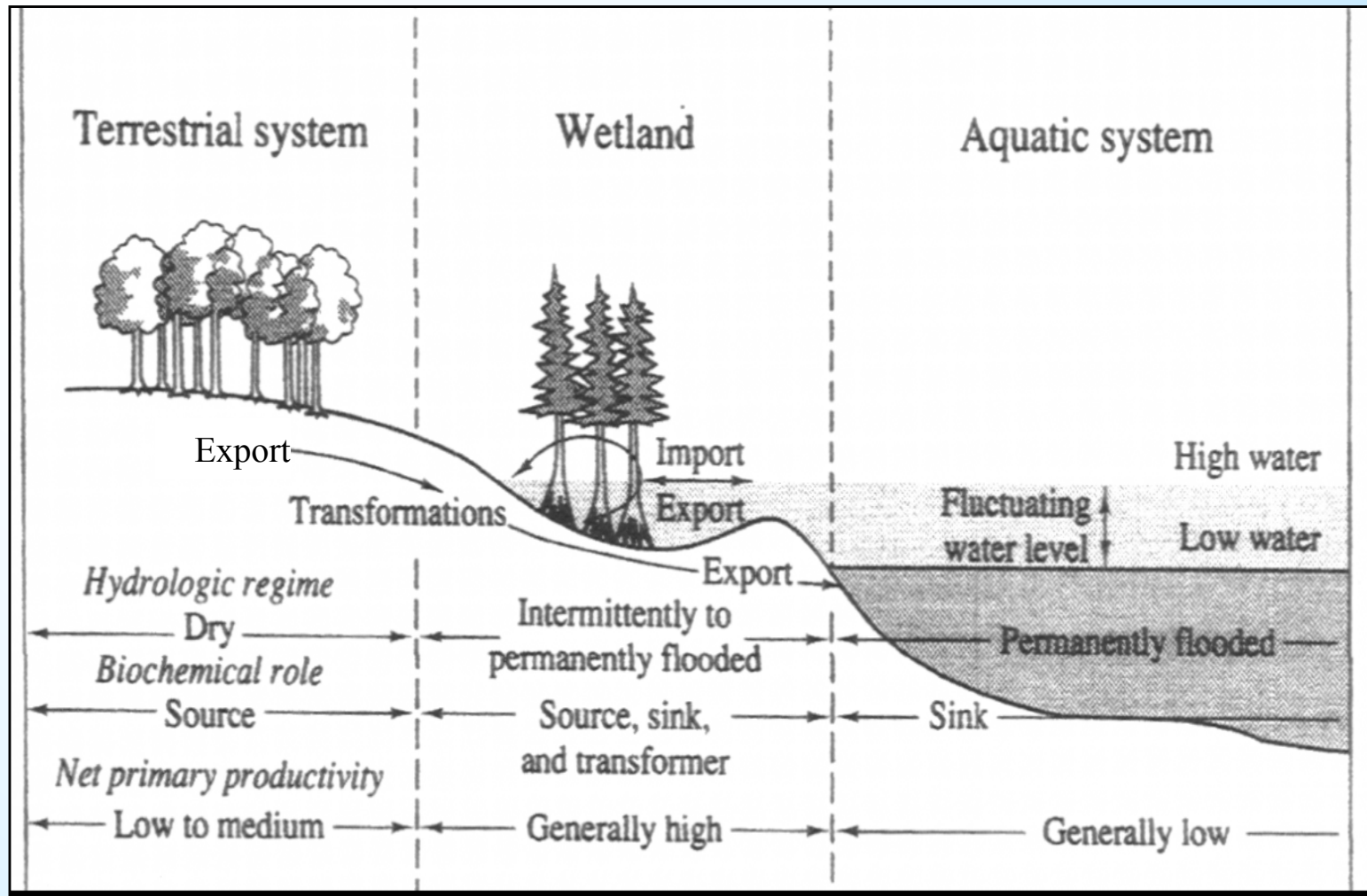
[https://www.youtube.com/watch?v=Gfch\\_b45zoQ#action=share](https://www.youtube.com/watch?v=Gfch_b45zoQ#action=share)





# Wetlands Are the Interface Between Terrestrial and Aquatic Systems

- Terrestrial (dry) systems tend to have medium NPP, high + NEP
- Wetlands have high NPP, + or - NEP
- Aquatic systems have low NPP, - NEP

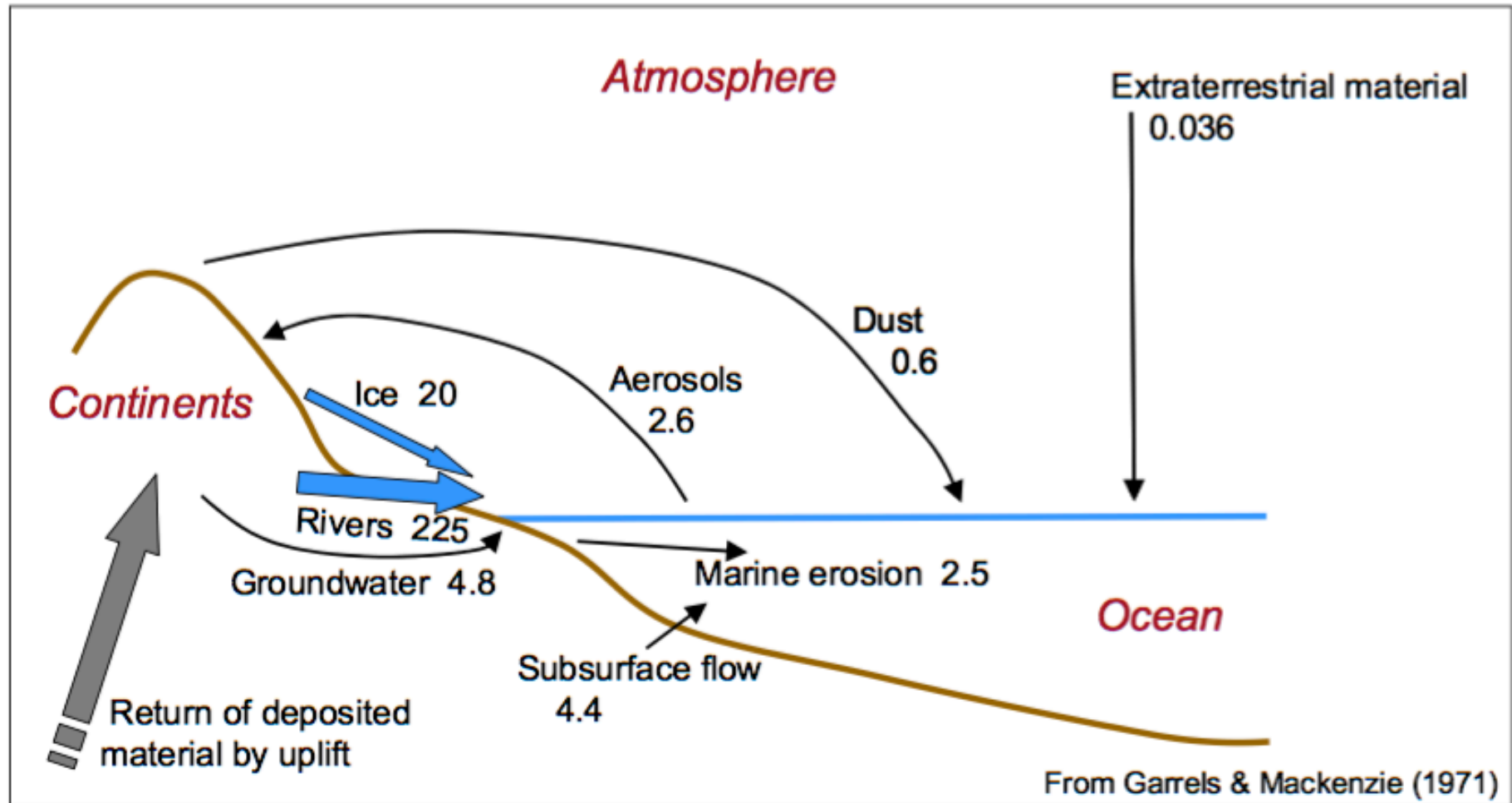


Drained wetlands or aquatic systems are major sites of “old C” oxidation

NPP = net primary production

NEP = net ecosystem production (P-R)

