Multi-Level Chemical Biomarker Sampling in the Lower Mississippi River/Louisiana Margin

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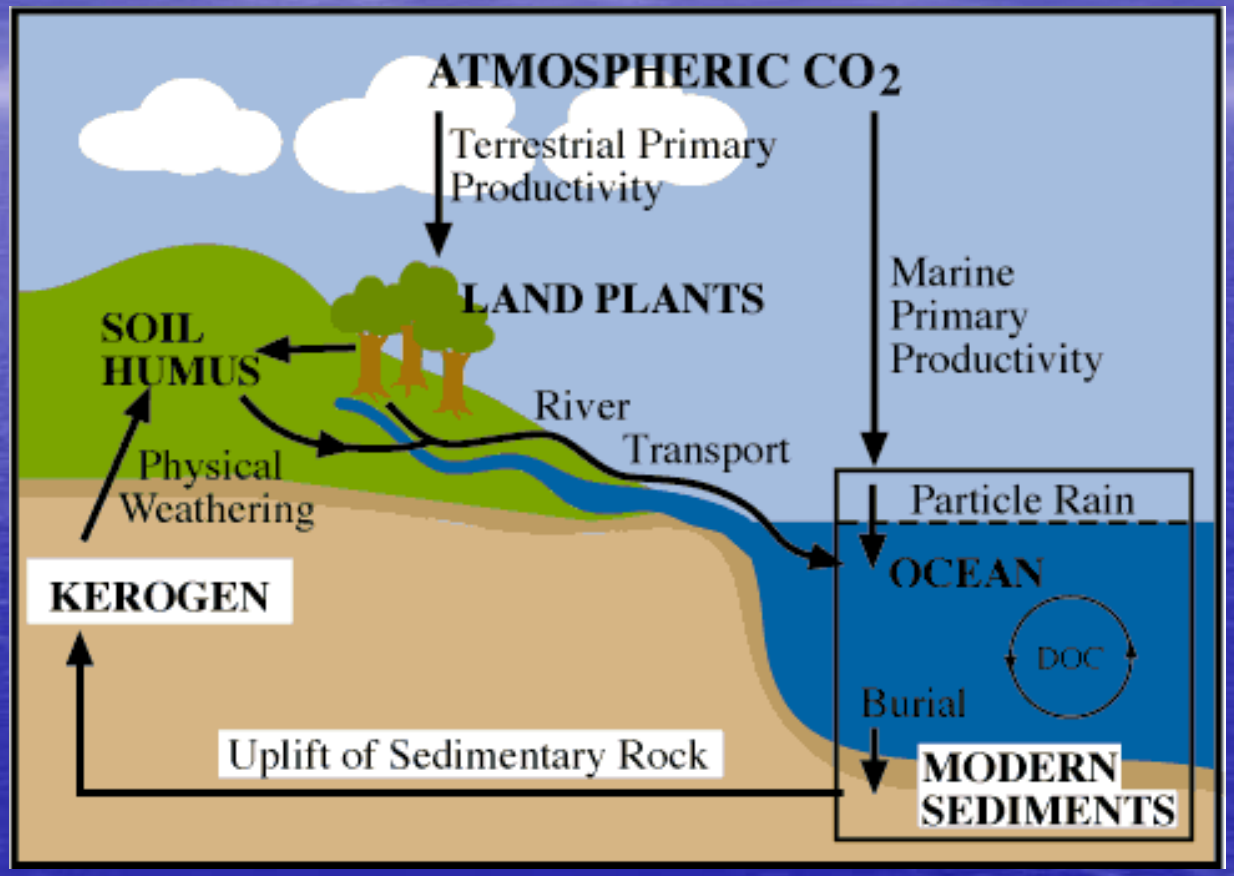
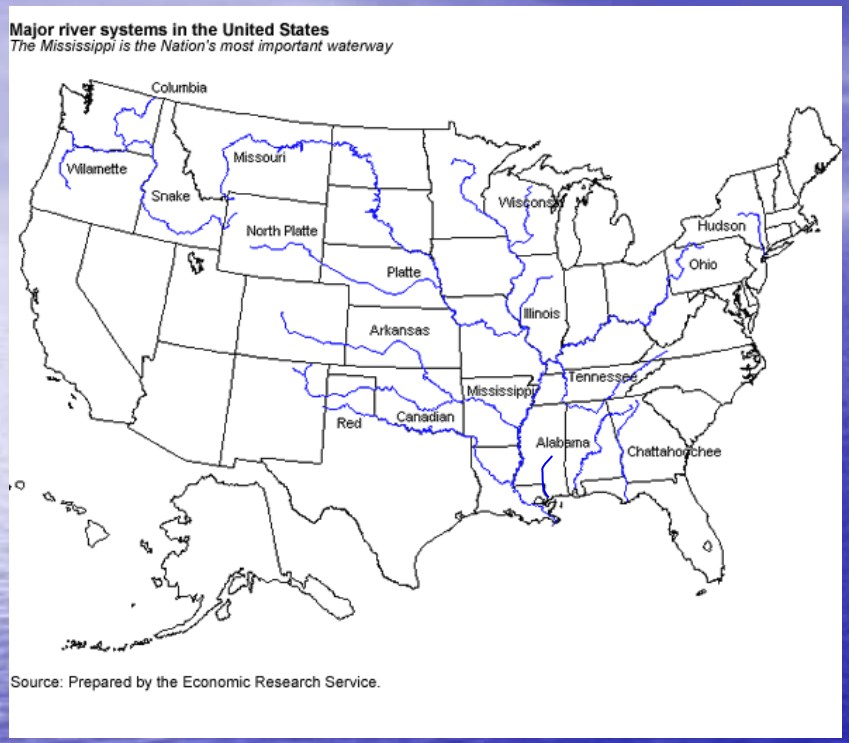
Organic Carbon Inputs From Rivers

4×10^{14} g of organic carbon transported via rivers each year

40% of global inputs transported by 20 largest rivers

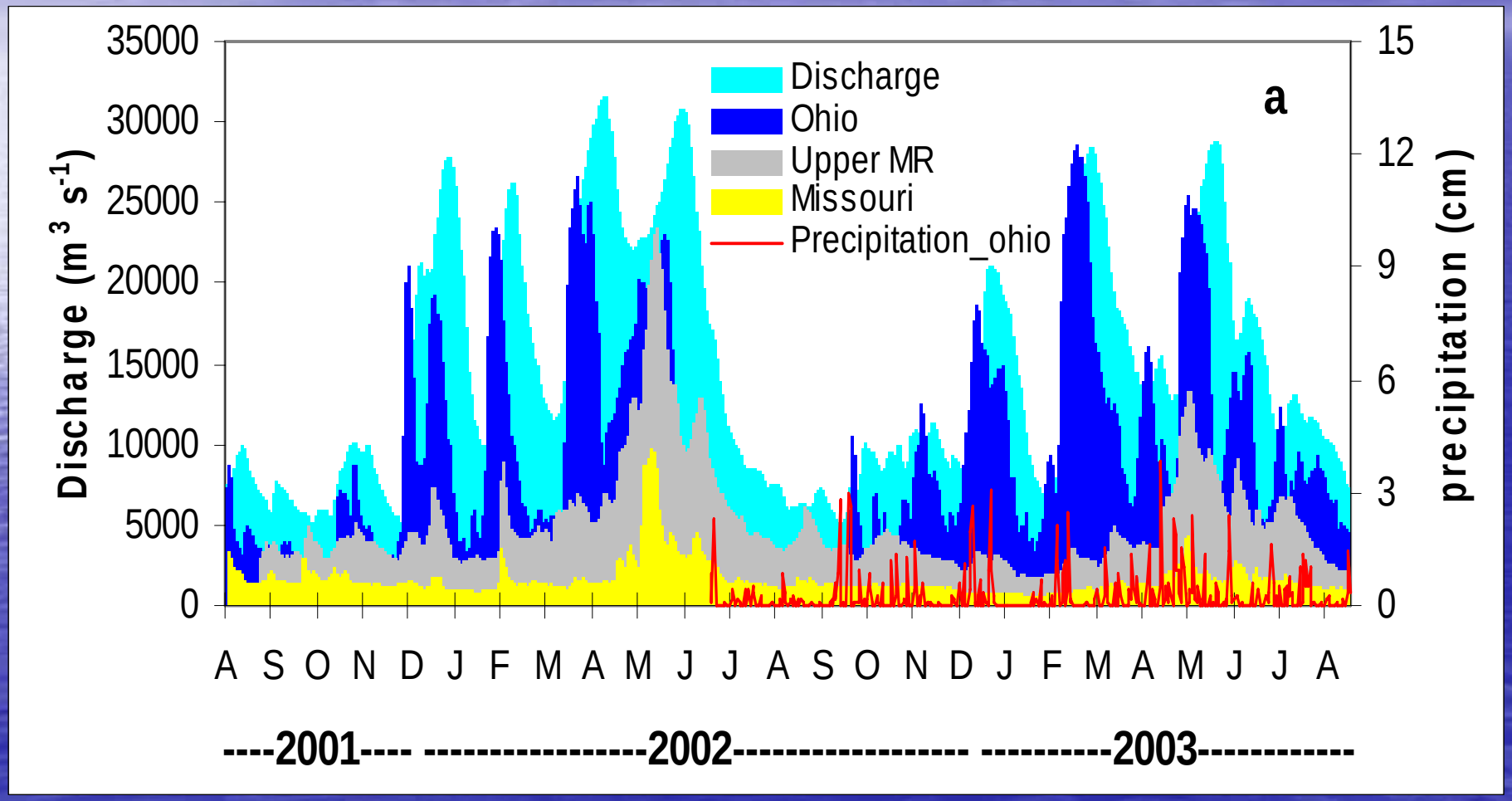


Temporal Sampling

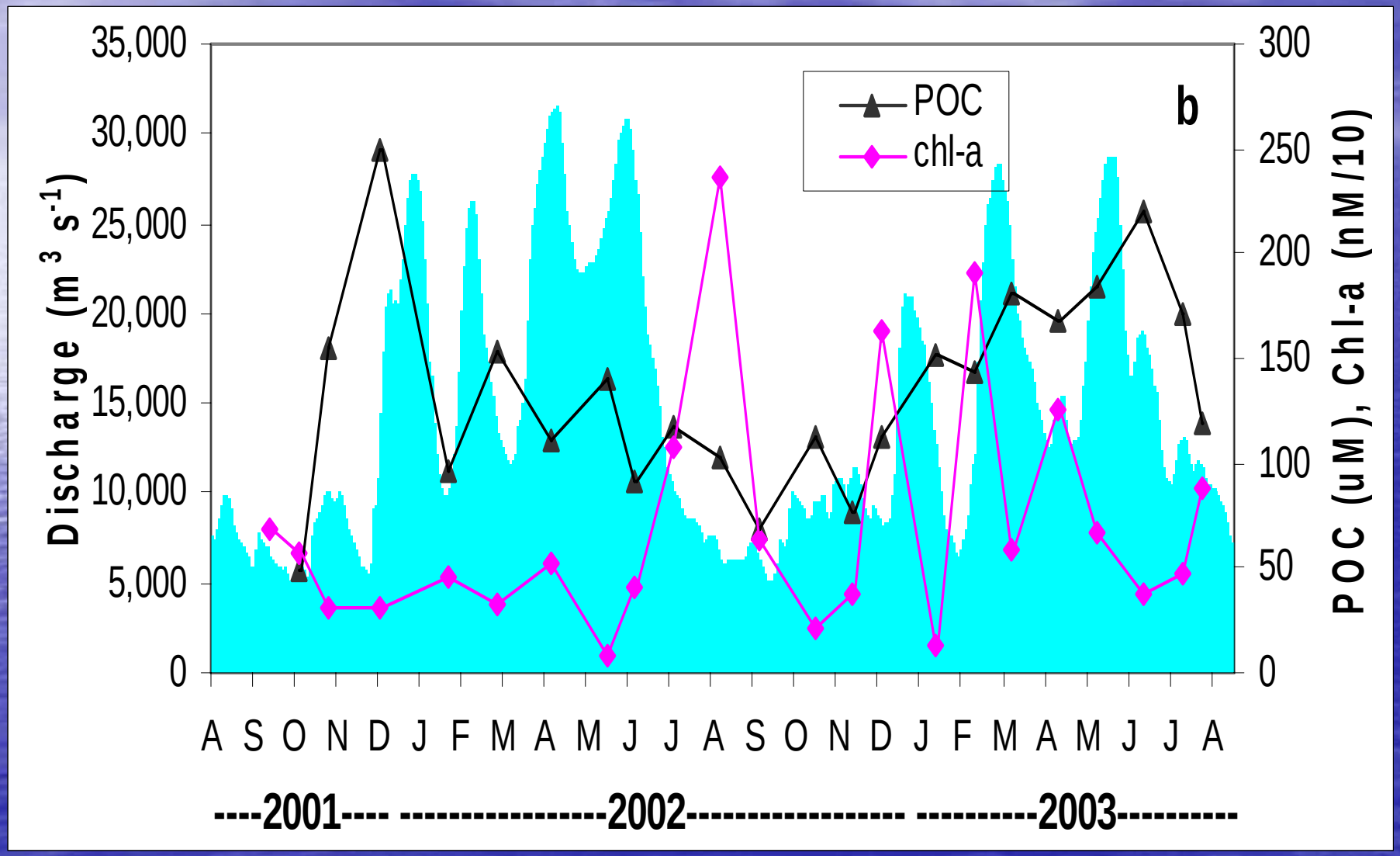


Mississippi River Sampling : Sept.2001-August 2003

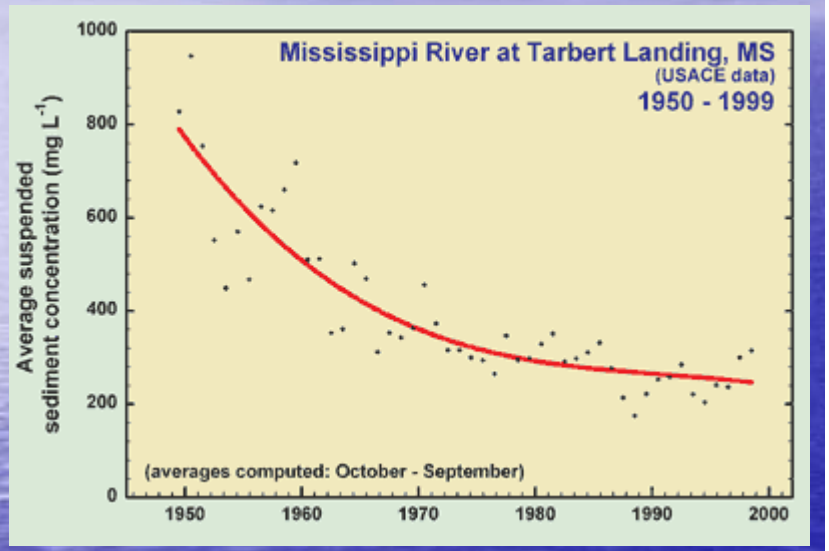
Discharge Patterns of Mississippi, Ohio, and Missouri Rivers

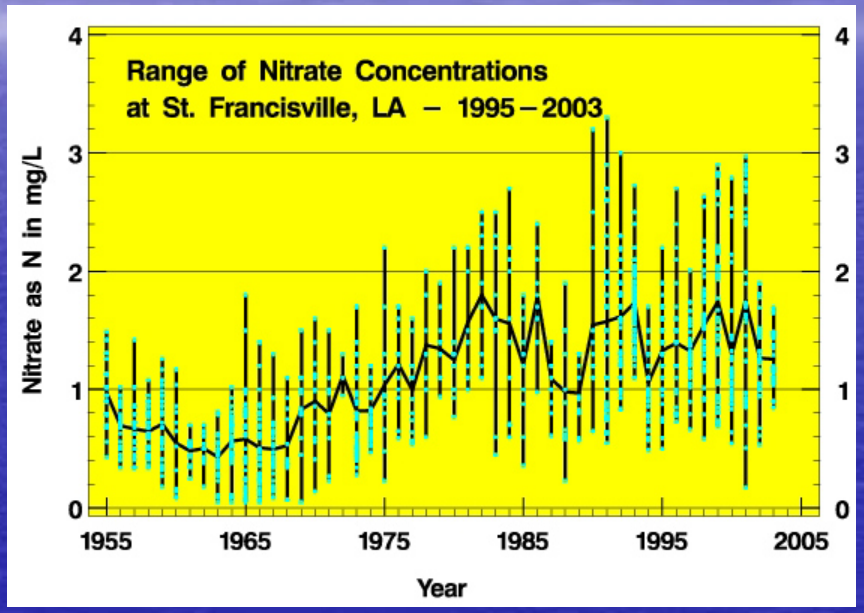


Particulate Organic Carbon and Chlorophyll-a



Temporal Changes in the Suspended Particulate Matter and Nitrate Concentration in the Lower MR

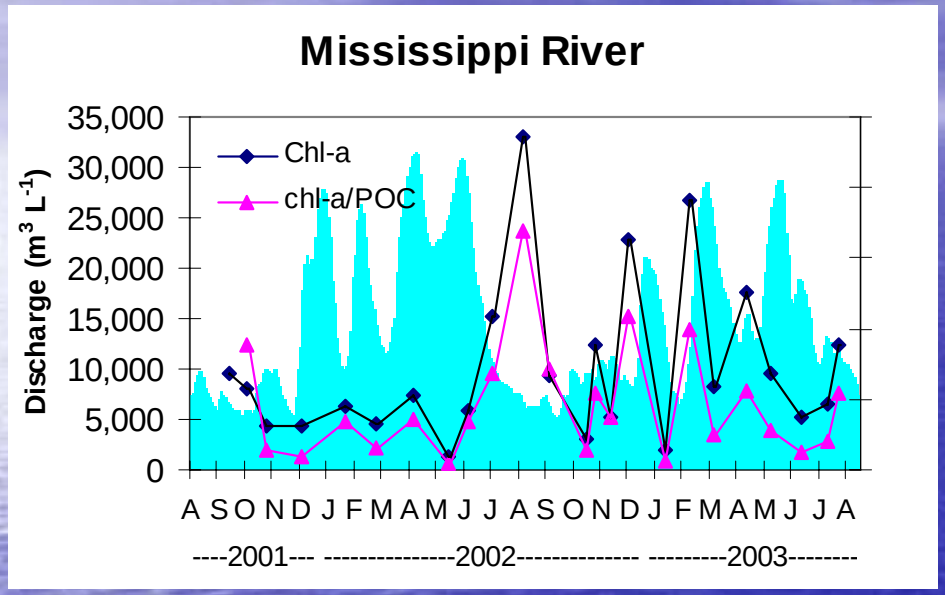




- SPM concentration decrease from 800 mg/L in 1950 to 250 mg/L in 1990 due to dam construction in the upper river (USACE data in http://gulfsci.usgs.gov/missriv/reports/ofrshelf/)

- Average nitrate concentration increase from 0.6-0.7mg/L in 1950s too 1.5 mg/L in 2000s because of utilization of chemical fertilizers (USGS data in co.water.usgs.gov/hypoxia/html/graphics4.html)

Phytoplankton Abundance (represented by chl-a)