# Masses of Materials Entering/Leaving the Ocean

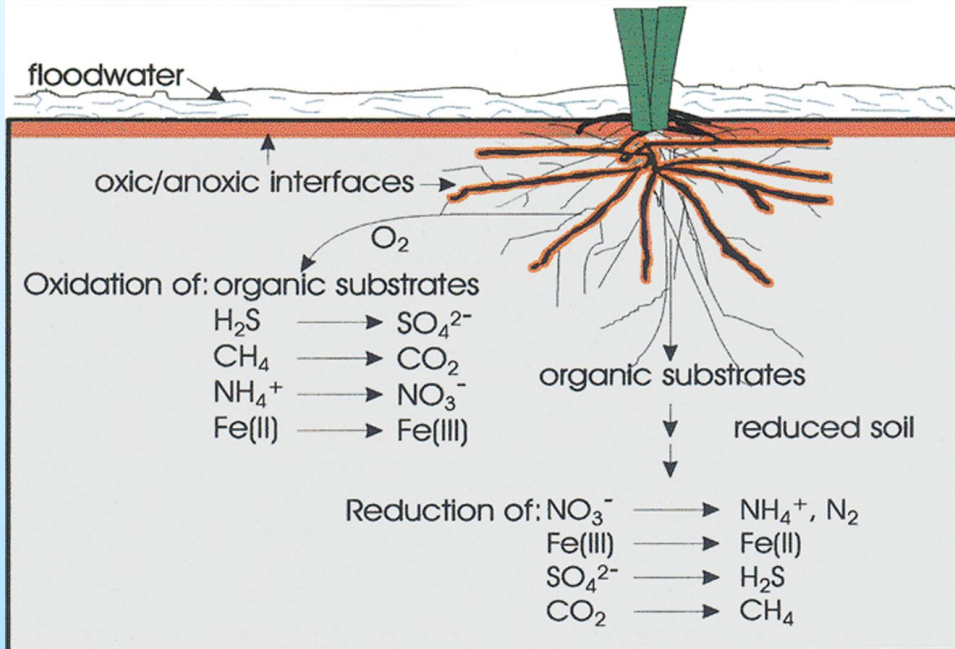


Transport rates are  $10^{14}$  g/year

Dissolved solids in global ocean =  $470 \times 10^{20}$  g

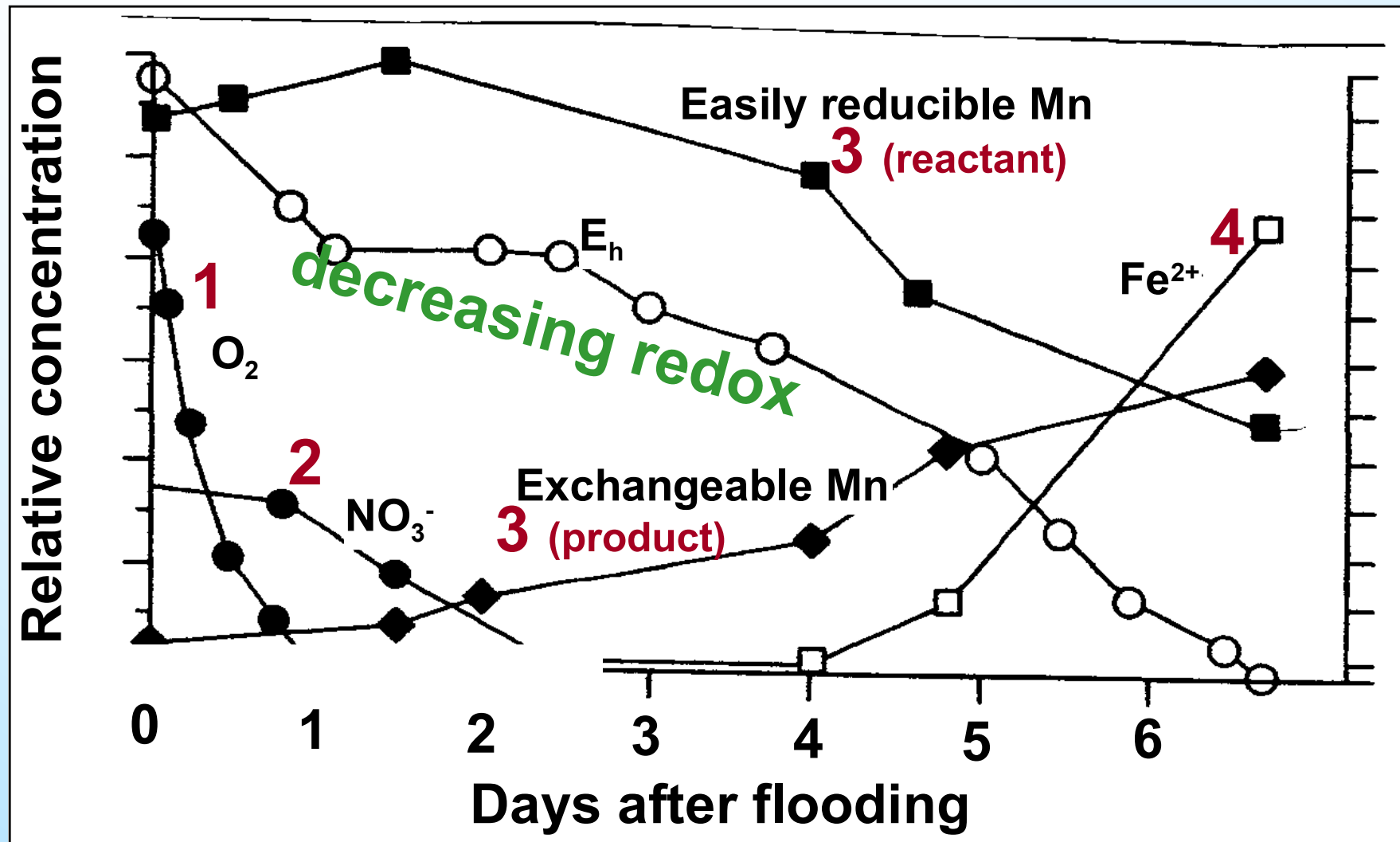


# Drained Soil vs. Flooded Soil



# Example: Changing Composition in Flooded Soils

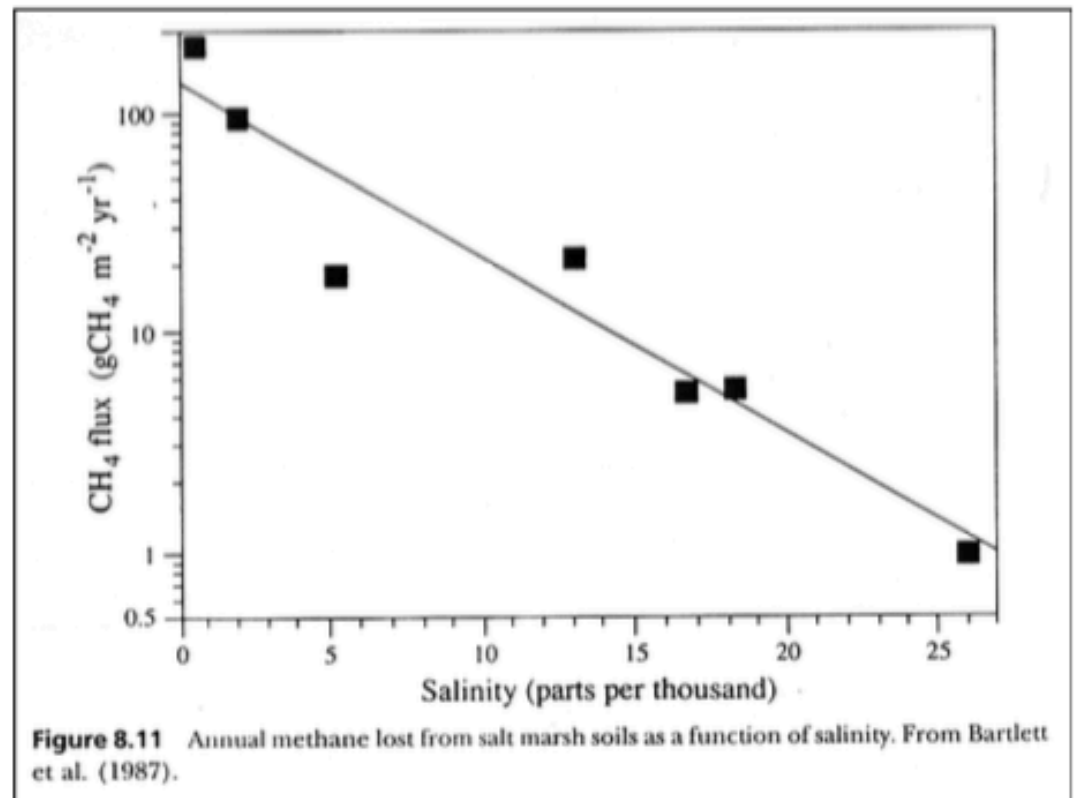
Temporal pattern reflects decreasing energy yield:



# 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:

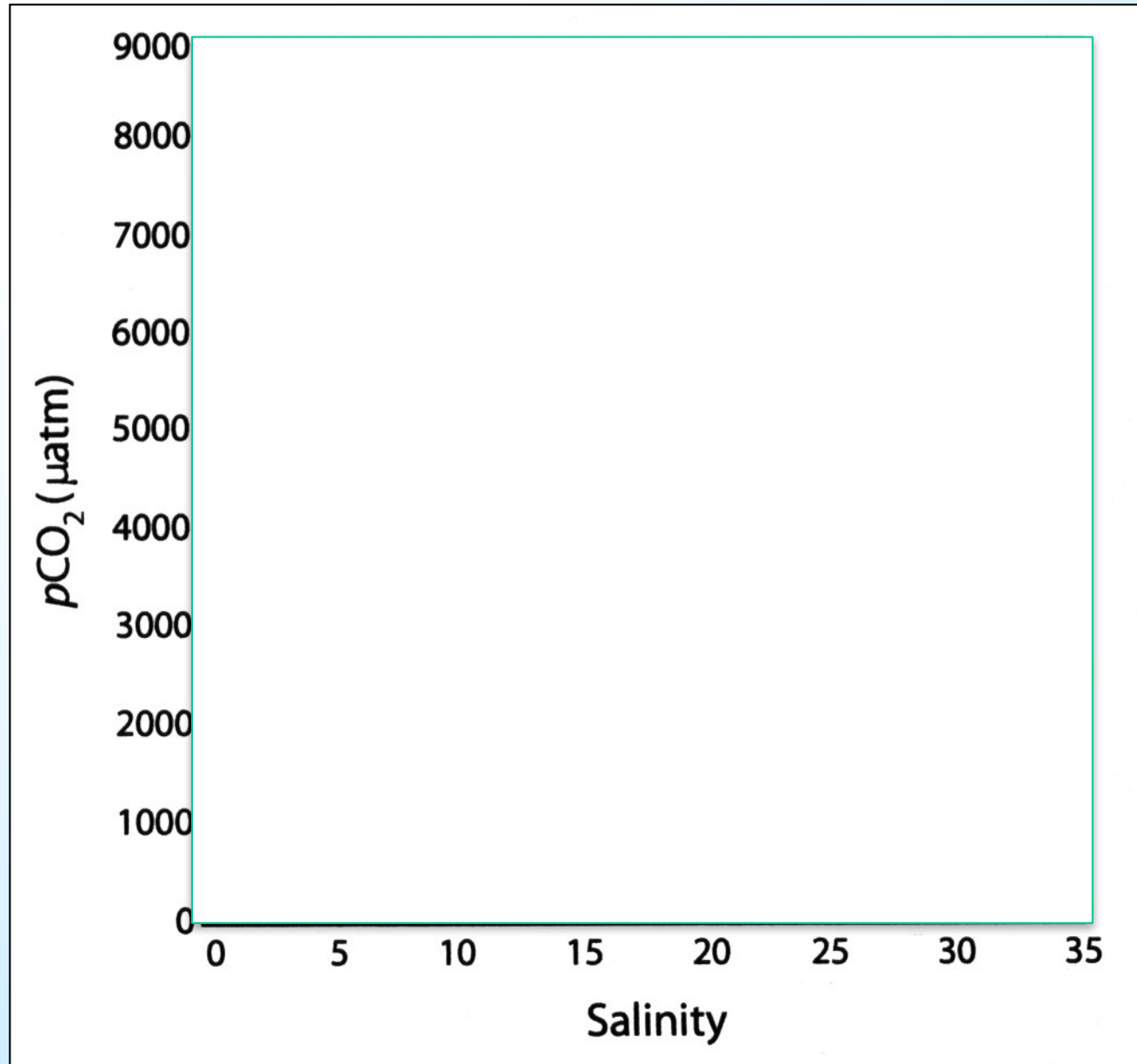
| Organic matter oxid | Oxidant                        | Reductant                   |
|---------------------|--------------------------------|-----------------------------|
| Aerobic oxidation   | O <sub>2</sub>                 | H <sub>2</sub> O            |
| Manganese reduction | MnO <sub>2</sub>               | Mn <sup>2+</sup>            |
| Nitrate reduction   | HNO <sub>3</sub>               | N <sub>2</sub>              |
| Iron reduction      | Fe <sub>2</sub> O <sub>3</sub> | Fe <sup>+2</sup>            |
| Sulfate reduction   | SO <sub>4</sub> <sup>2-</sup>  | S <sub>2</sub> <sup>-</sup> |
| Methanogenesis      | CO <sub>2</sub>                | CH <sub>4</sub>             |