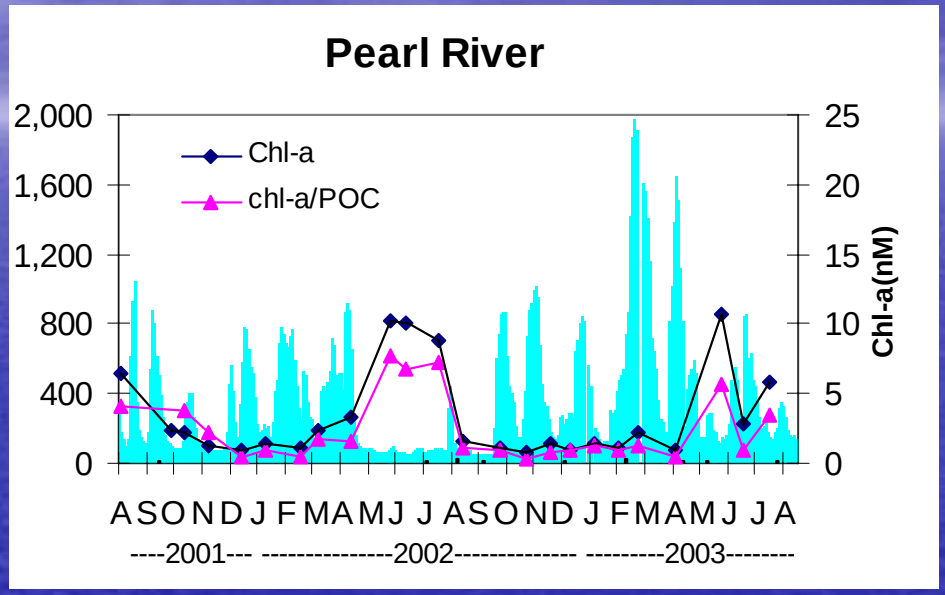
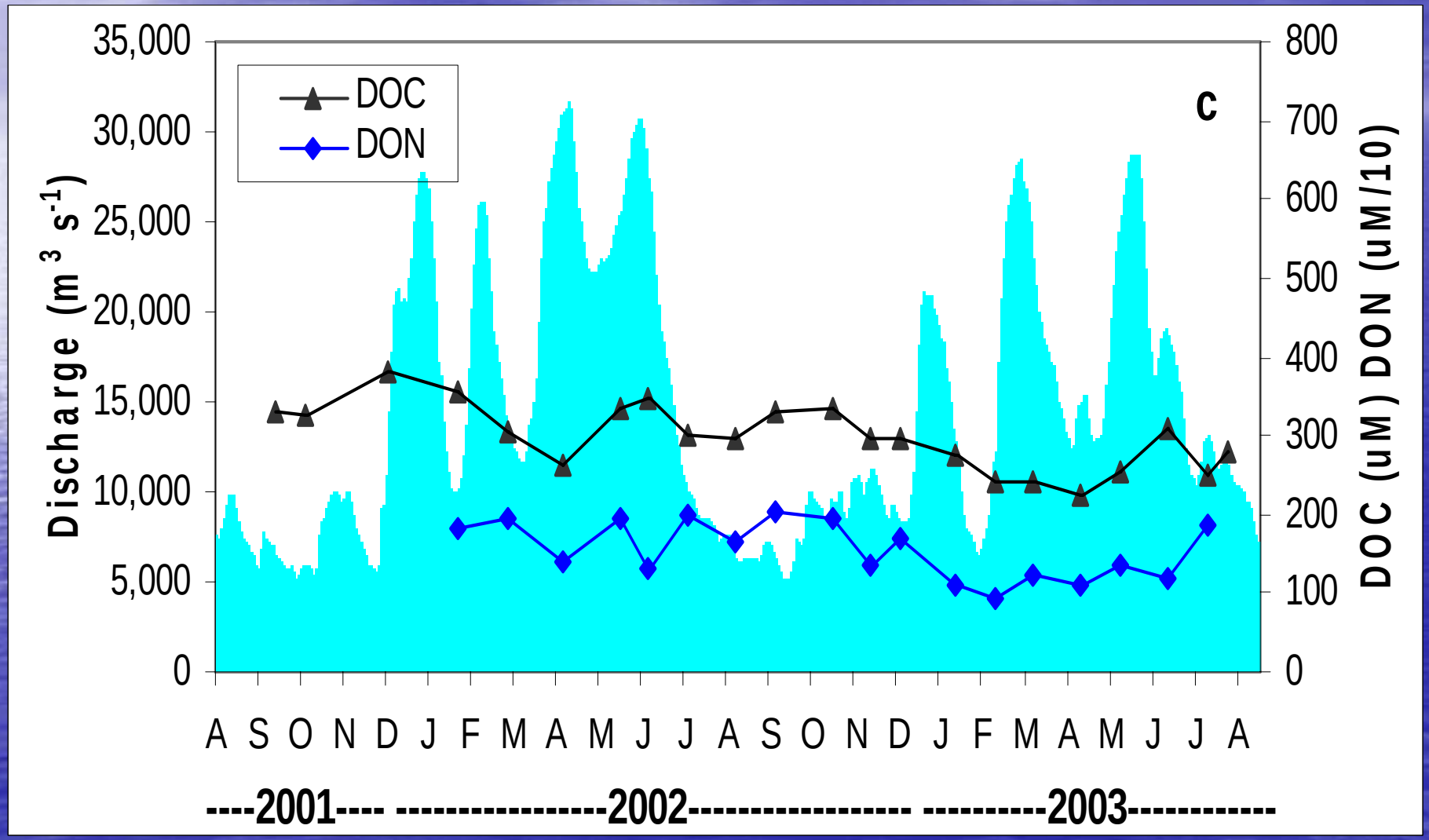


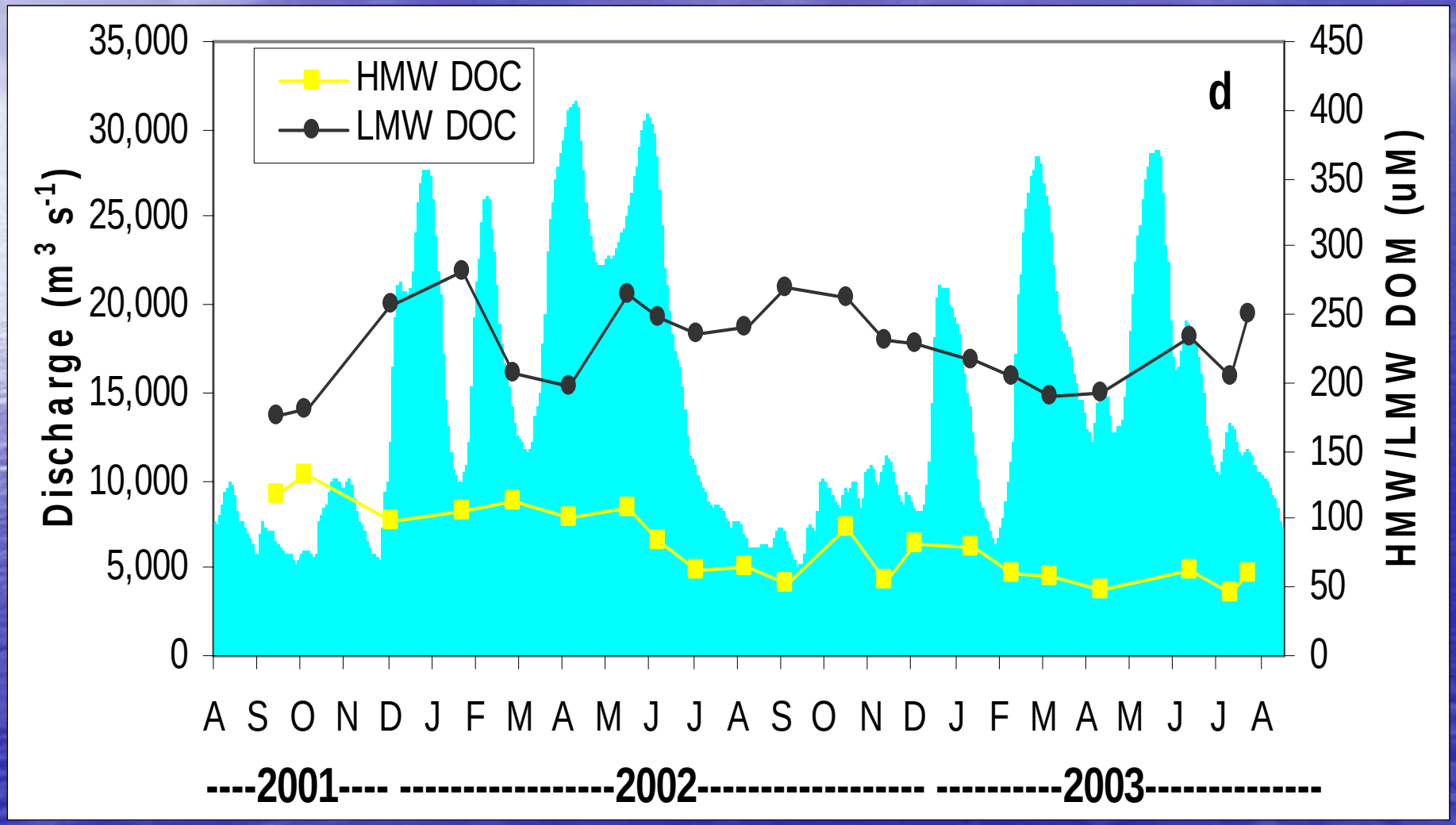
Table 1 Comparation of Chl-a concentration in MR, PR with other aquatic systems

	Range (uM)	Average(uM)	Source
Lower Mississippi	0.8 - 23.6	7.1	This study
Pearl	0.8 - 10.7	3.4	This study
Columbia (USA)	1.1 - 22.2		Sullivan et al. 2001
Ohio (USA)	1.1 - 17.7		Sellers and Bukaveckas, 2003
MR Plume	0.44 - 31.1	3.2/6.9	Wysocki, et al., 2005
Lake Pontchartrain (U	0.3 - 7.7	2.6	Bianchi and Argyrou, 1997
Plumes in Baltic Sea		6.5-13.1	Wasmund et al., 1999
Suwannee (USA)	< 0.1		
Amazon	0.17-2.38		Saliot et al., 2001

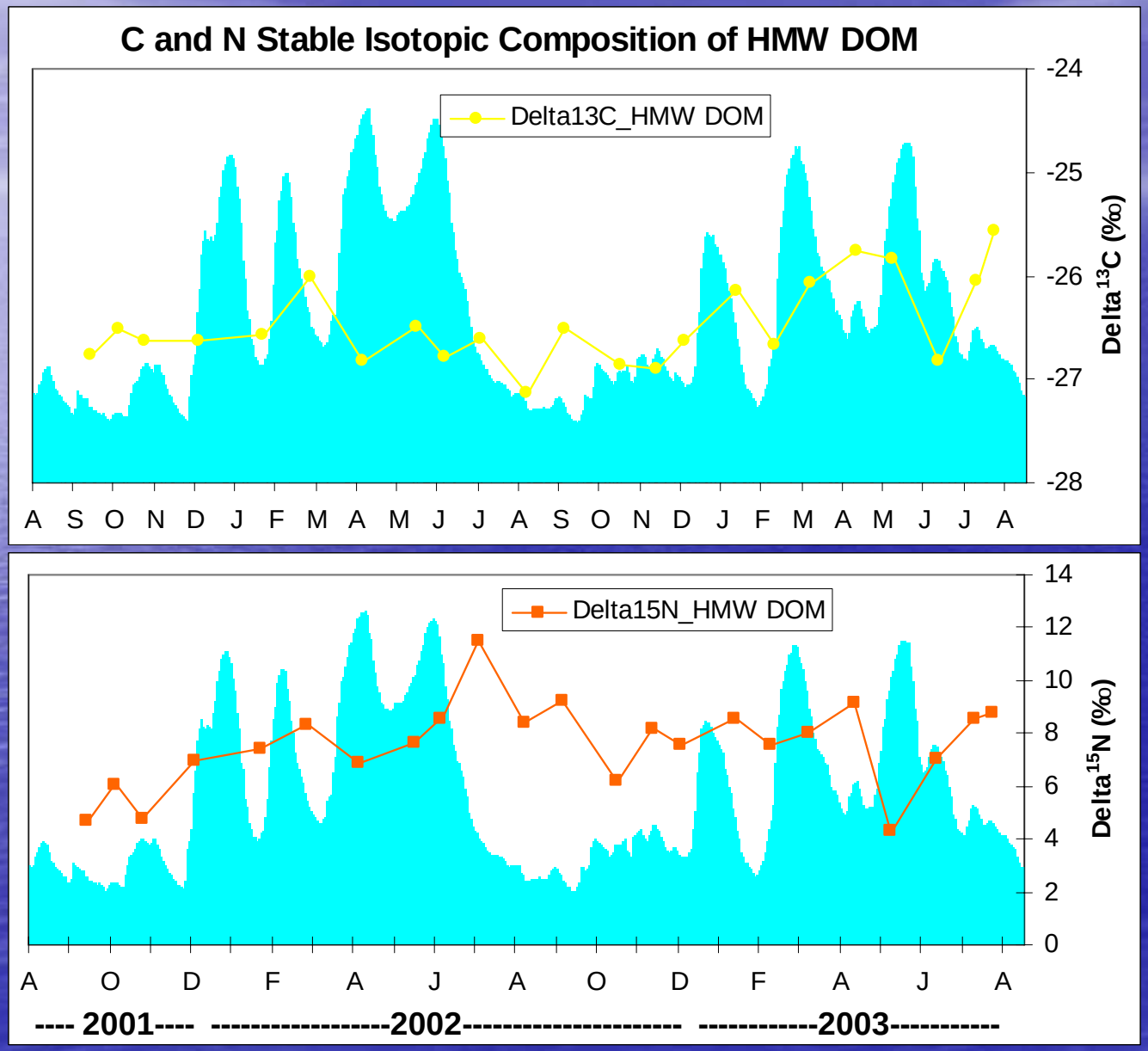
Dissolved Organic Carbon and Nitrogen



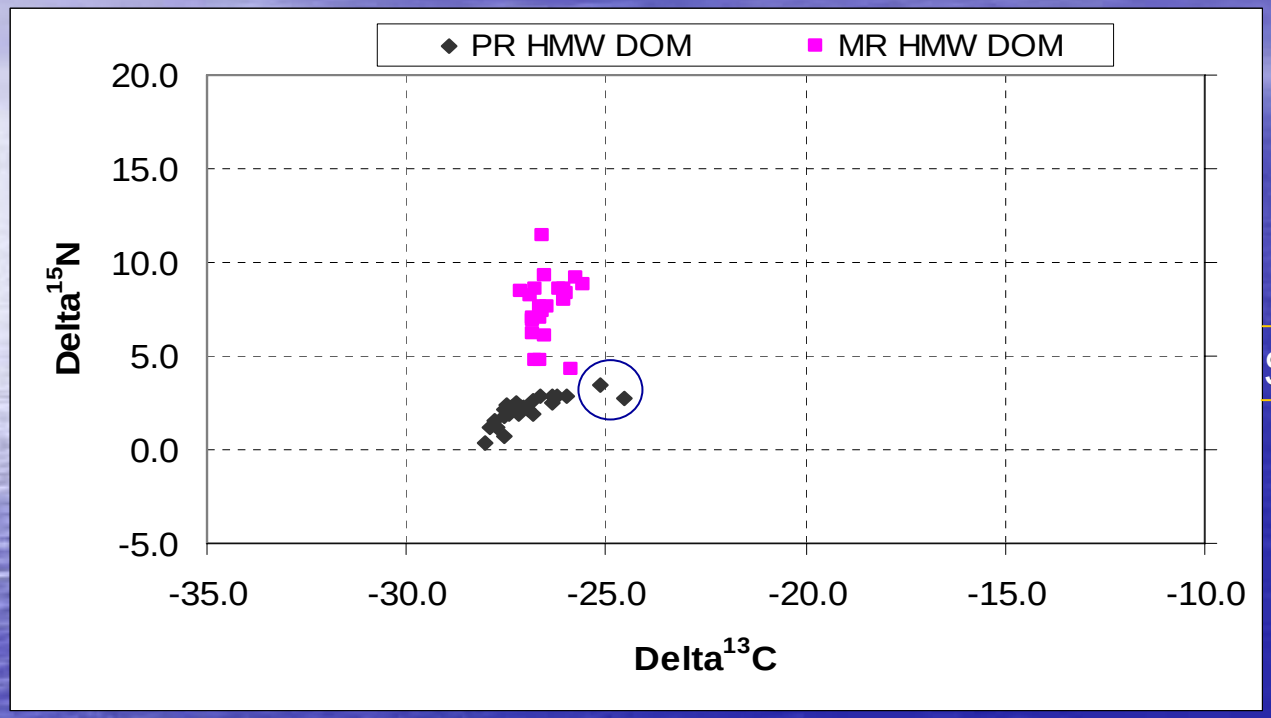
High-Molecular Weight (> 1 kDa) (colloidal) and Low Molecular (< 1kDa) Organic Carbon

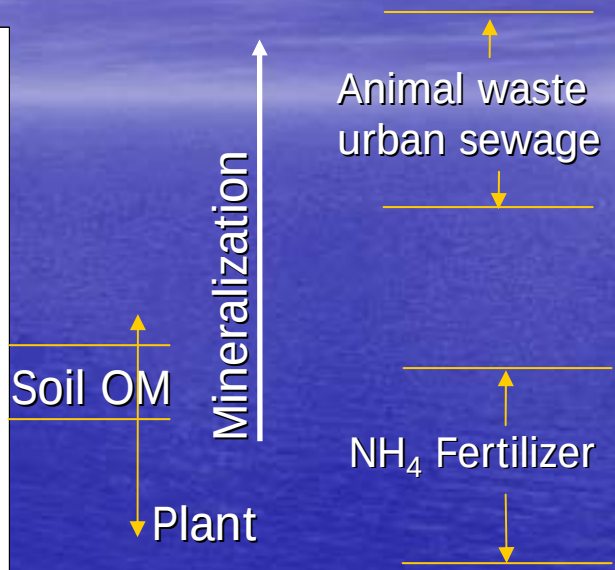


Stable Isotopic Composition of HMW DOM



$\delta^{13}C$ and $\delta^{15}N$ of HMW DOM



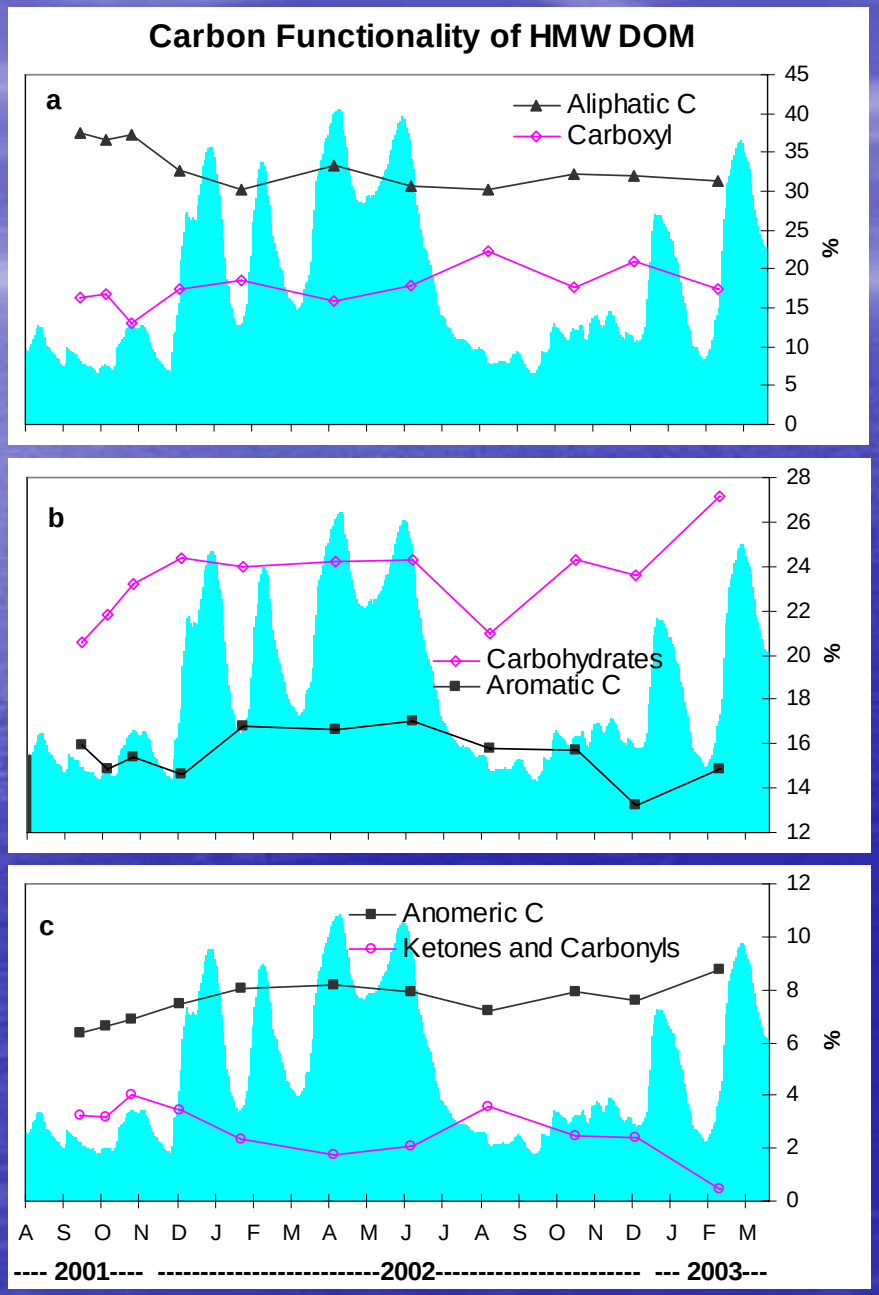


C_3 plant or soils

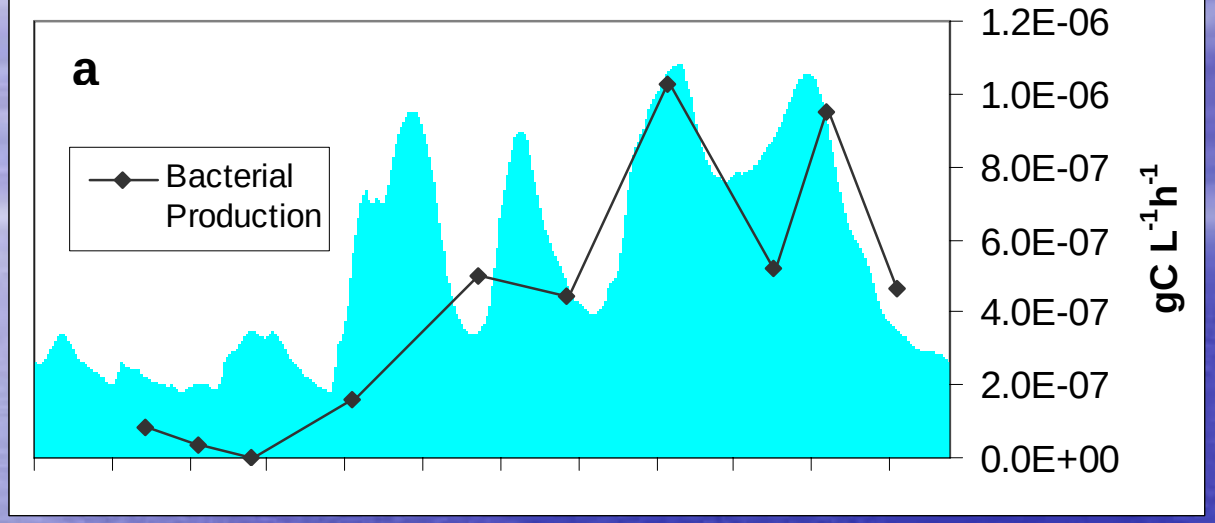
C_4 plant or soils

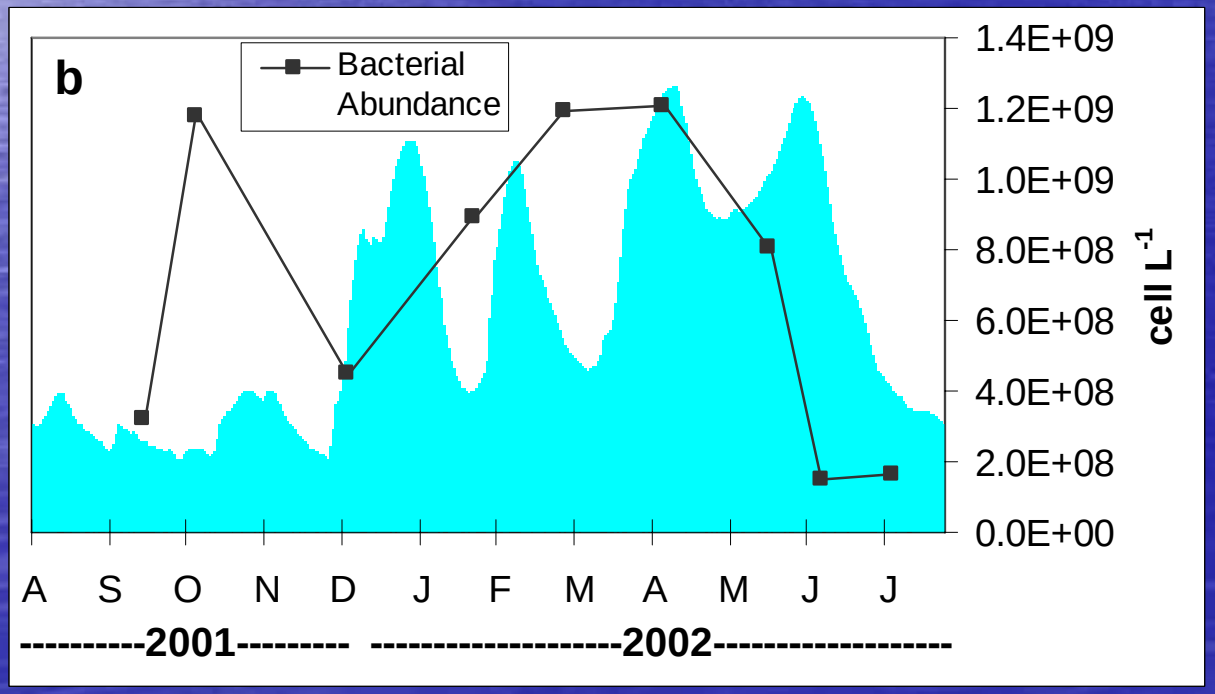
- HMW DOM in the lower MR was more enriched in 15N than the PR, partly due to preferential loss of light isotopes during long-term *in-situ* processing of organic matter in large river systems.

^{13}C-NMR Analysis of HMW DOM

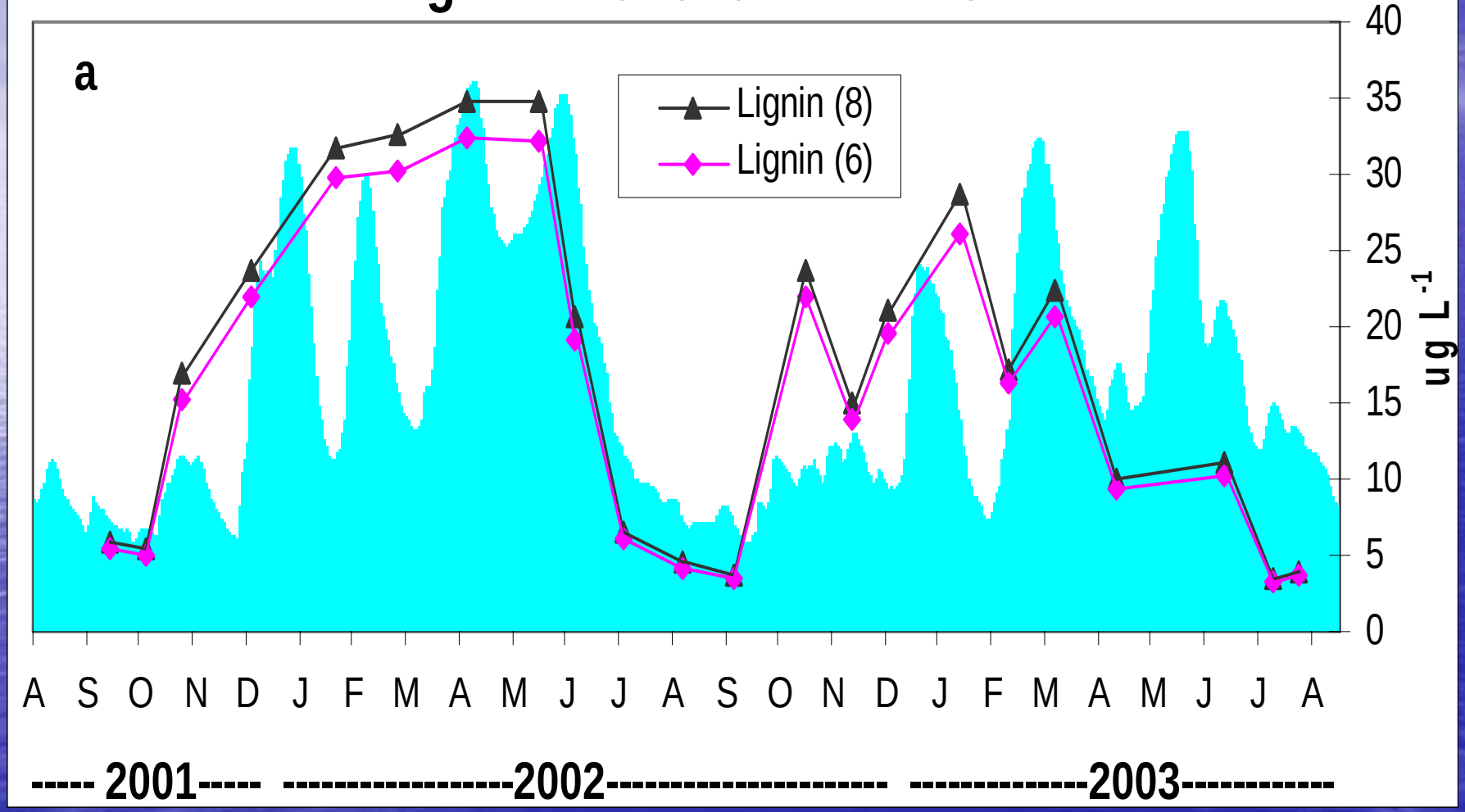


Bacteria Producation and Abundance



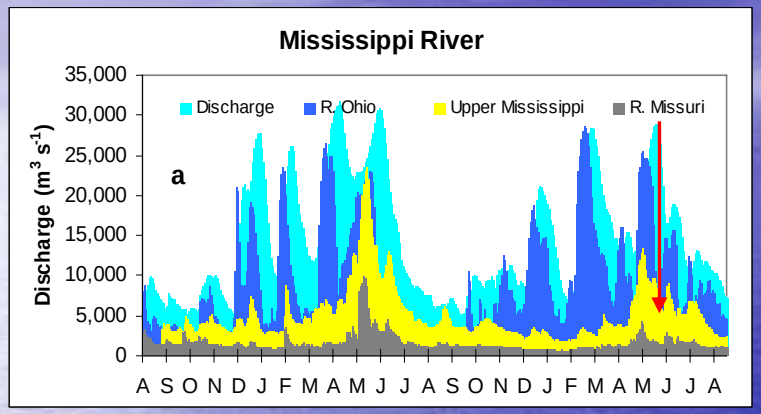


Lignin Phenol of HMW DOM

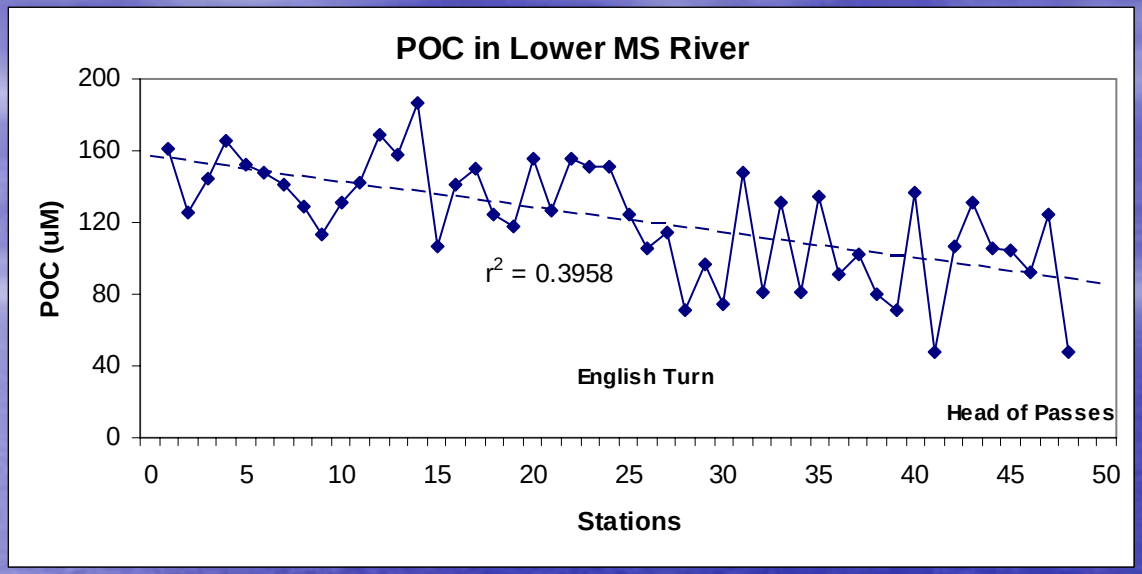


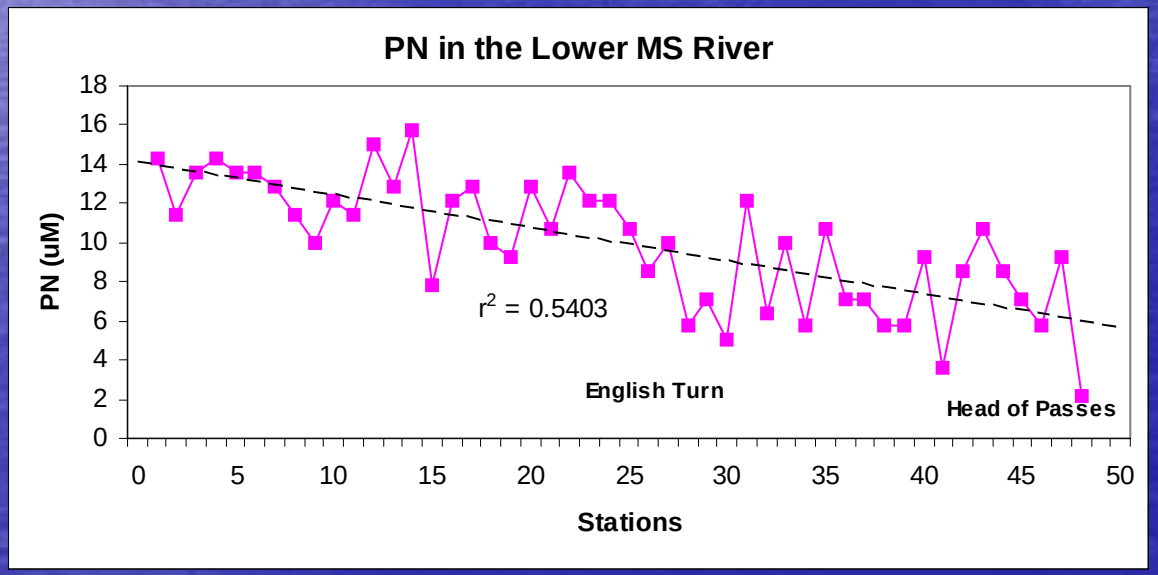
Spatial Sampling

June 20-24, 2003



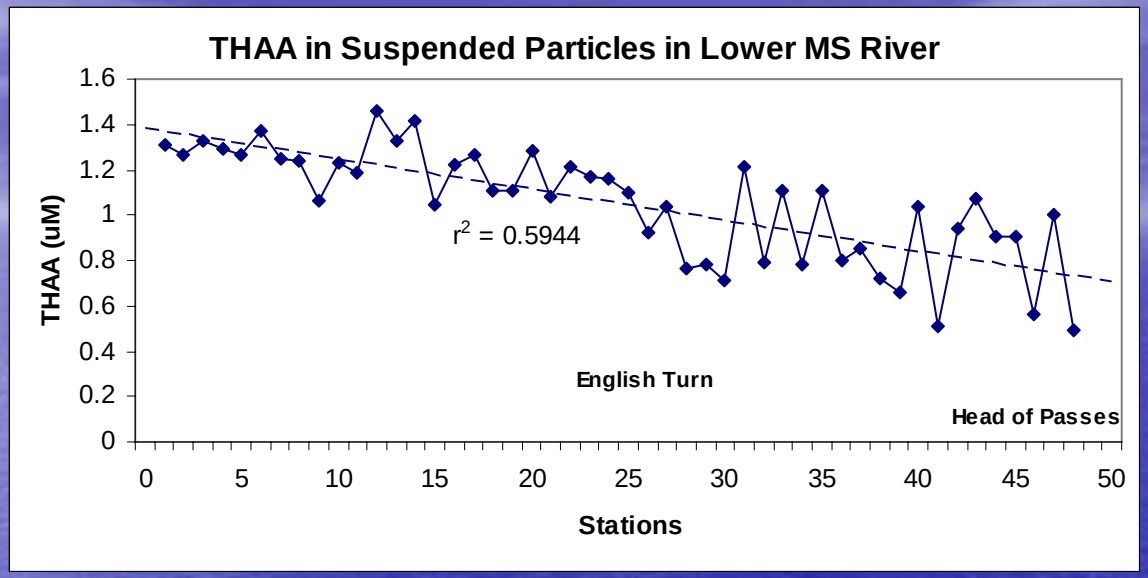
During June 2003, a period of mid-level discharge (17,400 m^{-3} s^{-1}), a parcel of water in the lower Mississippi River was sampled every 2 h during its 4 d transit from river-mile 225 near Baton Rouge, Louisiana, USA to river-mile 0 at Head of Passes, Louisiana, USA.