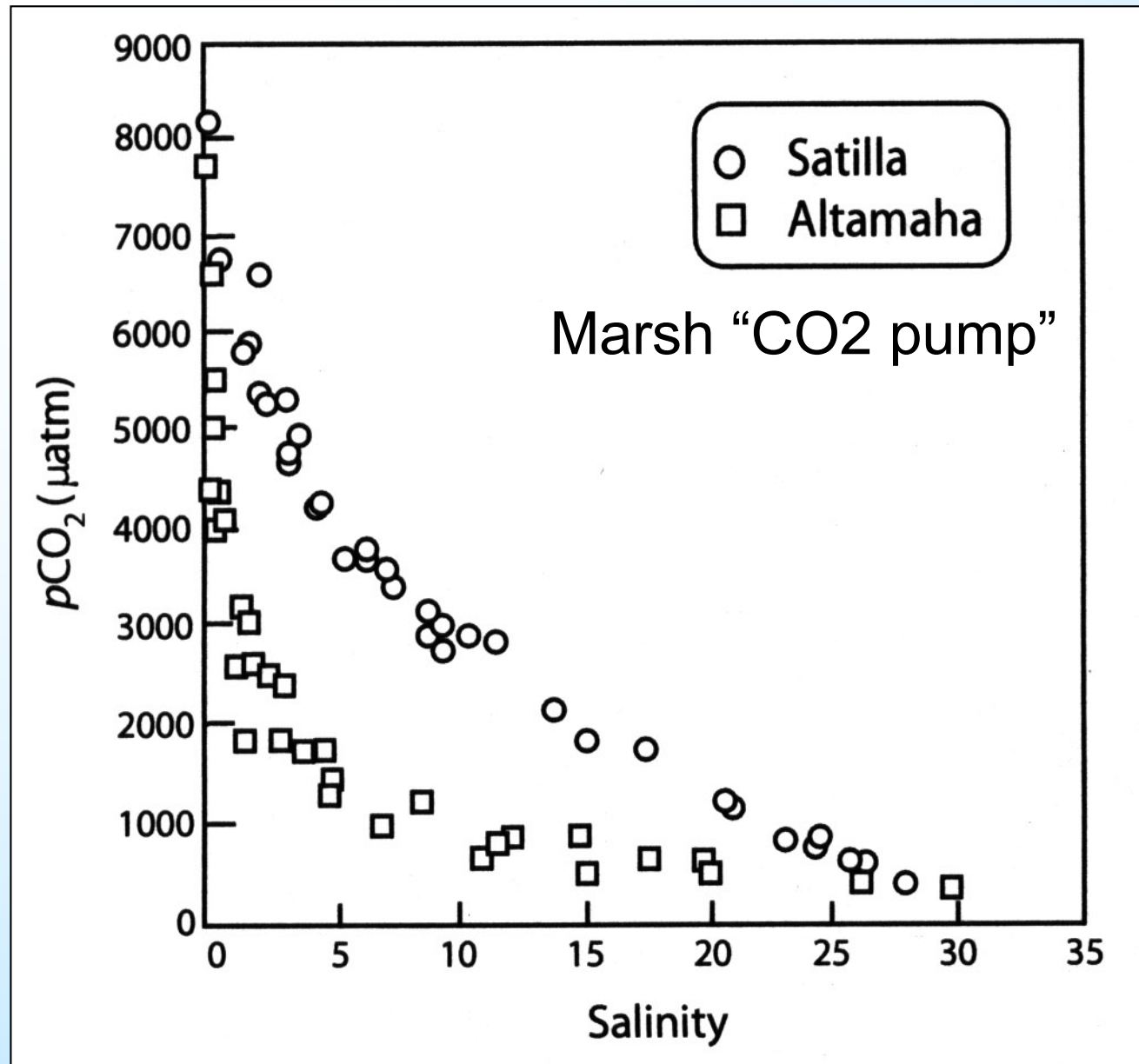


What about  $p\text{CO}_2$  along a salinity gradient then?

Is this a mixing line or something different?



Highest  $p\text{CO}_2$  is found in the lowest salinity waters (<10), with corresponding  $\text{CO}_2$  fluxes 20-250  $\text{mol m}^{-2} \text{y}^{-1}$ .



(in Bianchi 2007)

Table 5.4 Average  $p\text{CO}_2$  ranges for various U.S. and European estuaries.

| Estuary                                       | Number of transects | Average $p\text{CO}_2$ range (ppmv) |
|---|---------------------|-------------------------------------|
| Altamaha (USA) <sup>a</sup>                   | 1                   | 380–7800                            |
| Scheld (Belgium/The Netherlands) <sup>b</sup> | 10                  | 496–6653                            |
| Sada (Portugal) <sup>b</sup>                  | 1                   | 575–5700                            |
| Satilla (USA) <sup>a</sup>                    | 2                   | 420–5475                            |
| Thames (UK) <sup>b</sup>                      | 2                   | 485–4900                            |
| Ems (Germany/The Netherlands) <sup>b</sup>    | 1                   | 560–3755                            |
| Gironde (France) <sup>b</sup>                 | 5                   | 499–3536                            |
| Douro (Portugal) <sup>b</sup>                 | 1                   | 1330–2200                           |
| York (USA) <sup>c</sup>                       | 12                  | 352–1896                            |
| Tamar (UK) <sup>b</sup>                       | 2                   | 390–1825                            |
| Hudson (NY, USA) <sup>d</sup>                 | 6                   | 517–1795                            |
| Rhine (The Netherlands) <sup>b</sup>          | 3                   | 563–1763                            |
| Rappahannock (USA) <sup>c</sup>               | 9                   | 474–1613                            |
| James (USA) <sup>c</sup>                      | 10                  | 284–1361                            |
| Elbe (Germany) <sup>b</sup>                   | 1                   | 580–1100                            |
| Columbia (USA) <sup>e</sup>                   | 1                   | 590–950                             |
| Potomac (USA) <sup>c</sup>                    | 12                  | 646–878                             |
|   | Average             | 531–3129                            |