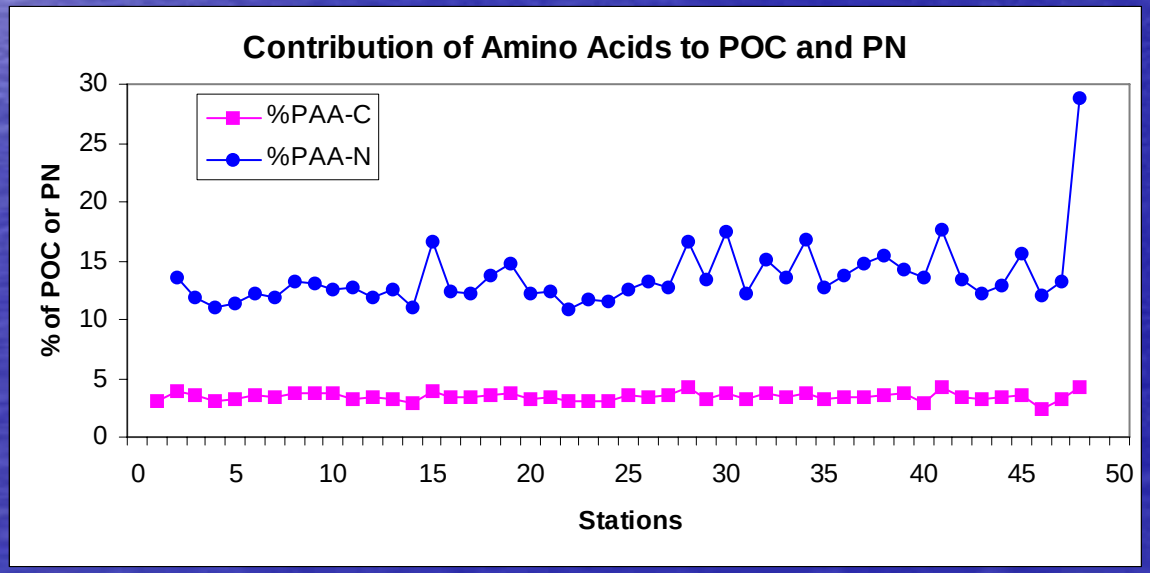

POC in Lower MS River
POC (uM)
200
160
120
80
40
0
0
5
10
15
20
25
30
35
40
45
50
Stations
r2 = 0.3958
English Turn
Head of Passes

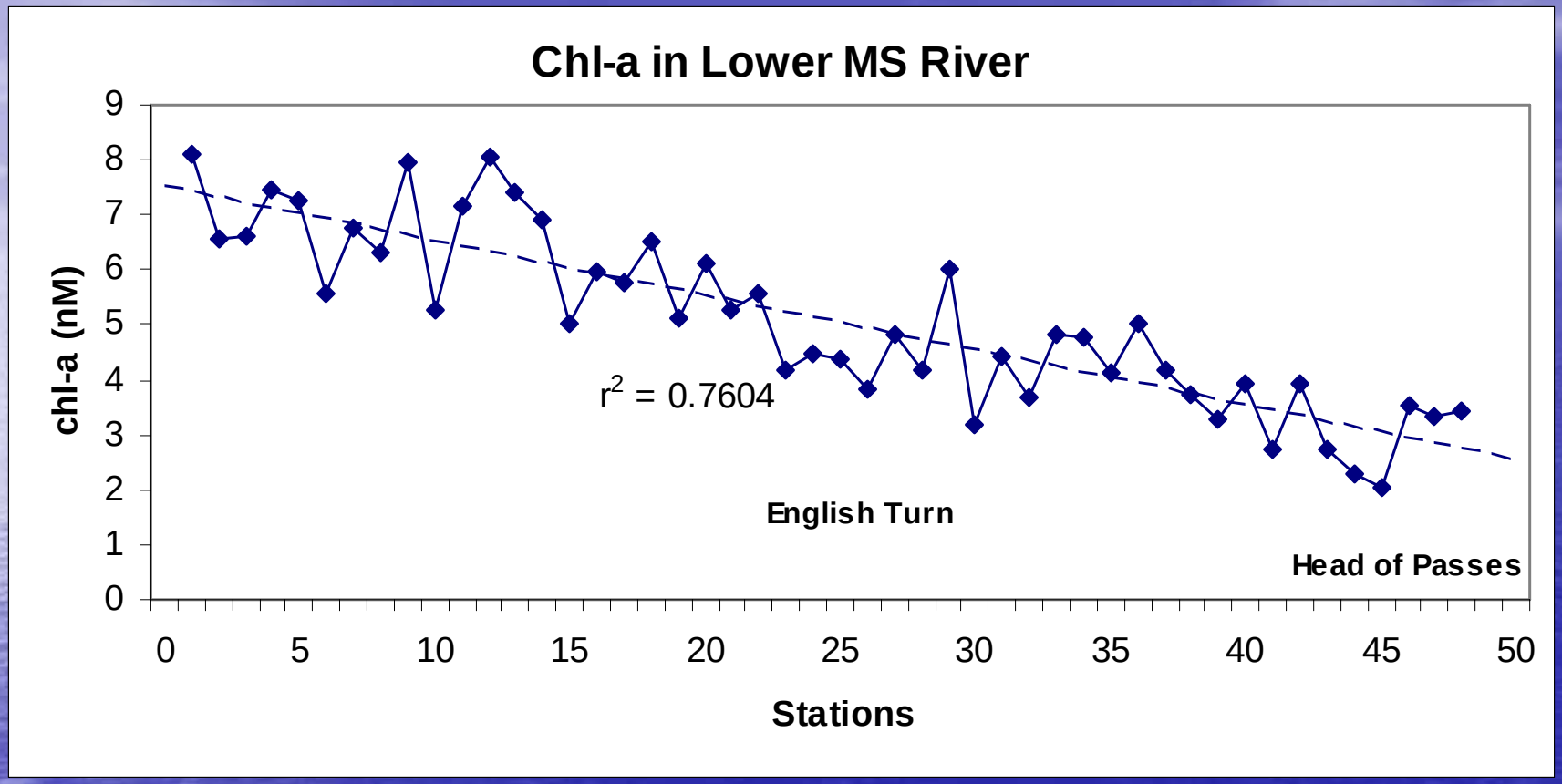

PN in the Lower MS River
PN (uM)
18
16
14
12
10
8
6
4
2
0
0
5
10
15
20
25
30
35
40
45
50
Stations
r2 = 0.5403
English Turn
Head of Passes

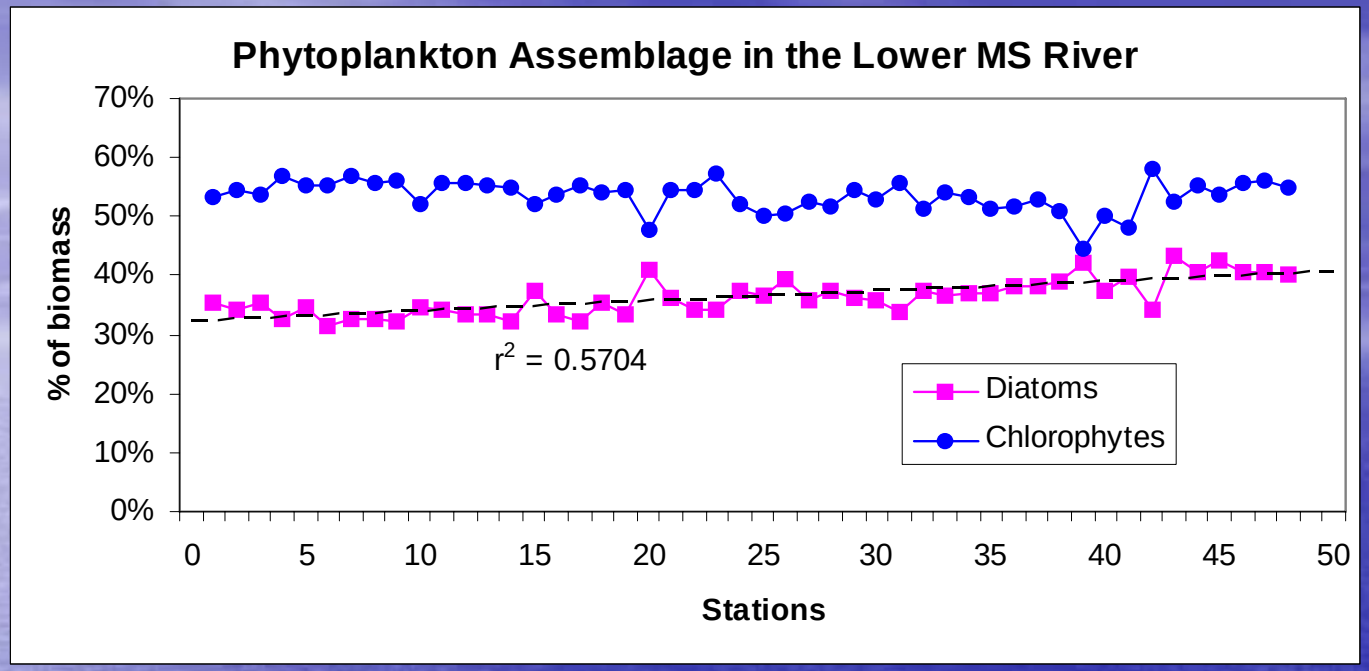
Total Hydrolyzable Amino Acids in POM

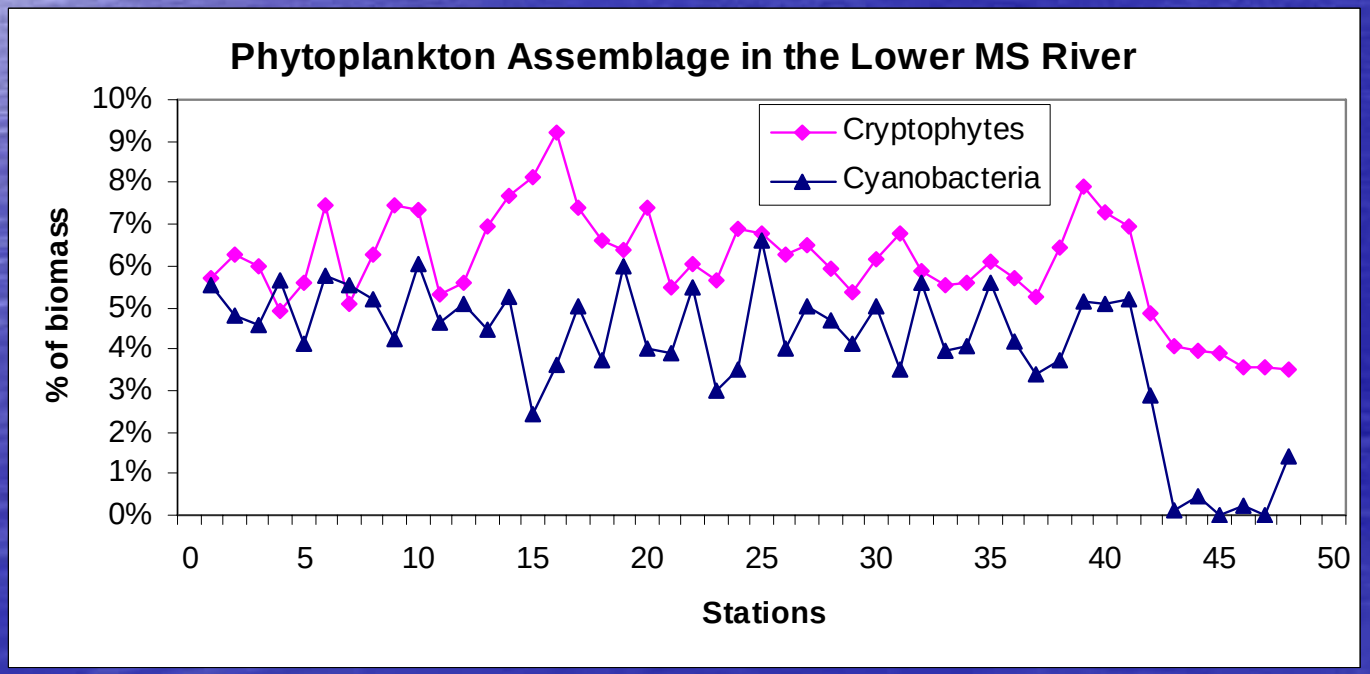
THAA highly corrected with PN (r^2 = 0.94)






Chl-a in Lower MS River
chl-a (nM)
9
8
7
6
5
4
3
2
1
0
0
5
10
15
20
25
30
35
40
45
50
Stations
r2 = 0.7604
English Turn
Head of Passes

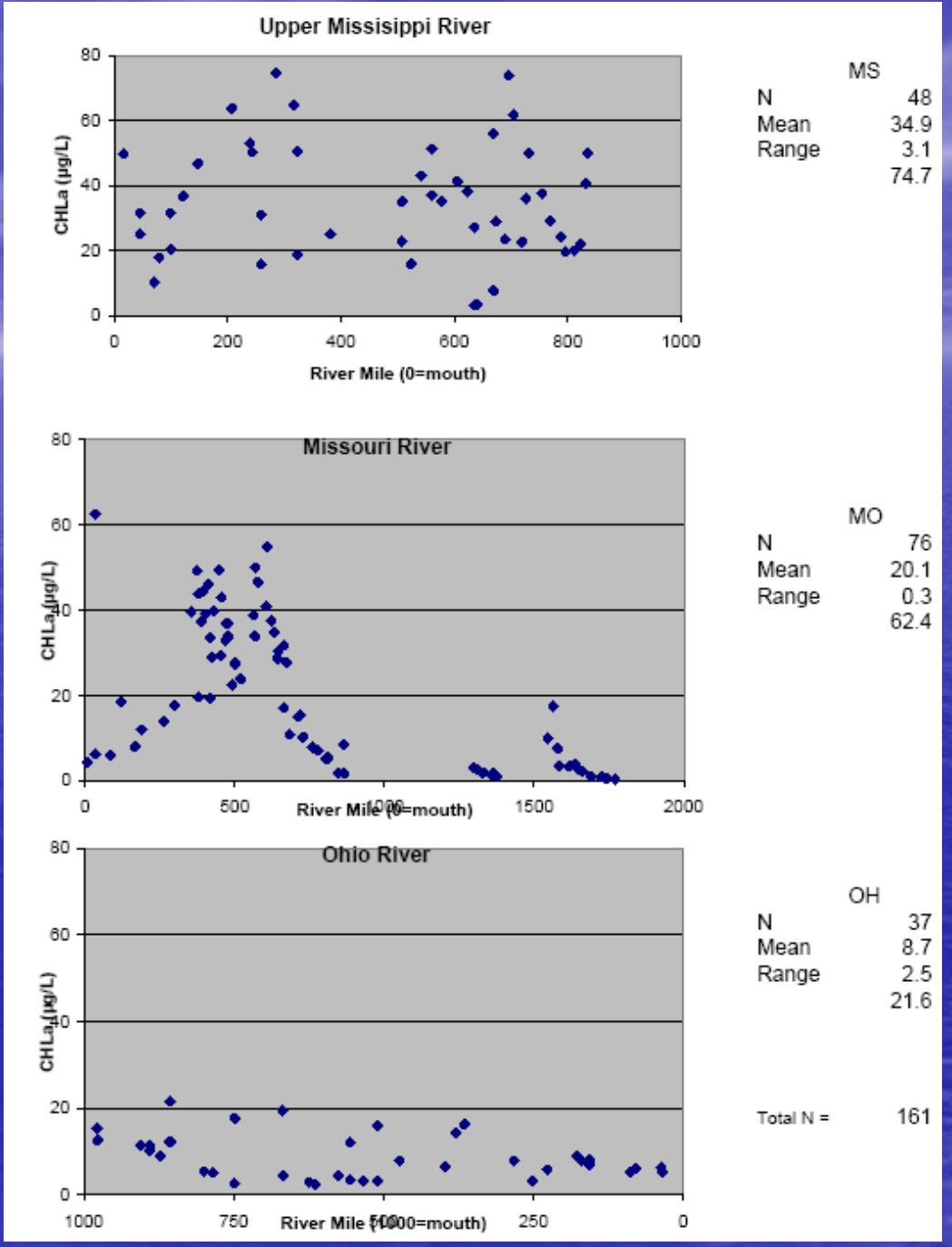

Phytoplankton Assemblage in the Lower MS River
% of biomass
70%
60%
50%
40%
30%
20%
10%
0%
0
5
10
15
20
25
30
35
40
45
50
Stations
r2 = 0.5704
Diatoms
Chlorophytes

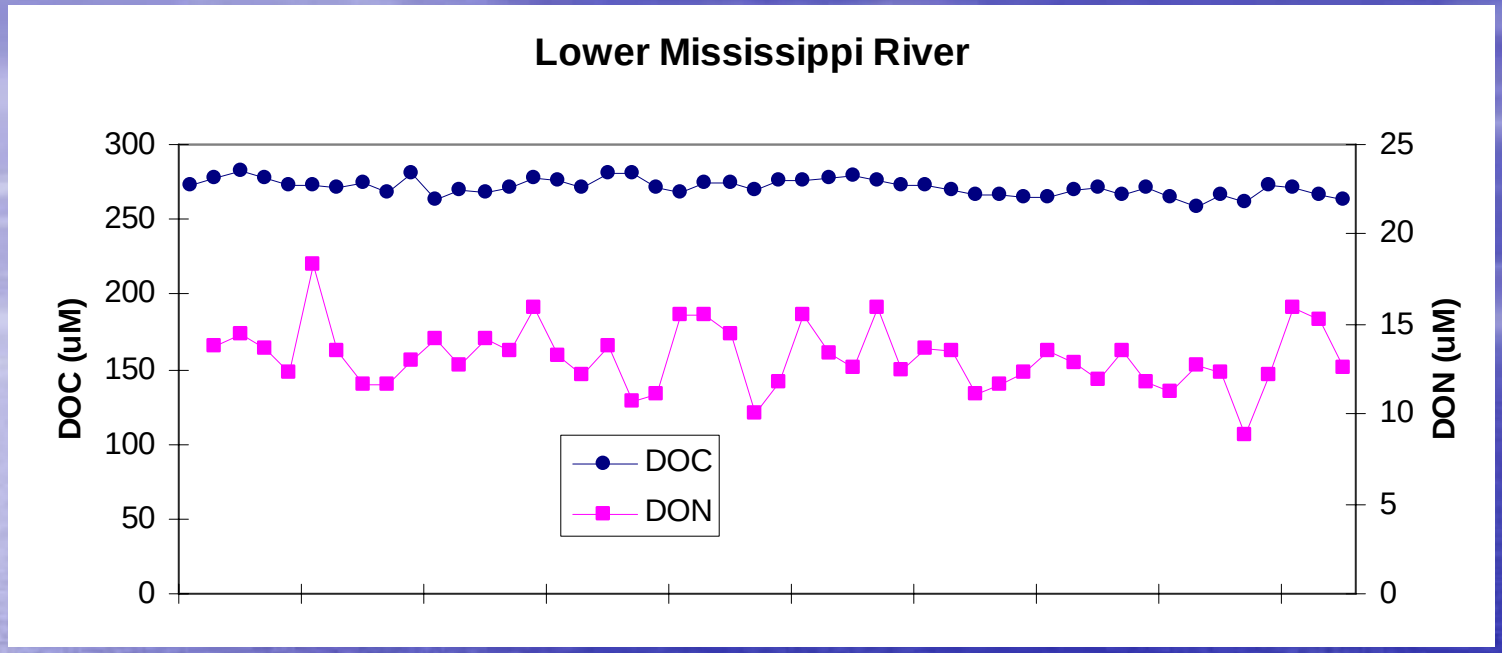

Phytoplankton Assemblage in the Lower MS River
% of biomass
10%
9%
8%
7%
6%
5%
4%
3%
2%
1%
0%
0
5
10
15
20
25
30
35
40
45
50
Stations
Cryptophytes
Cyanobacteria