# An Example of Seasonal Effects

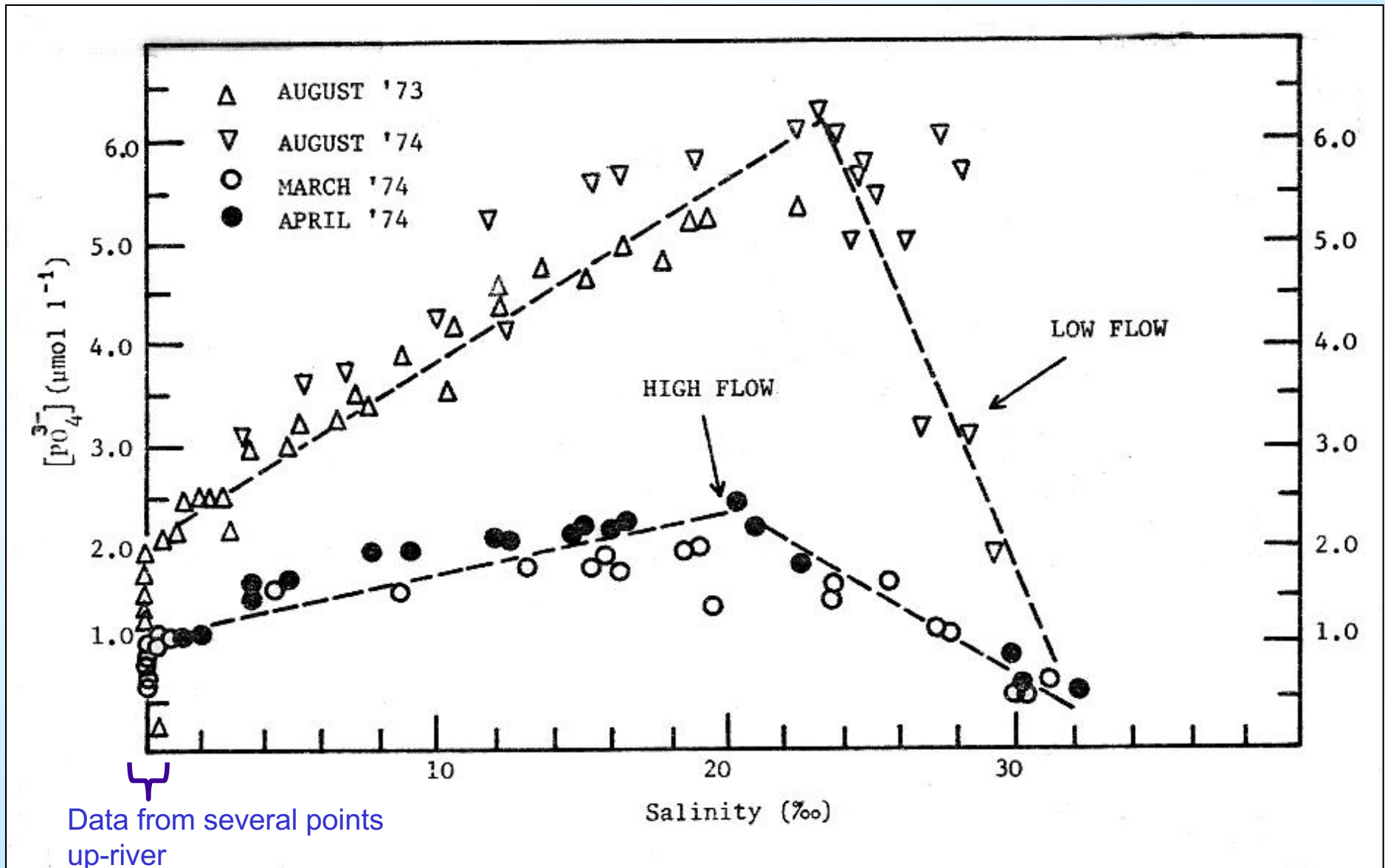


FIG. 41.8. Phosphate (molybdate-reactive) as a function of salinity in the Hudson Estuary (after Simpson *et al.*, 1975). Results for high-flow and low-flow conditions are illustrated.

**Table 1.3. Factors which impose temporal variability on the composition of water at a fixed geographical position in an estuary**

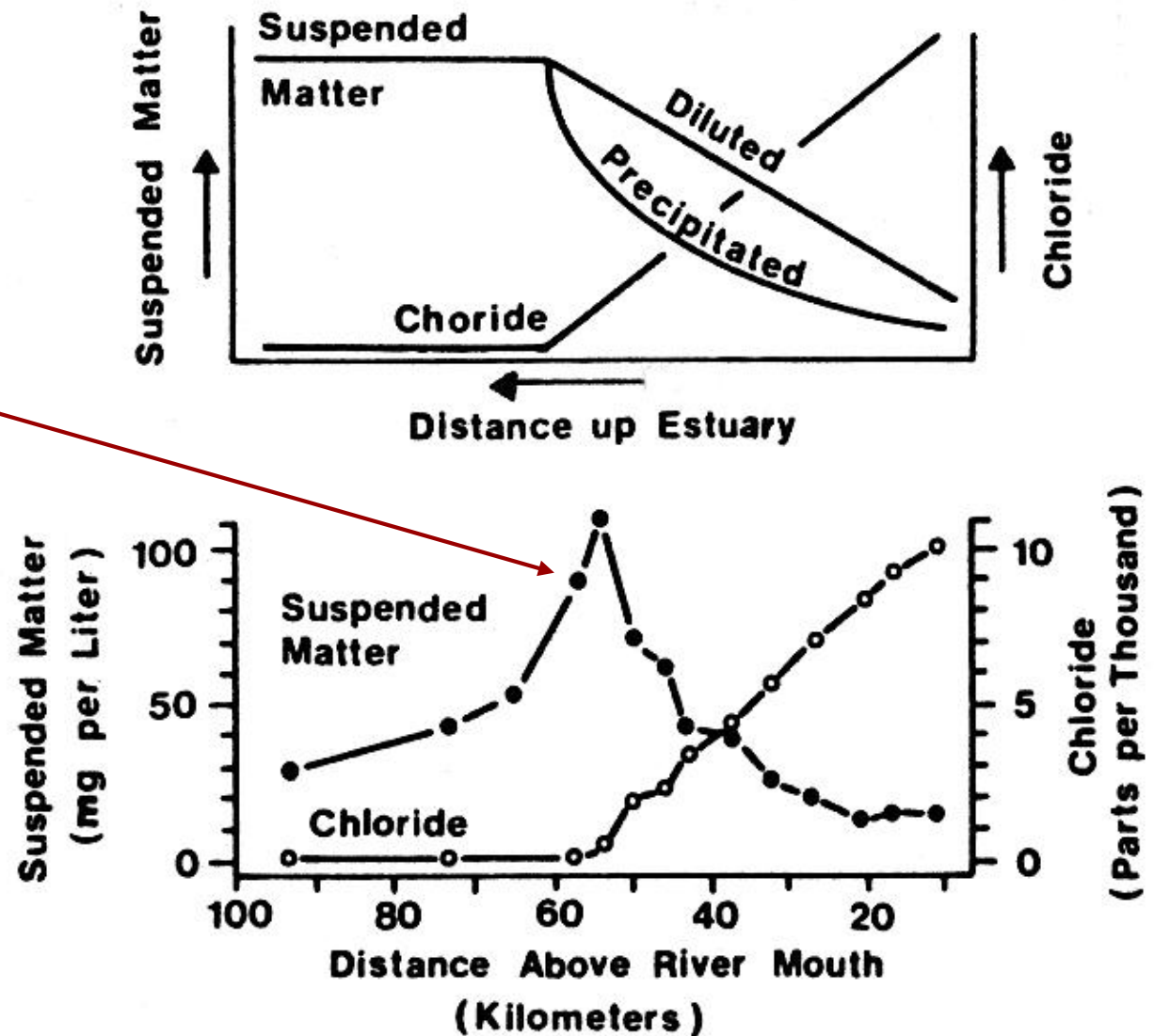
| Form of variability  | Frequency   | Process   |
|--|---|---|
| <b><u>Cyclic fluctuations about average conditions</u></b>   |   |   |
| 1. Small scale random fluctuations about mean level or trend | < Seconds to minutes  | Turbulent eddy structure of water in mixing regime  |
| 2. Variability around mean level or trend                    | Minutes to hours  | Eddying; incompletely mixed inputs; temporary isolation of water, e.g. in bays or over mud flats                                  |
| 3. Regular interruptions to mean level or trend              | Often tidal   | Intermittent discharge  |
| 4. Regularly cyclic  | Usually 12½ hours, with spring/neap variations in amplitude | Tidal advection   |
| 5. Regularly cyclic  | Annual  | Biological and/or climatic cycles   |
| <b><u>Intermittent fluctuations</u></b>                      |   |   |
| 1. Irregular interruptions to mean level or trend            | —   | Irregular discharge   |
| 2. Intermittent significant change in water characteristics  | Often annual, i.e. more probable at certain times of year   | Climatic effects, e.g. exceptionally high or low fresh water run-off; storm surges; biological instability (plankton blooms)      |
| 3. Permanent discontinuity in water characteristics          | —   | Change in exploitation, e.g. new discharge. Natural phenomenon, e.g. morphological adjustment to estuarine bed form, rechanneling |
| <b><u>Trend</u></b>  |   |   |
| 1. Persistent year to year trend                             | —   | Change in exploitation, e.g. continuous increase or decrease in discharge. Natural estuarine evolution, e.g. continuing siltation |