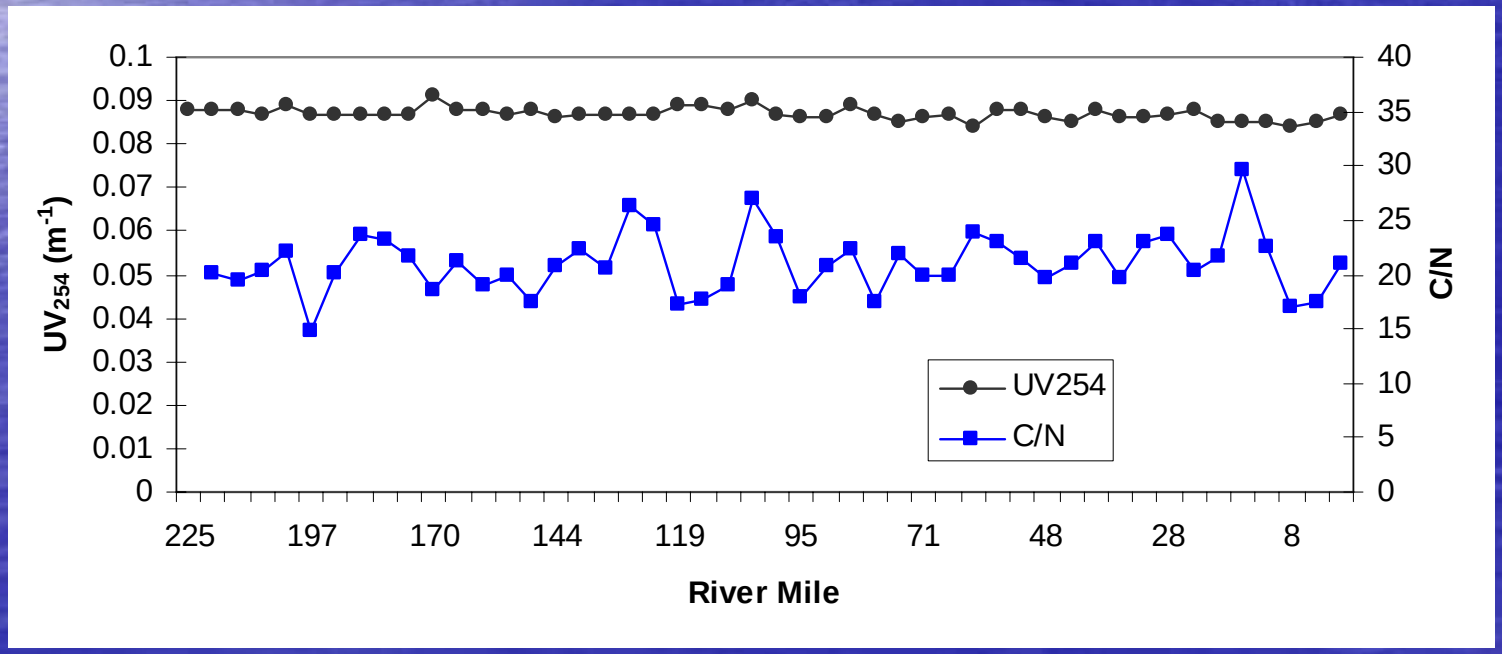
Phytoplankton Abundance in Primary Tributaries of the MR

(EPA EMAP GRE chl-a data, 2004)

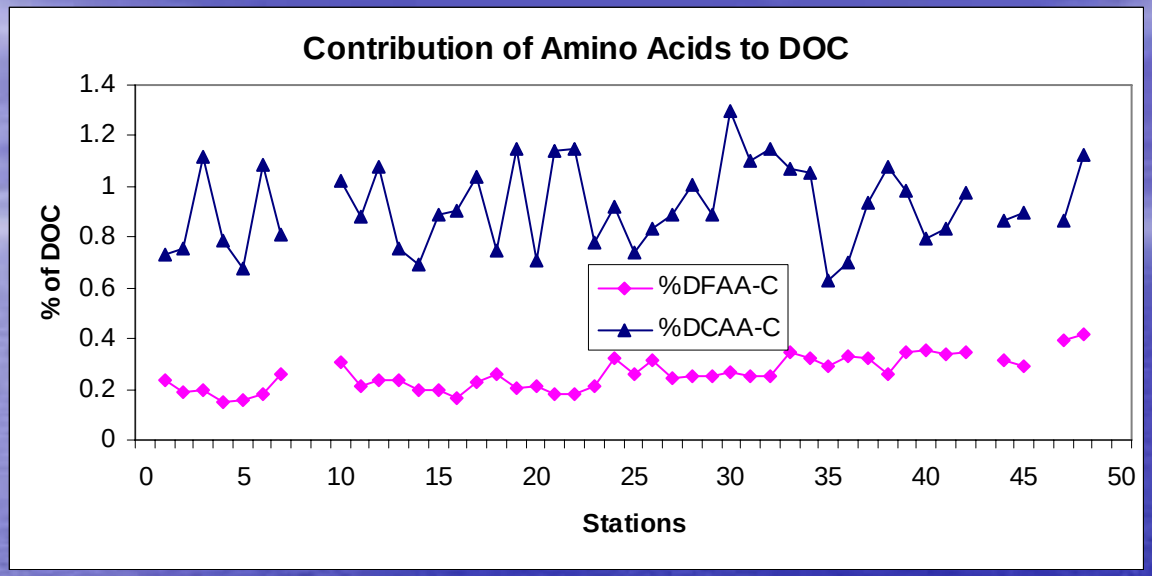
Exportation of phytoplankton biomass from backwater reservoirs, navigation locks, and wetland of tributaries during high-flow periods

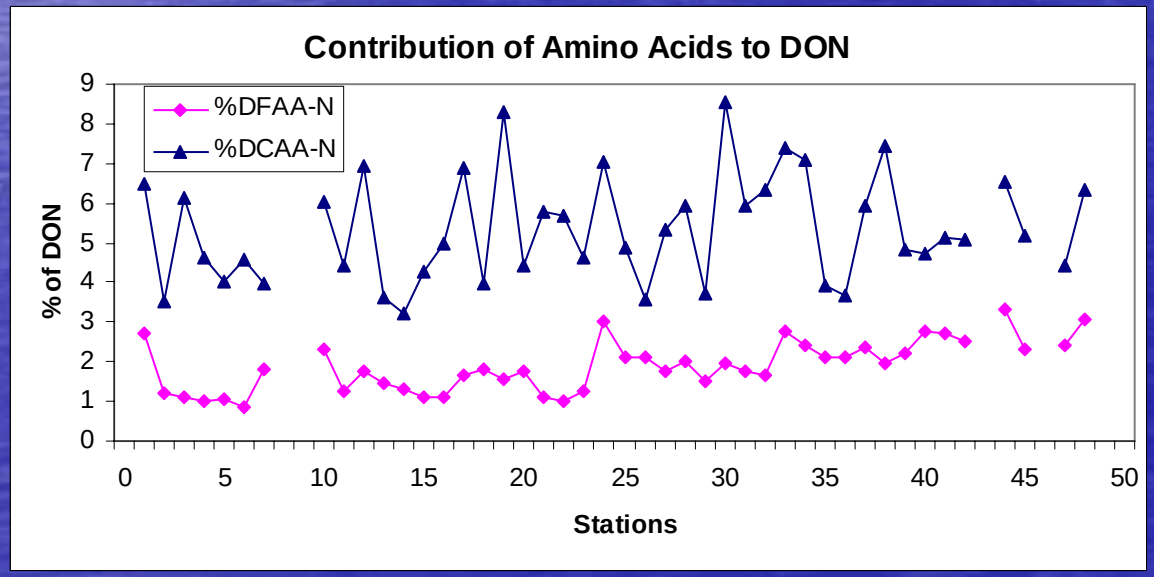



Lower Mississippi River
DOC (uM)
DON (uM)
300
250
200
150
100
50
0
25
20
15
10
5
0
DOC
DON

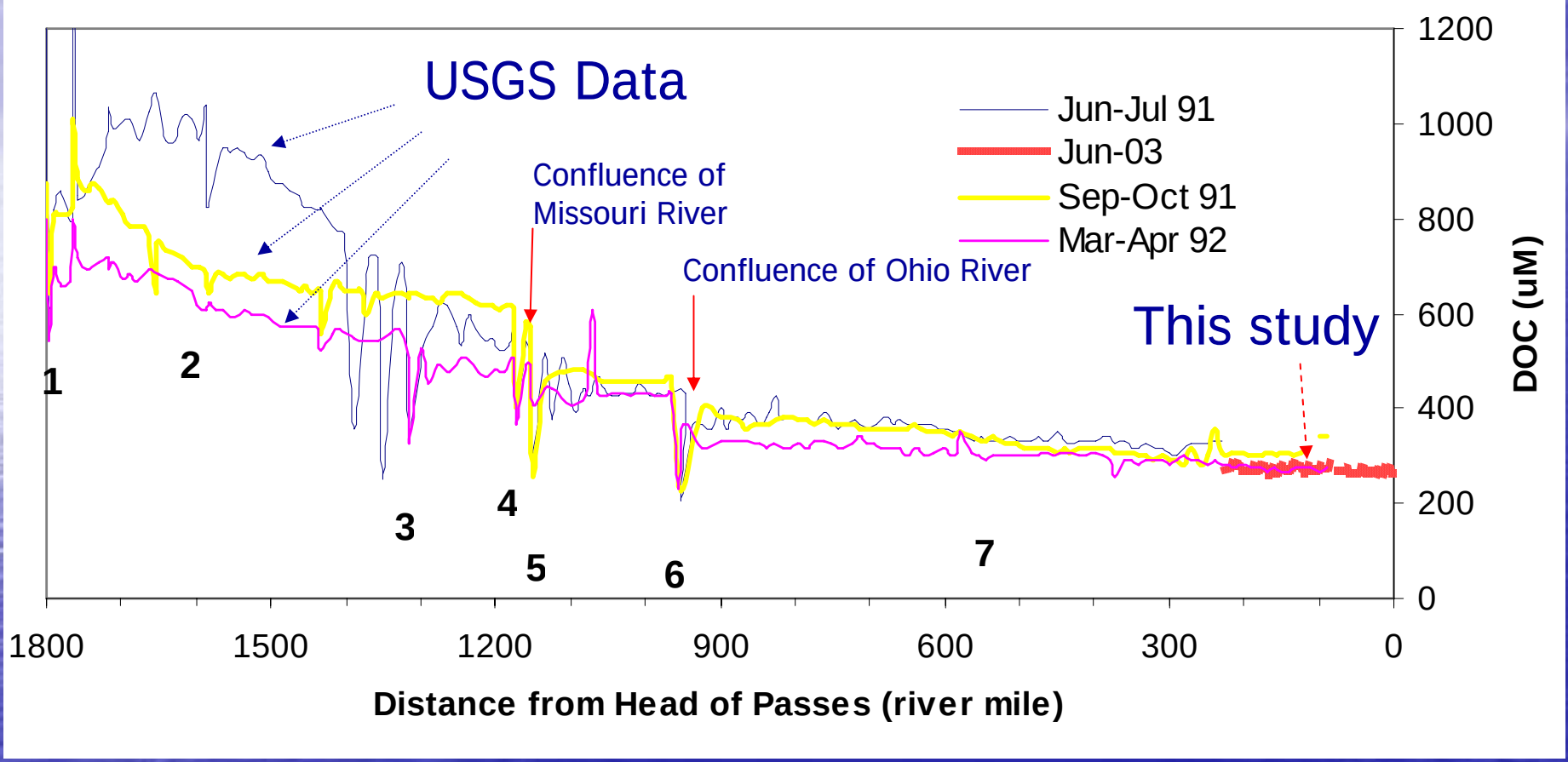

UV254 (m-1)
C/N
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
40
35
30
25
20
15
10
5
0
UV254
C/N
225
197
170
144
119
95
71
48
28
8
River Mile

Dissolved Free and Combined Amino Acids in DOM





DOC in the Mississippi River From Headwater to Head of Passes



- DOC gradually decreases, most of the decrease occurred in upper MR (by 30-48%), very little (6-8%) in lower river
- Large decrease in DOC below the confluence of the Missouri River and Ohio River, likely from dilution effect and *in-situ* processing

Mean Global Fluvial Loadings of Organic Carbon to the Oceans

Reference	DOC	POC	TOC
Smith and Hollibaugh (1993)	164	197	386

Units = 10^{11} mol C yr^{-1}

Mean Annual Fluvial Loadings of Organic Carbon from the Mississippi River

	DOC	POC	TOC
(July 1998 - June 1999)	3.0 (62%)	1.8 (38%)	4.8
This Study- Global Percent:	1.8	0.9	1.2

Units = 10^{11} mol C yr^{-1}

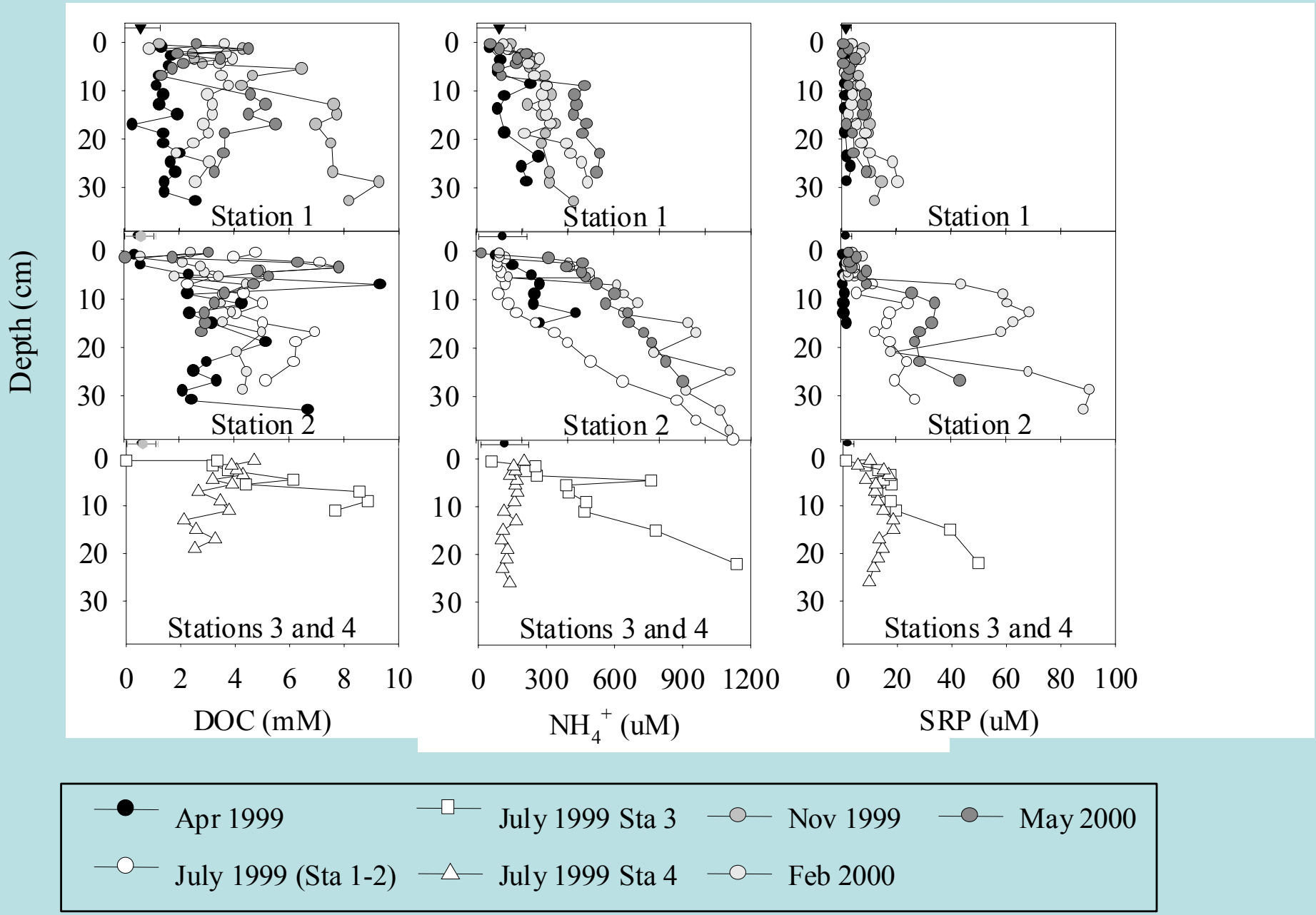
Bianchi et al. (2003)

Background: Seasonal Sediment Storage in Rivers

Presently, only about 10% of the sediments eroded from land are being discharged directly to the oceans by rivers, while the bulk of particulate terrestrial materials is being stored somewhere within the river system--between the uplands and the sea (Meade et al., 1990).

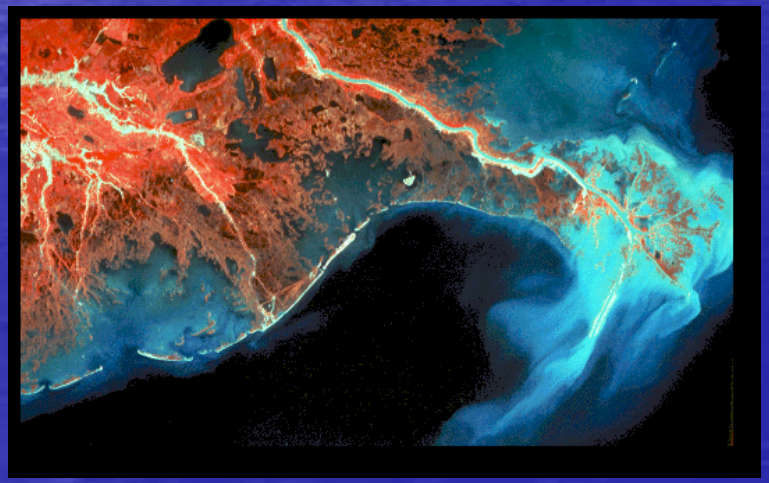
The seasonal storage and remobilization of sediments in rivers is a worldwide phenomenon that has been observed and described for rivers ranging in size from small streams to the Amazon, the world's largest river.