# The Mid-estuary Turbidity Maximum

Expected:

Turbidity max is due to both 1) chemical flocculation and 2) sediment resuspension

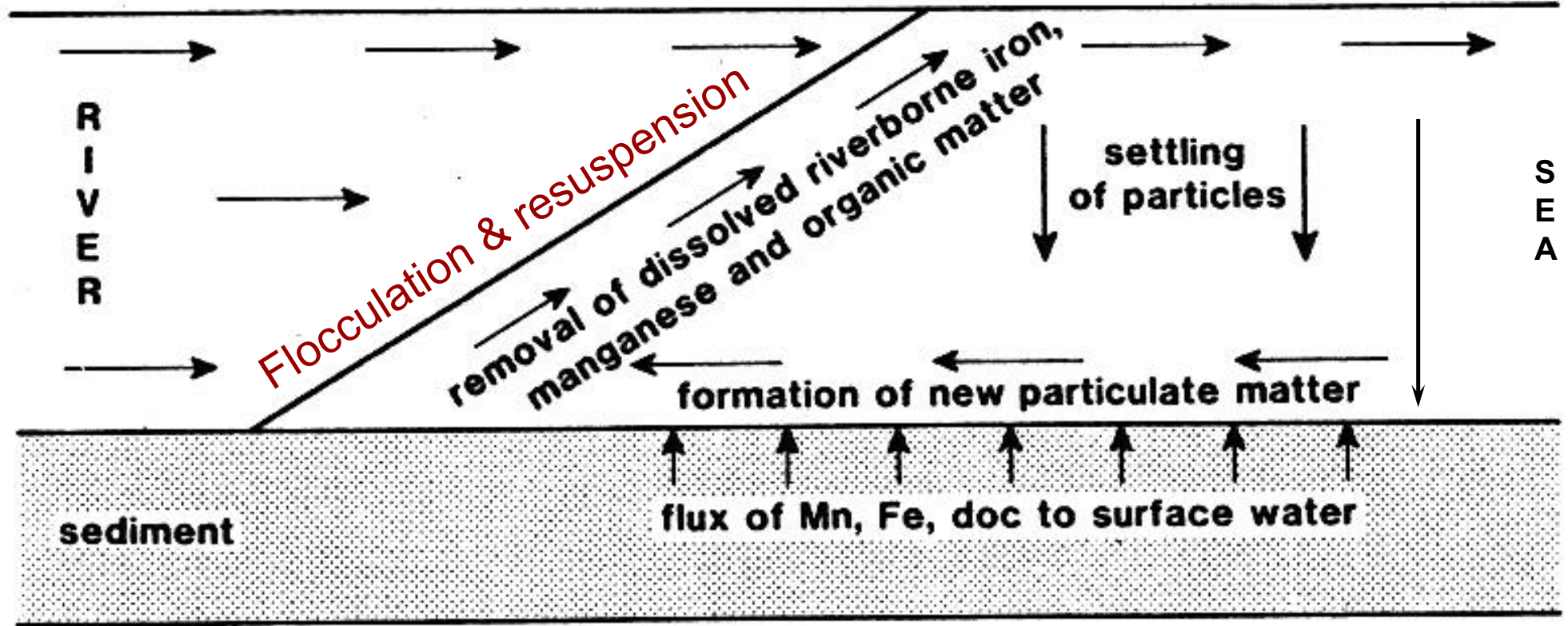
Measured:



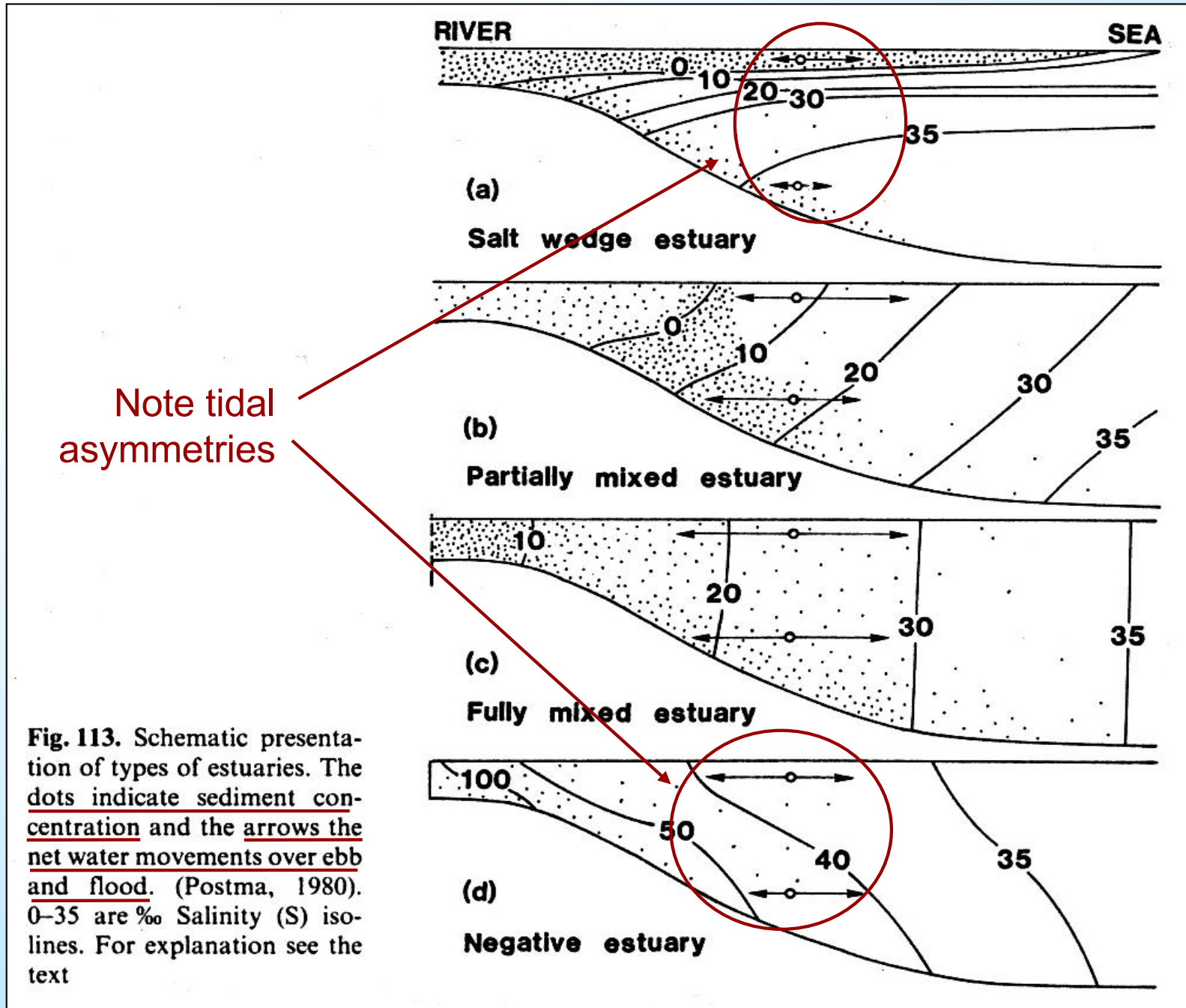
**Fig. 115.** Example of the non-conservative behaviour of suspended matter in estuaries and the formation of a turbidity maximum at the fresh-sea water interface (Meade, 1972)



# A Mid-estuary Trap for Riverborne Material



# Particle Distribution vs. Estuary Type



# Effects Of The Mid-estuary Particle Maximum

1. **Scavenging** of surface-active materials
  - 70-100% of riverine Fe is removed (most at low salinity)
  - 60-80% of humic acids are removed
  - 5% of total DOM is removed
2. Increased **turbidity**
  - Lower primary production
  - Reduction of photochemical reaction rates
3. Enhanced **transport** rates downstream / offshore
  - Enhanced sedimentation rates downstream / offshore



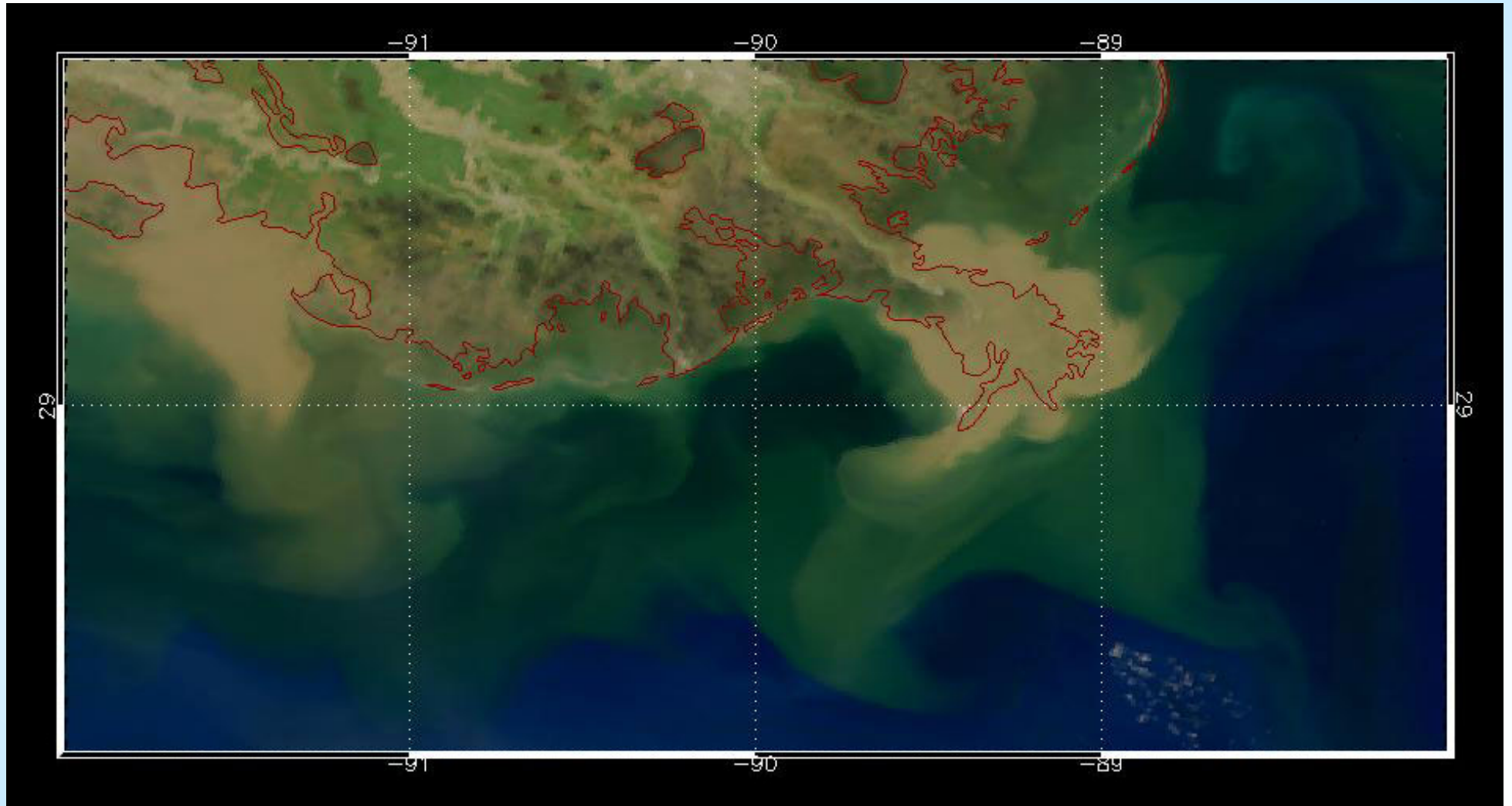
# Estuarine Plumes on the Continental Shelf



[cacique.uprm.edu/gers/anasco\\_plume.jpg](http://cacique.uprm.edu/gers/anasco_plume.jpg)