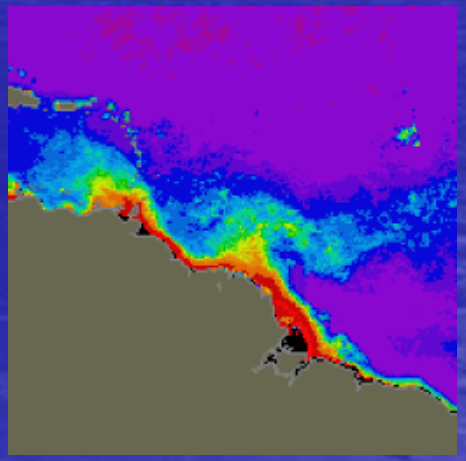
DOC, Ammonium, and SRP in River and Shelf Porewaters



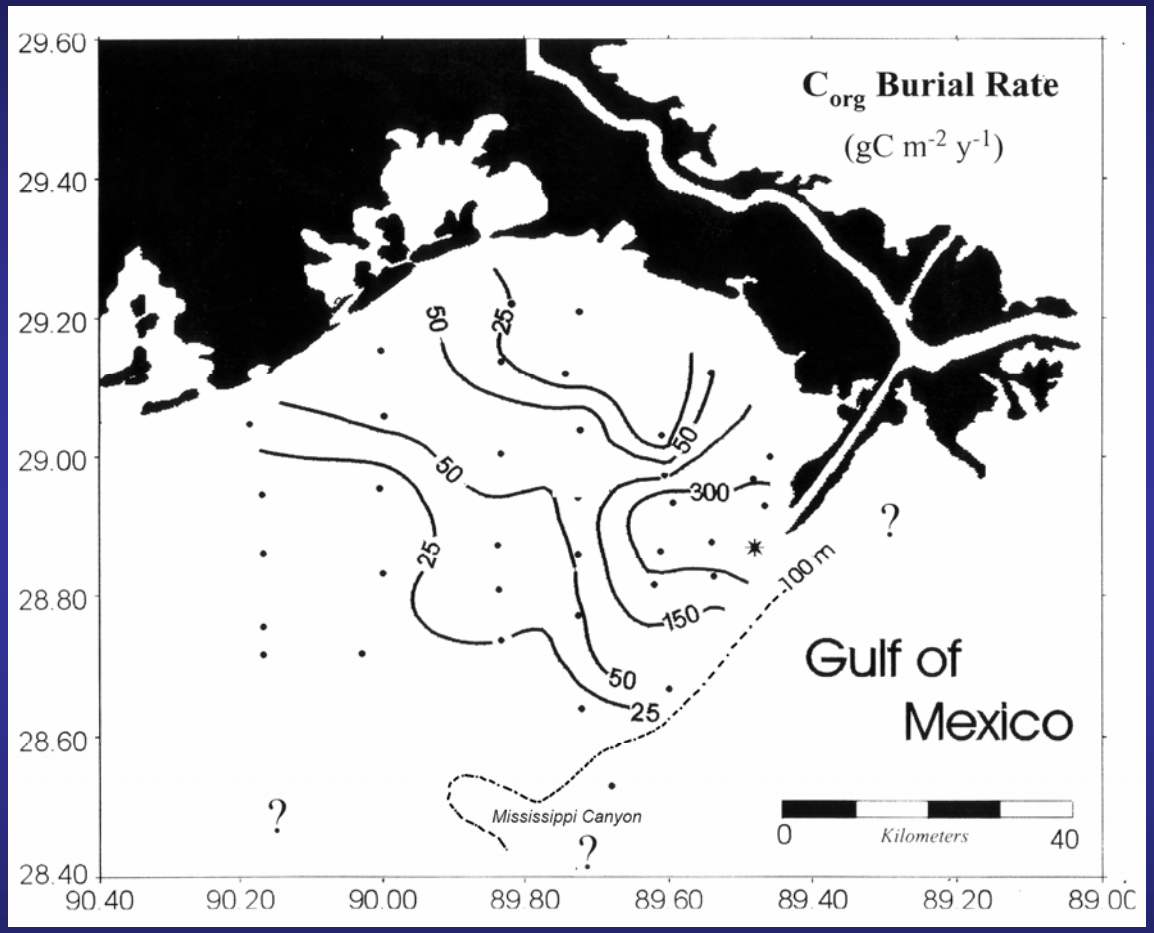
River-Dominated Ocean Margins (RiOMars)

Most of the terrestrial materials (organic carbon, macronutrients, micronutrients, major/minor elements, mineral matter) transported to the oceans enter via these margin environments

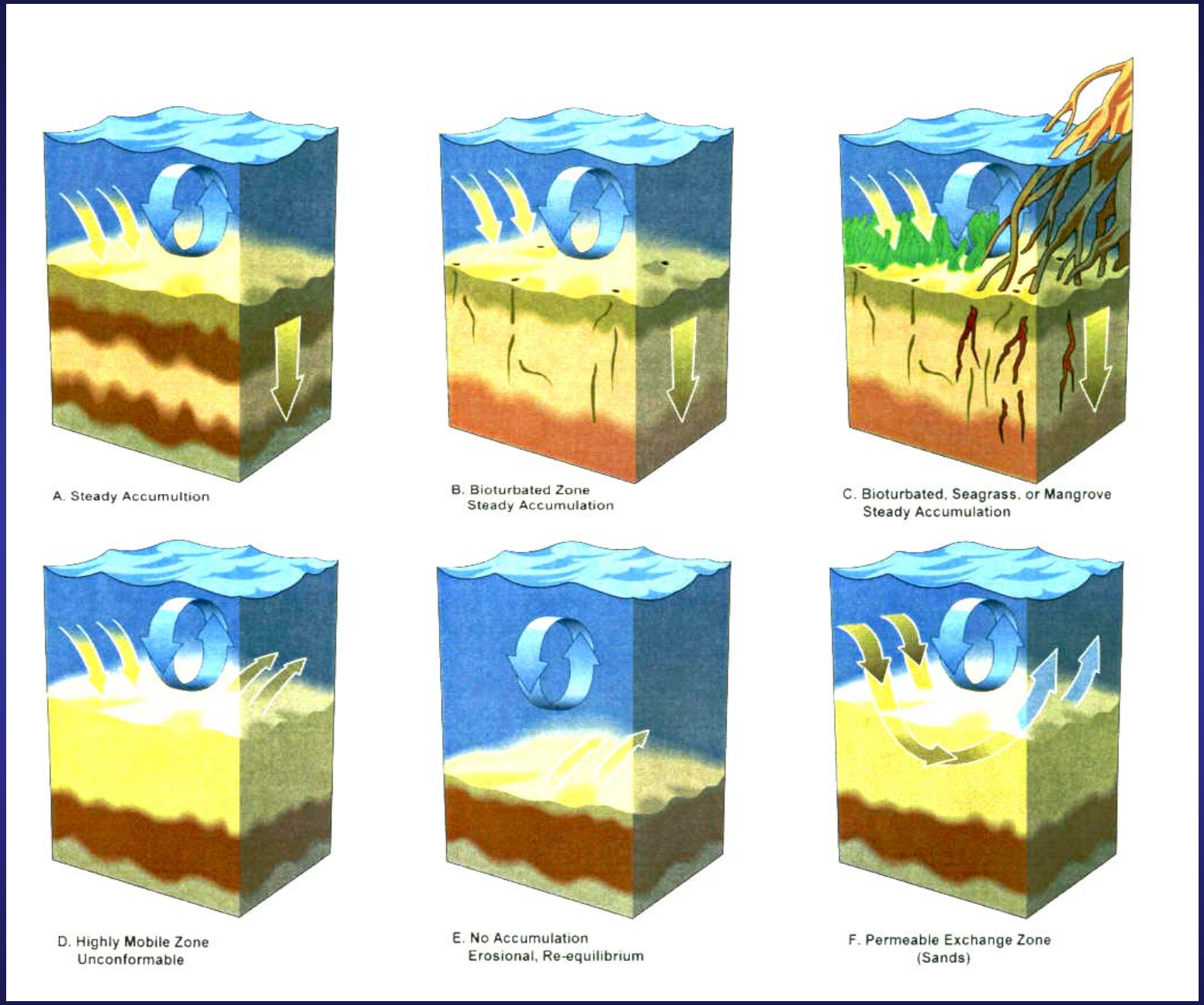




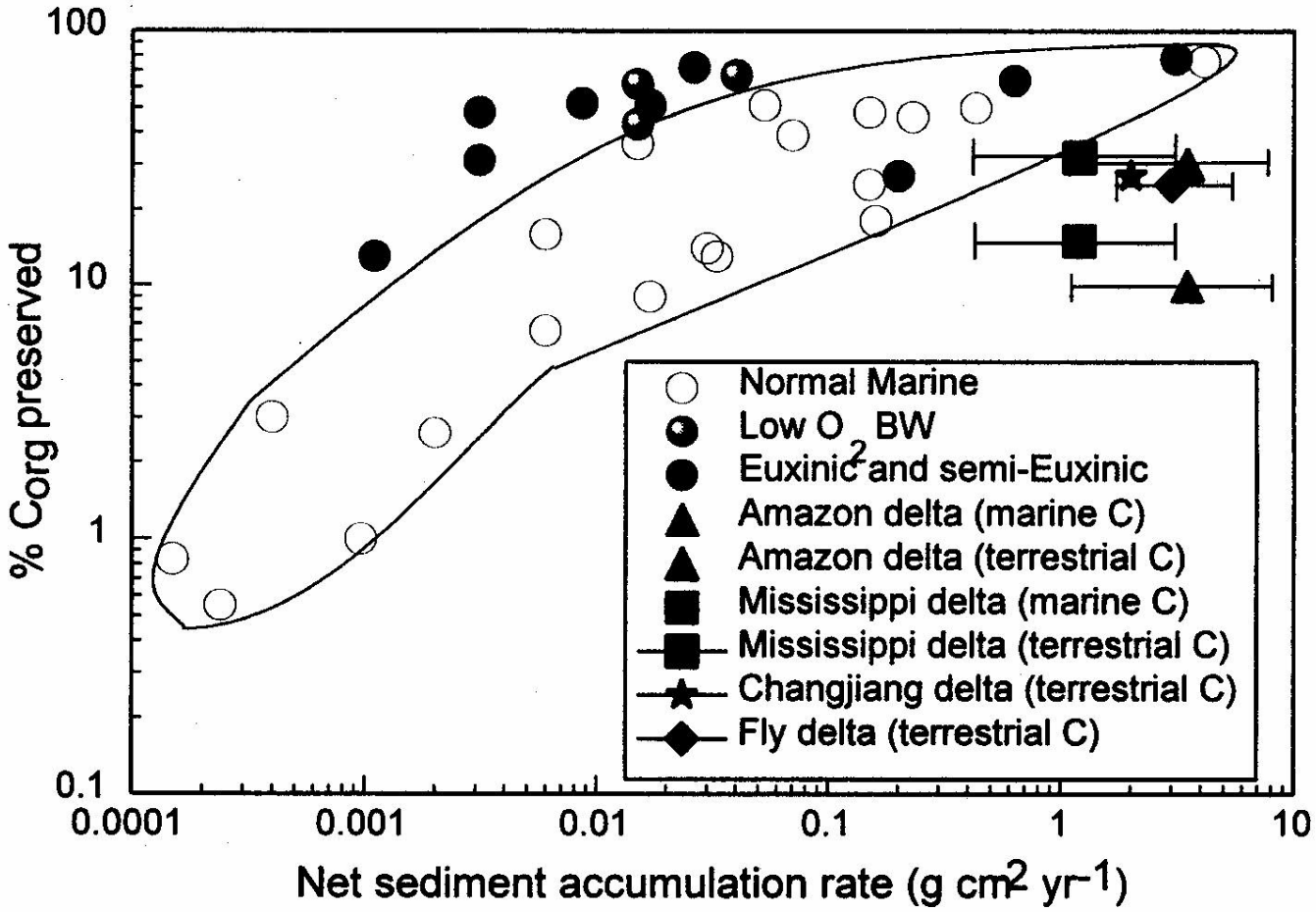
If a mass-balance approach is taken (using stable isotopes), the conclusion is that only 30% of the **terrestrial organic carbon** delivered to this depocenter over the past 100 years is preserved— the rest is remineralized (Eadie et al., 1994; Trefrey et al., 1994).



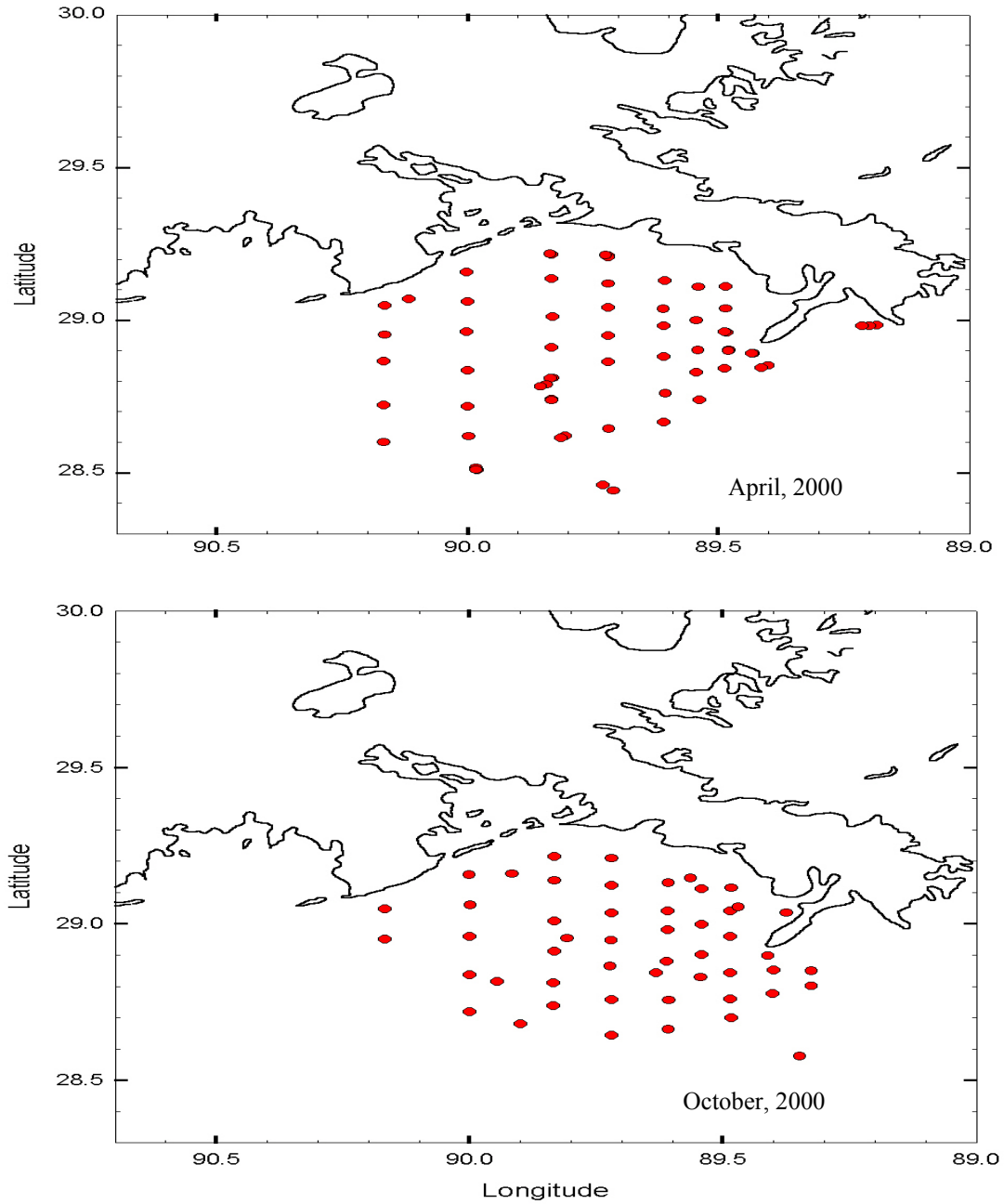
Other vascular plant sources or transported offshore?



Aller R.C. (2002) - modified by McKee et al. (2003)



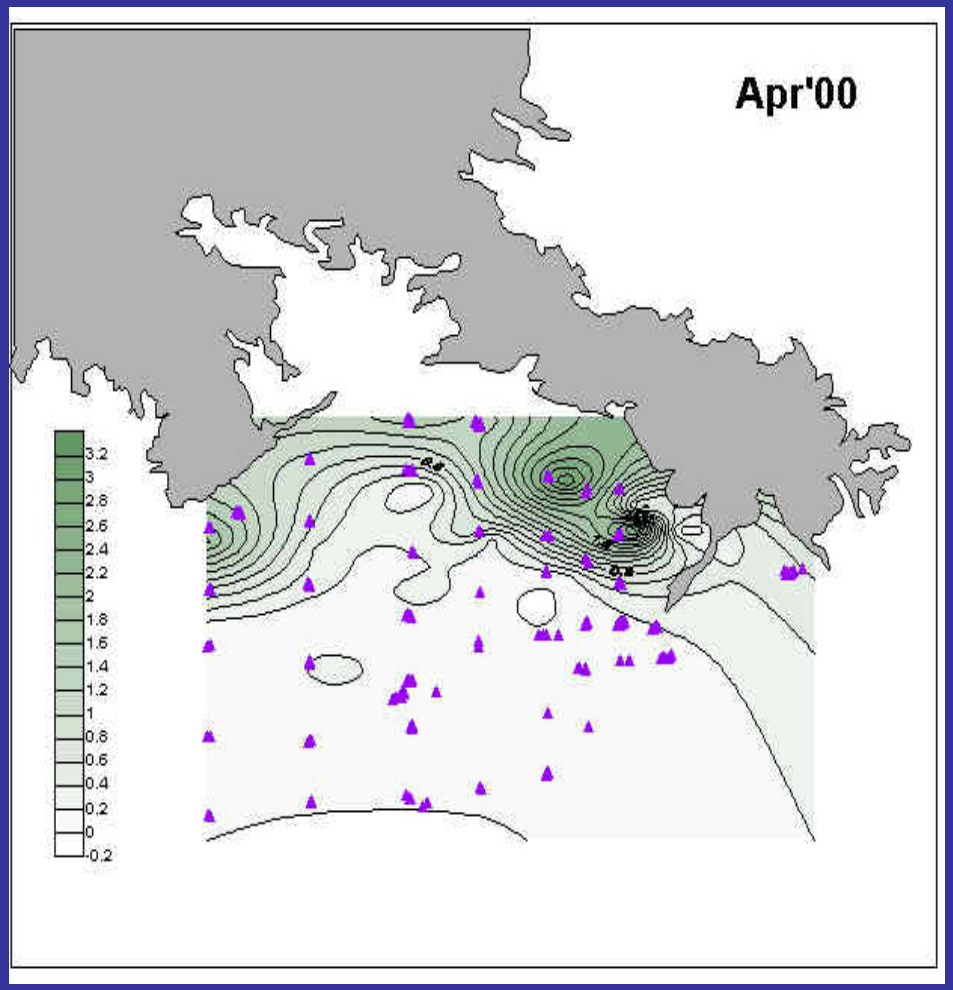
Aller R.C. (1998)

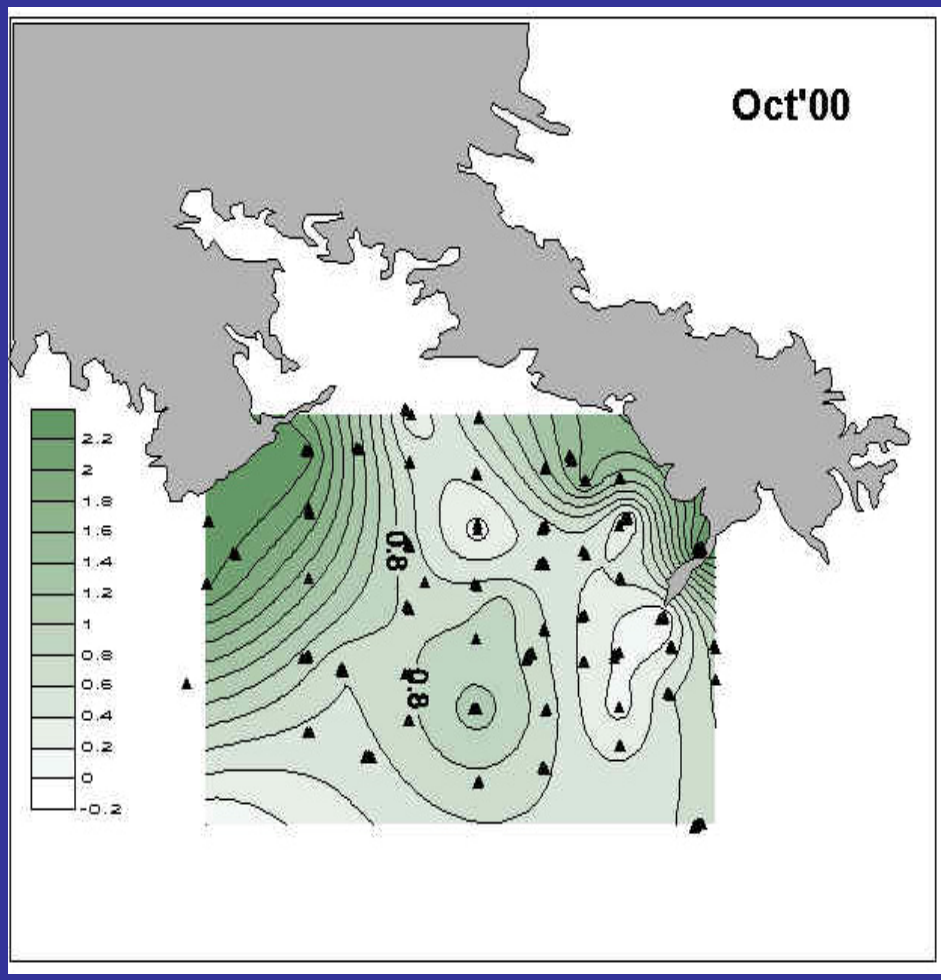


(Wysocki and Bianchi, unpublished)

N

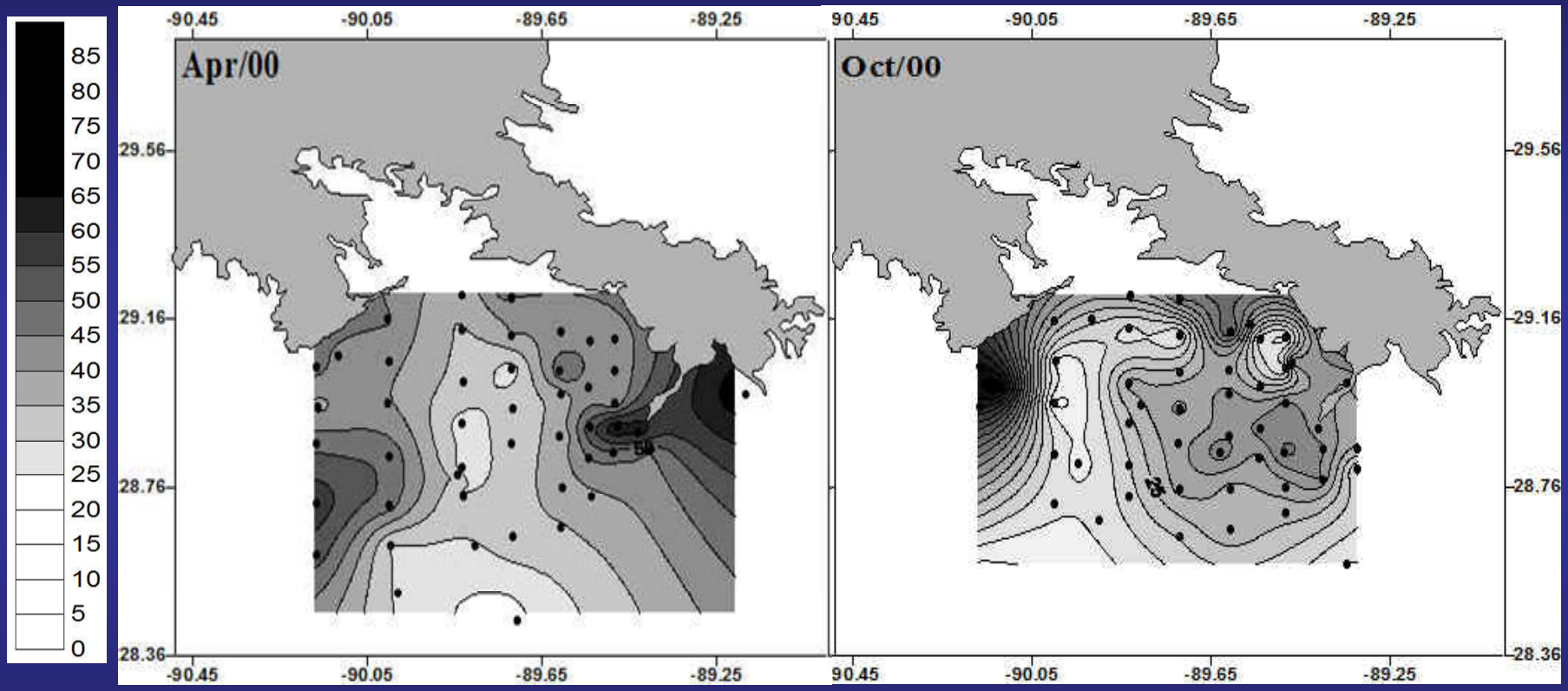
Lignin in Surface Sediment





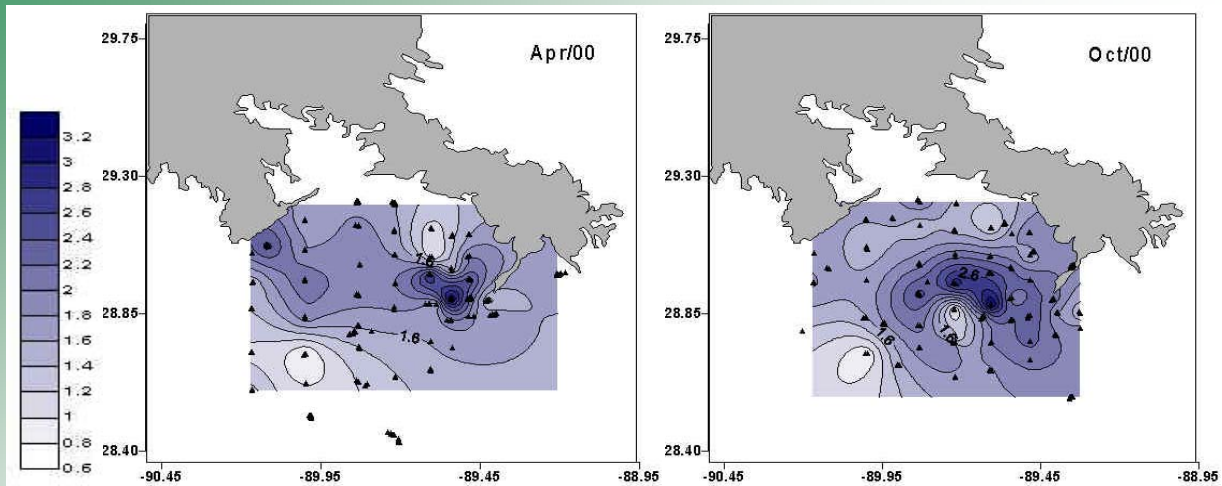
Lambda = TMAH products per 100 mg of sedimentary organic carbon

- **Distribution of terrestrial organic matter as a percentage of total organic carbon** according to equation 1.
- Mean values were 41.3% ± 9.9 in April (high flow) and 32.5% ± 15.7 in October (low flow).

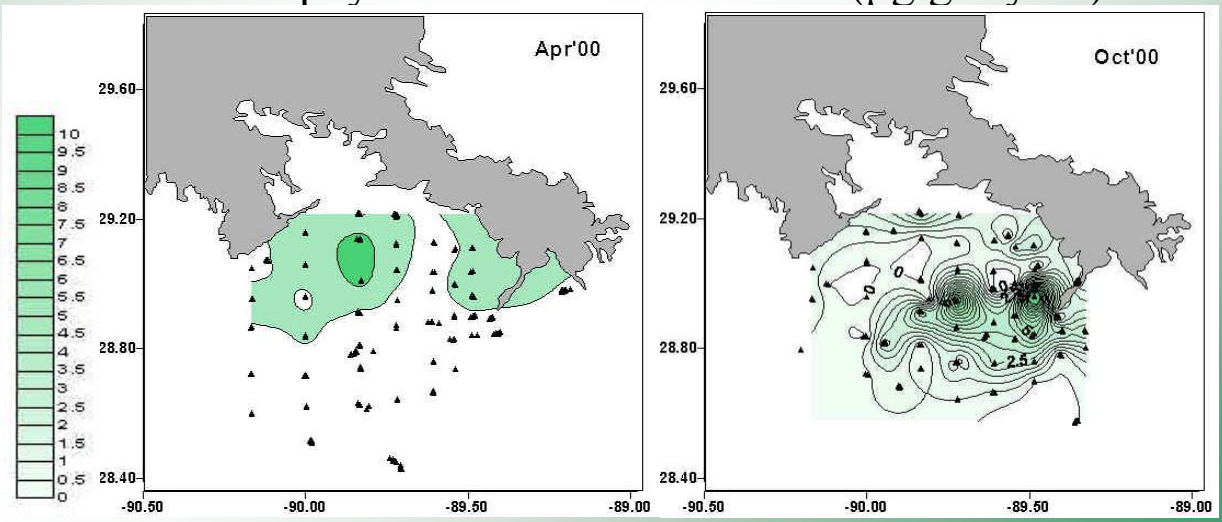


Using mixing model equations to calculate the relative amounts of C3 and C4 sources in the total terrestrial pool, it was determined that ~ 30-40% of the terrestrial inputs to the Louisiana shelf are from C3 sources.

Ad/Al ratios in surface sediments



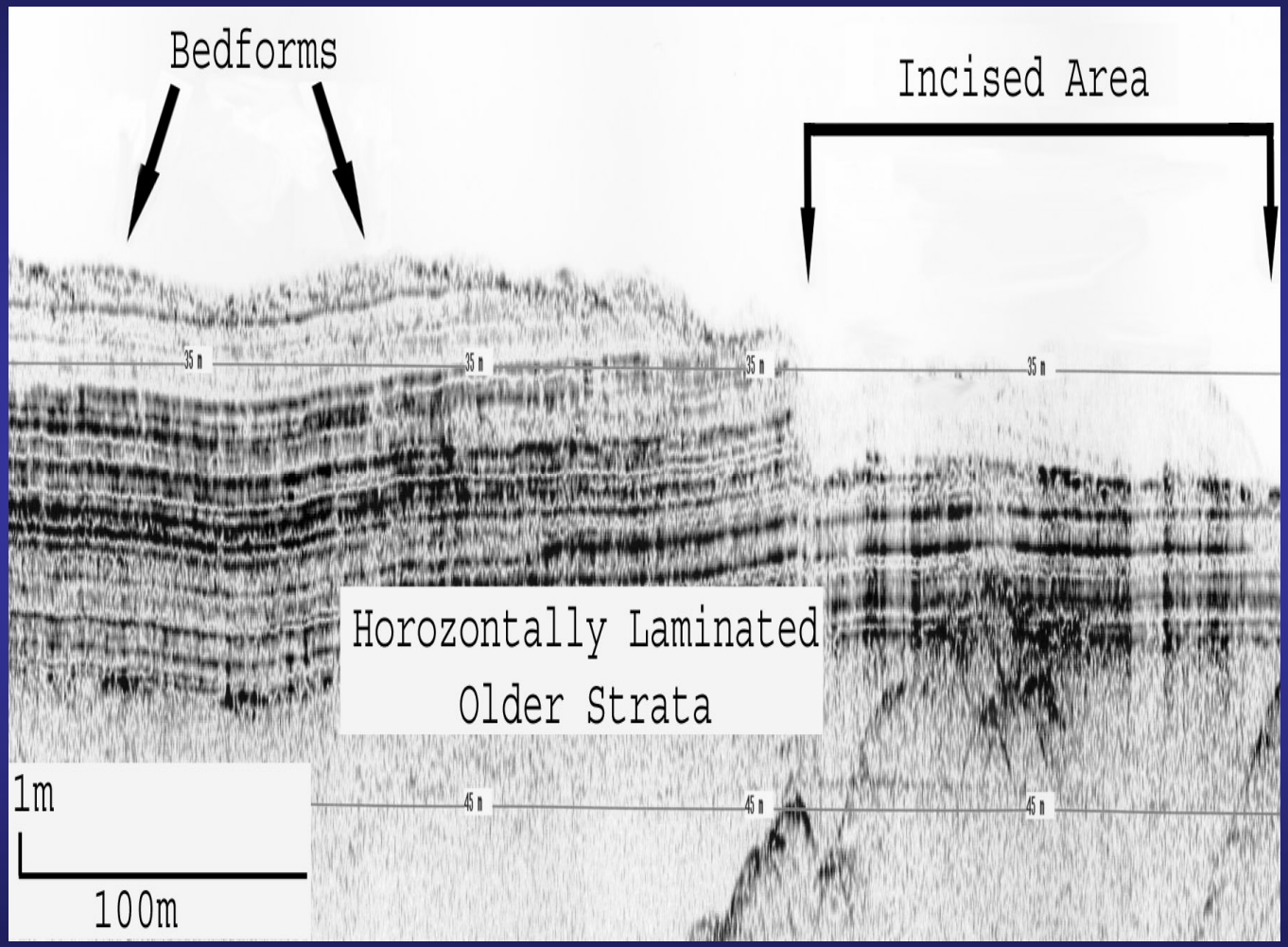
Chlorophyll *a* in surface sediments (µg/g dry wt)



April	October	
range: 0 – 2 µg/g	range: 0– 12 µg/g	Wysocki et al.
mean: 0.44 ± 0.09	mean: 1.75 ± 0.67	(unpublished)

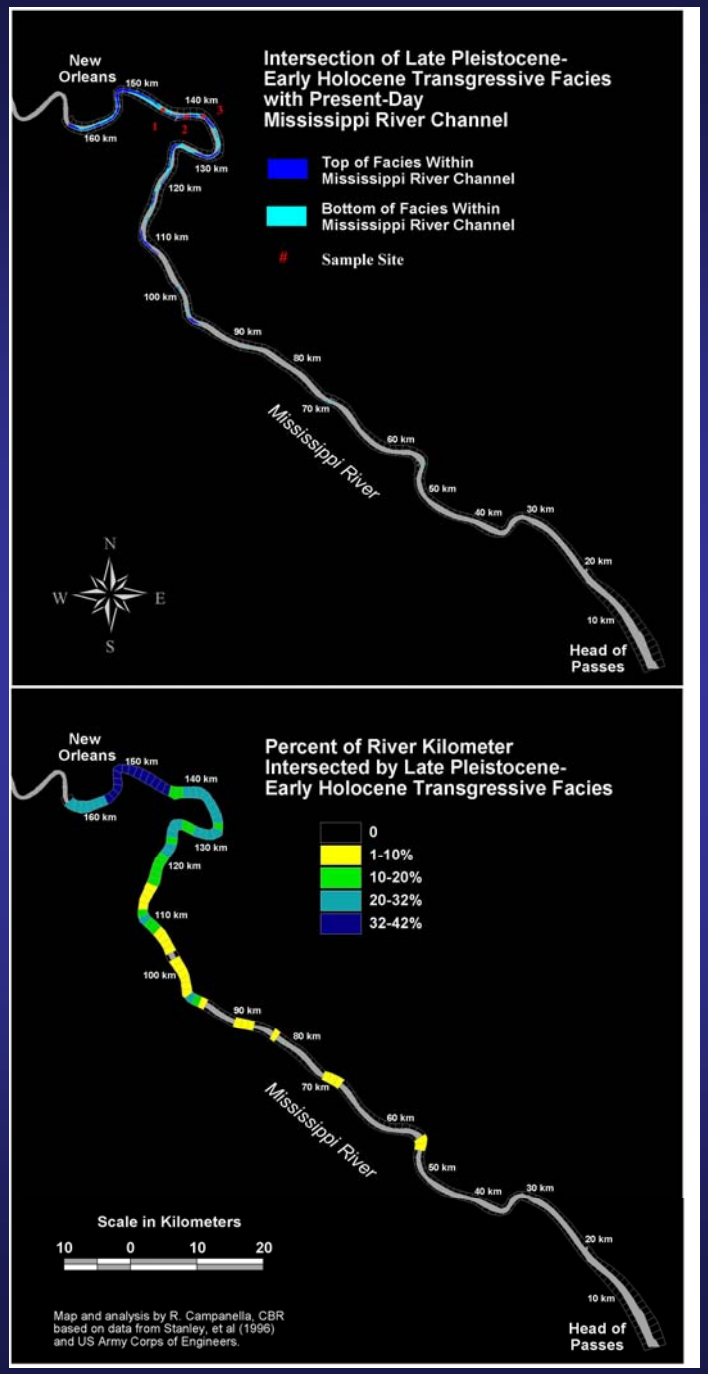
Co-metabolism: the set of processes whereby refractory organic material (e.g. terrestrial OC) is broken down more efficiently when mixed with labile material (e.g. marine OC),via higher microbial turnover rates

Lohnis (1926); Canfield (1993); Aller (1998)

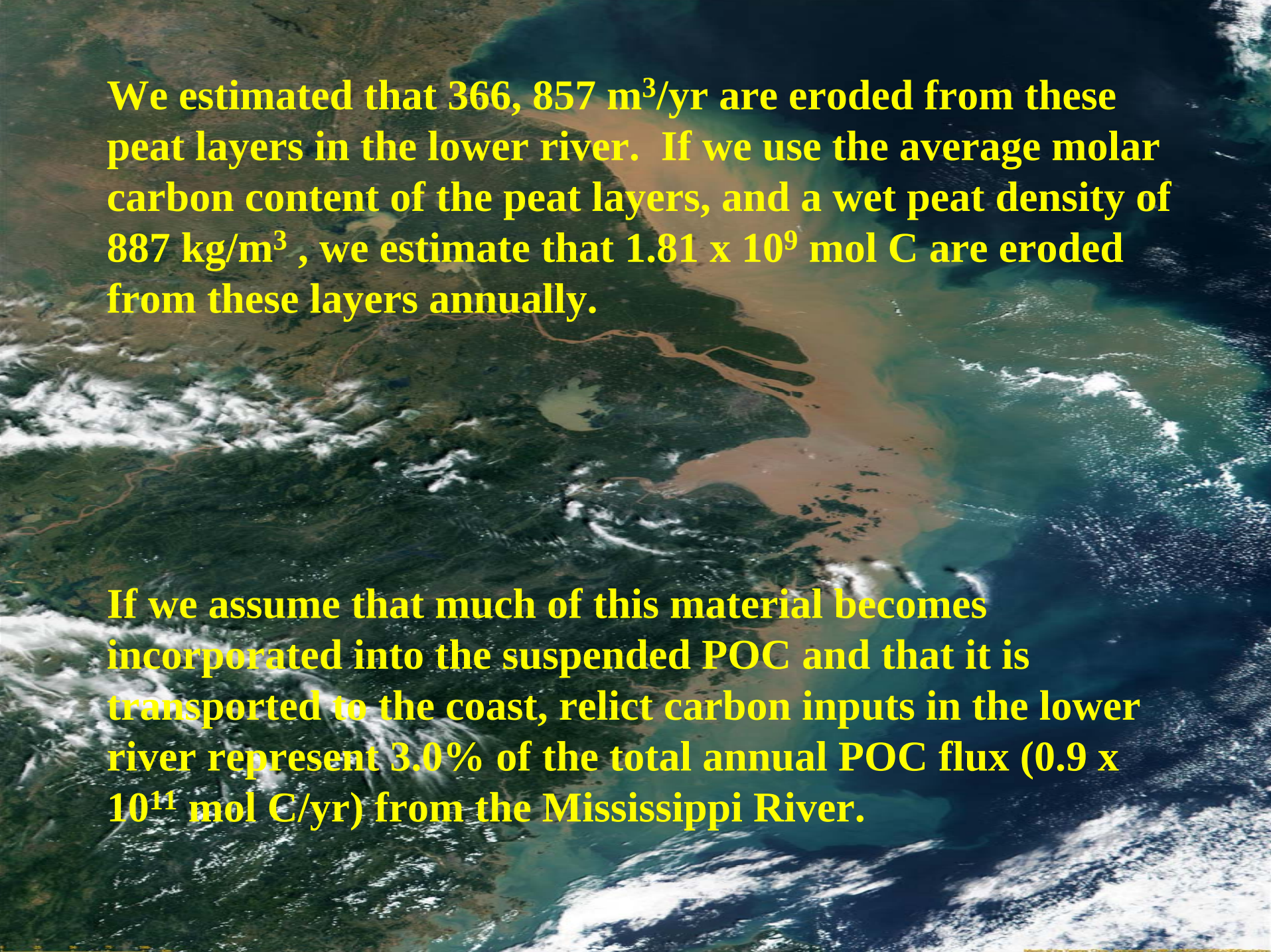


Radiocarbon ages of this peat material ranged from 2,140 to 4,210 yr BP in to 32,580 yr BP in Pleistocene clay layers below.