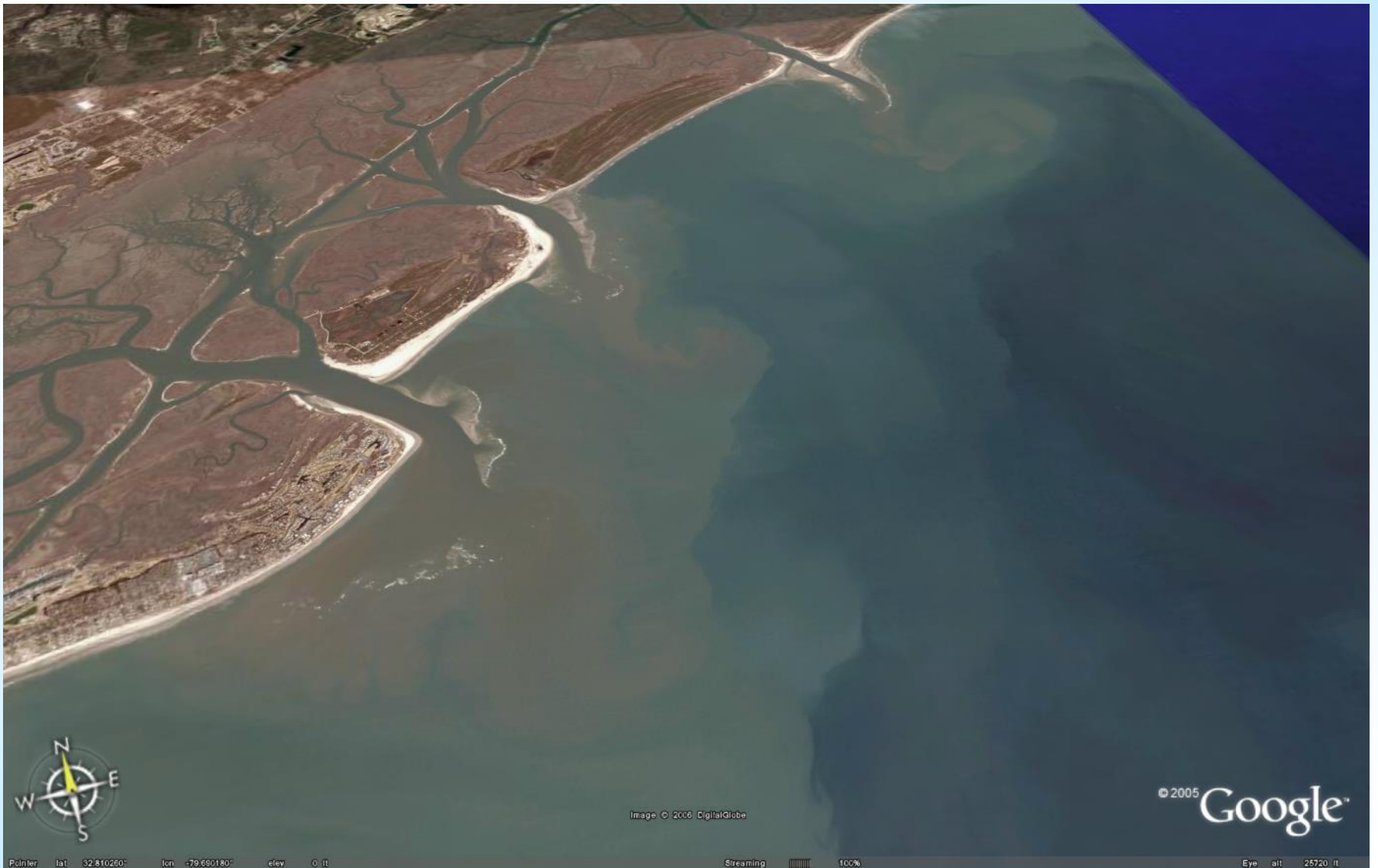


# Estuarine Plumes on the Continental Shelf



[gulfsce.usgs.gov/.../ofrshelf/images/seawifs.jpg](http://gulfsce.usgs.gov/.../ofrshelf/images/seawifs.jpg)

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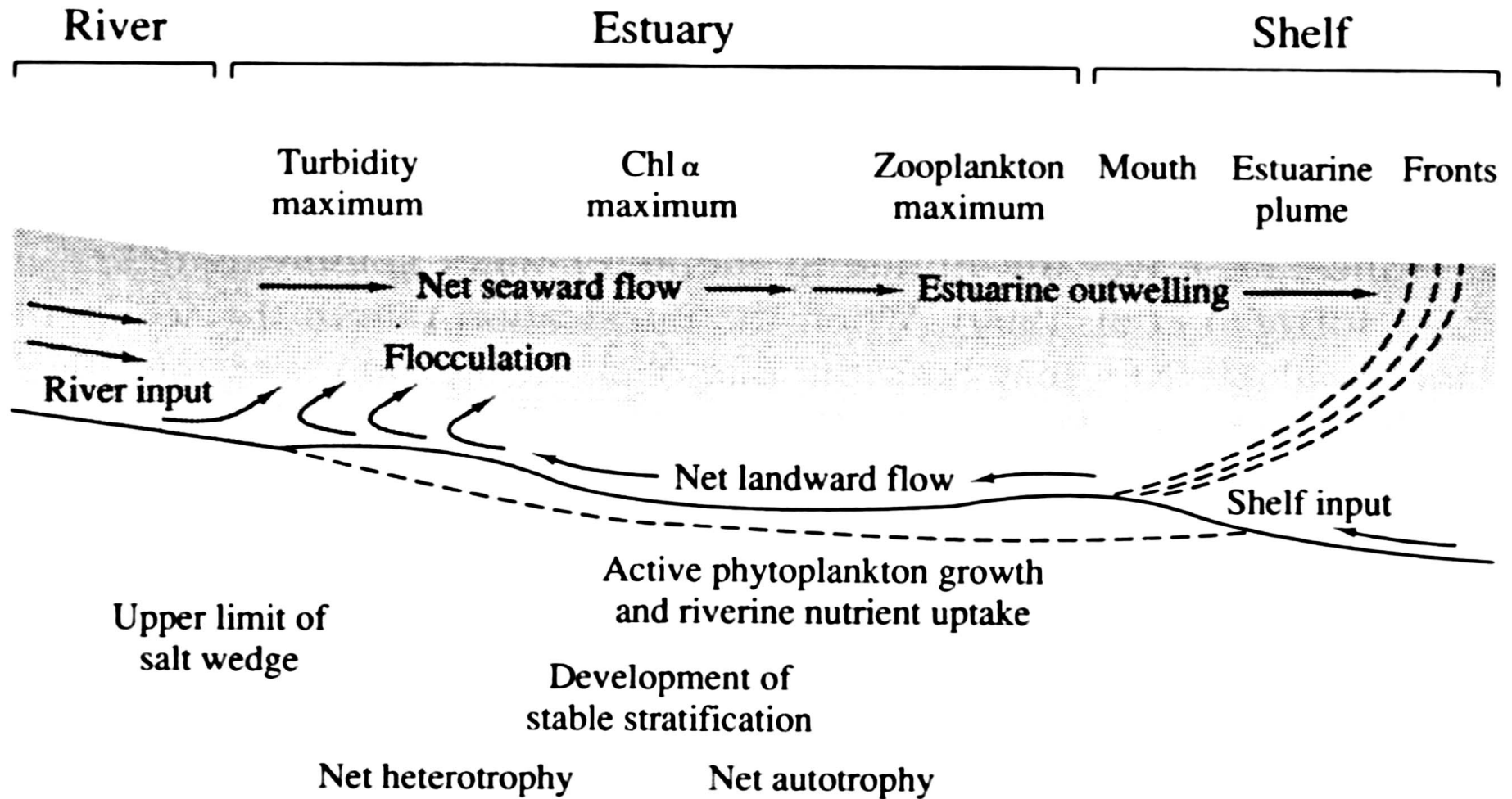
# Surface Runoff

## MANY POINTS OF ENTRY

Pollutants that are harmful to Hawaii's reefs can enter the ocean in many ways, including through storm drains and streams. Sediment runoff is a particular problem in some coastal areas, such as along East Honolulu's Maunalua Bay. The pollutants flush into Maunalua via nine major streams that have been altered to speed storm runoff and through dozens of neighborhood drainage systems that eventually empty into the streams or the bay. Other areas with similar sedimentation problems face the same challenge as East Honolulu: How to reduce the amount of dirt and other pollutants washing into the ocean.



# An Estuarine Summary



**Figure 8.13** Conceptual model of the chemical and biological structure in estuaries. As the suspended load settles from the entering river waters and nutrients are made available, phytoplankton production increases, fueling an increase in zooplankton production and higher trophic levels. From Fisher et al. (1988).