Galler et al., 2003, EOS



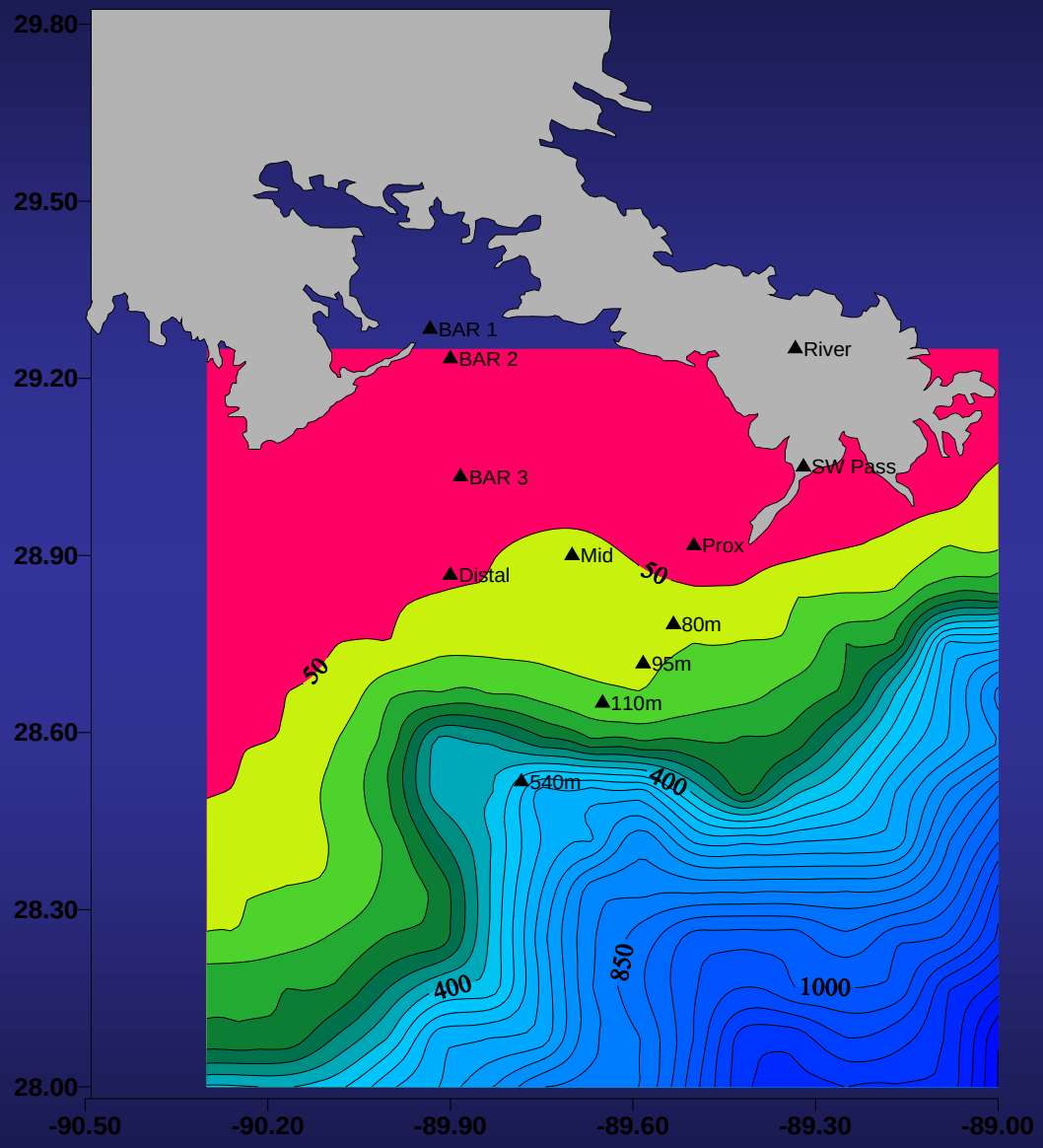
Decreases in the extent of relict outcropping down-stream is due to the seaward dip of the layer caused by it overlaying the dipping continental shelf.

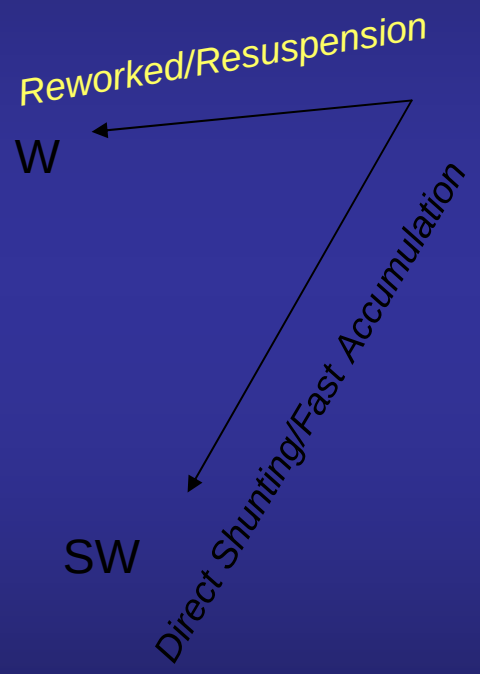


We estimated that 366, 857 m^3/yr are eroded from these peat layers in the lower river. If we use the average molar carbon content of the peat layers, and a wet peat density of 887 kg/m^3 , we estimate that 1.81 x 10^9 mol C are eroded from these layers annually.

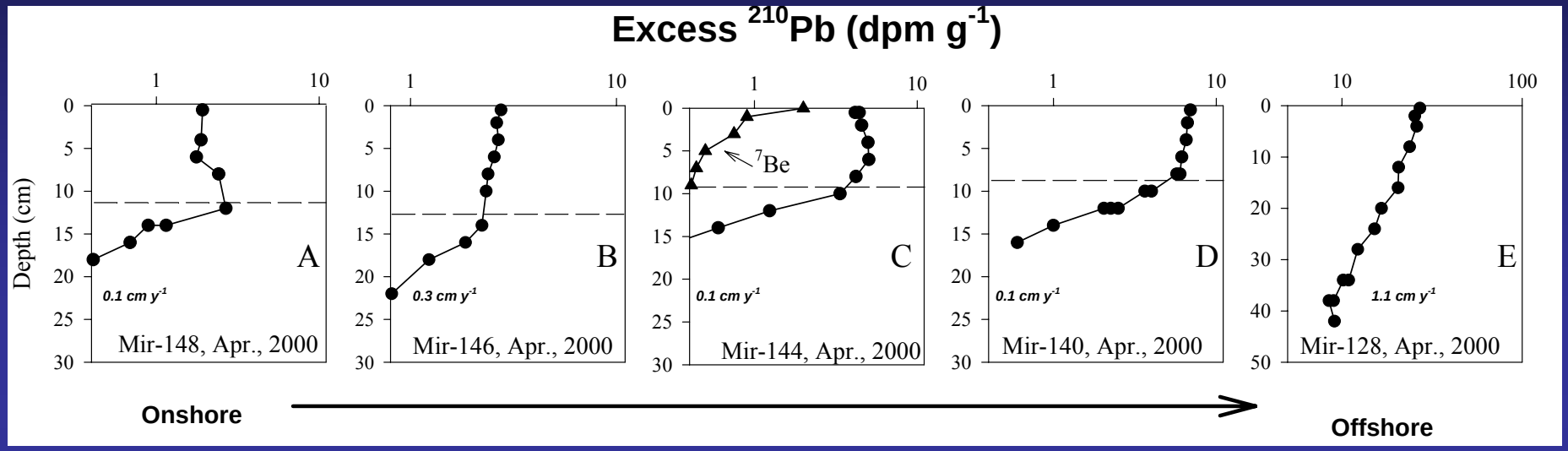
If we assume that much of this material becomes incorporated into the suspended POC and that it is transported to the coast, relict carbon inputs in the lower river represent 3.0% of the total annual POC flux (0.9 x 10^{11} mol C/yr) from the Mississippi River.

July Cruise Sampling Scheme





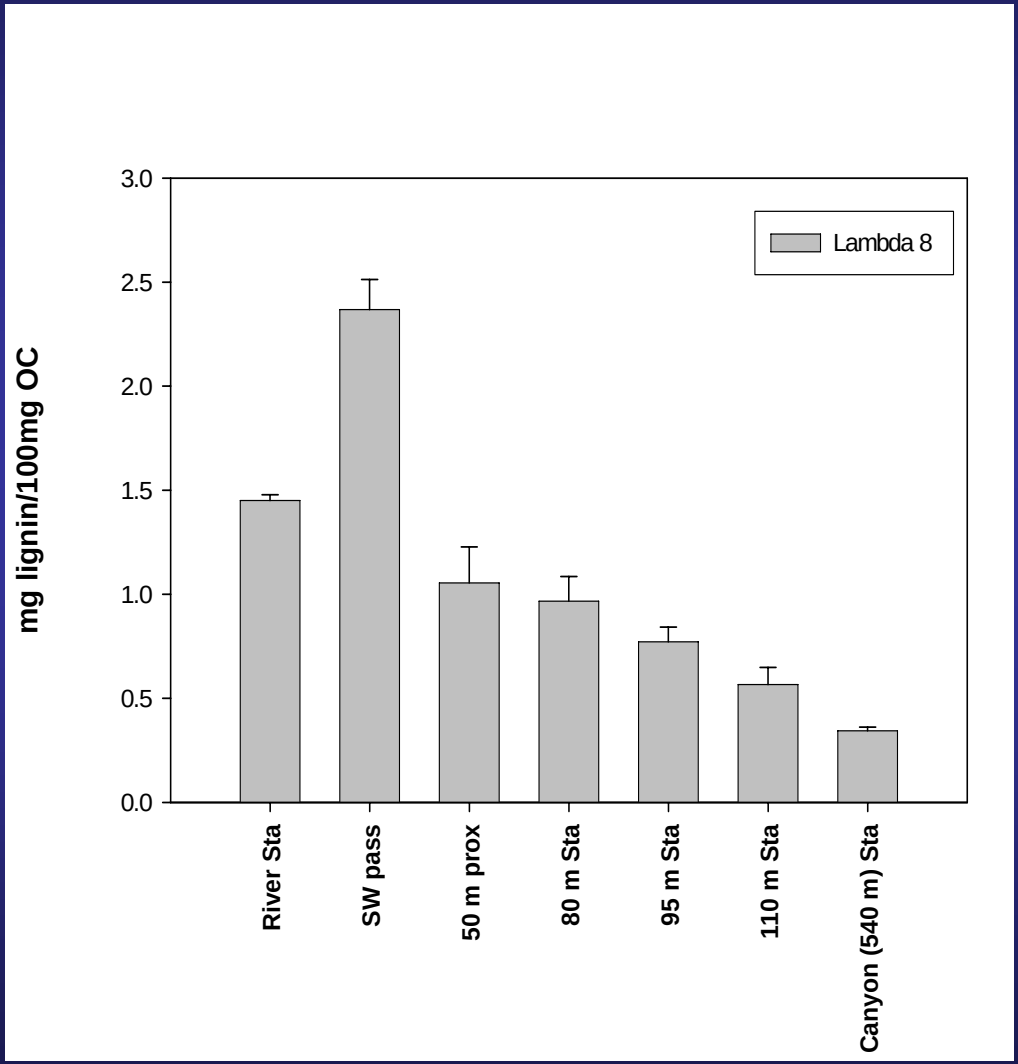
Cross-Shelf Stations

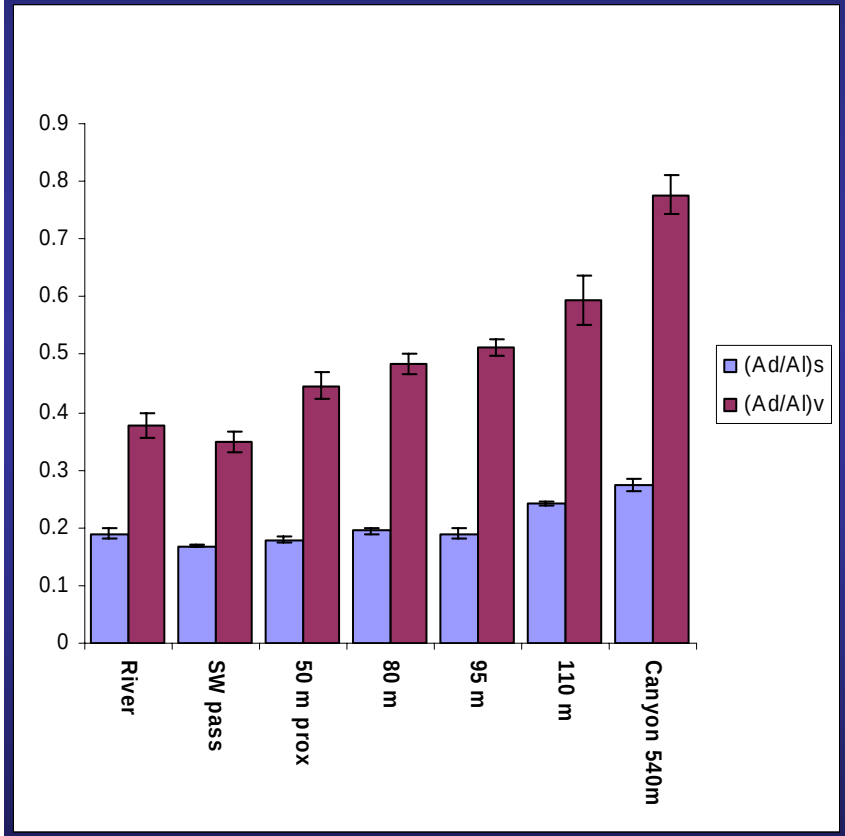


For the cross-shelf transect designated as transect A in Figure 5, sedimentation rates are relatively constant at 0.1 to 0.3 cm y^{-1} but increase to > 1 cm y^{-1} a the shelf break near the Mississippi Canyon.

McKee et al. (submitted)

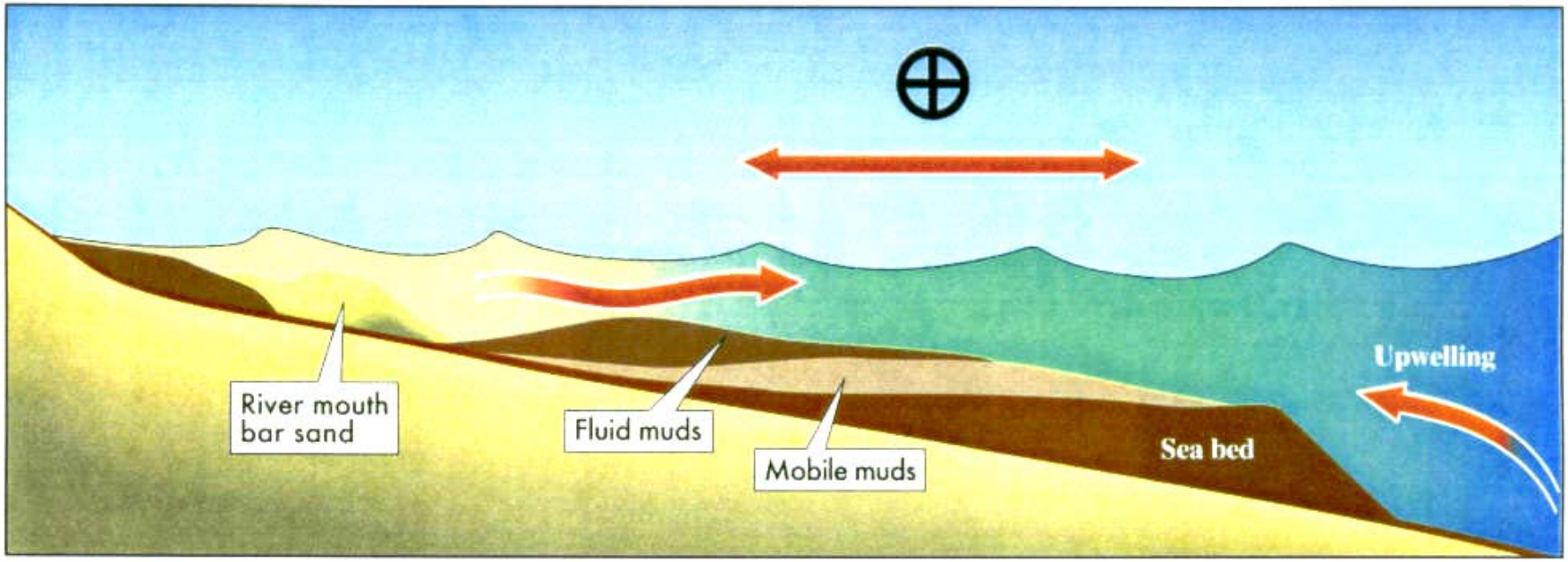
Sedimentary Lignin: Canyon Transect (0-1)





(Ad/Al)s-Syringic acid/Syringealdehyde
(Ad/Al)v-Vanillic acid/Vanillin

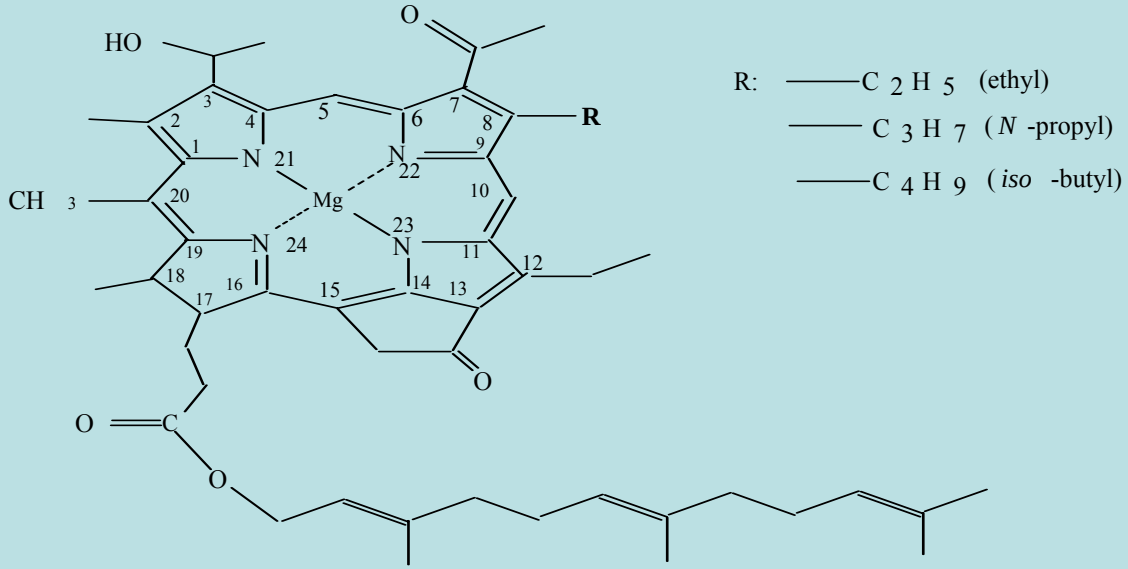
Clinoform Prograding over Relict Sands



Bacteriochlorophyll-*e*

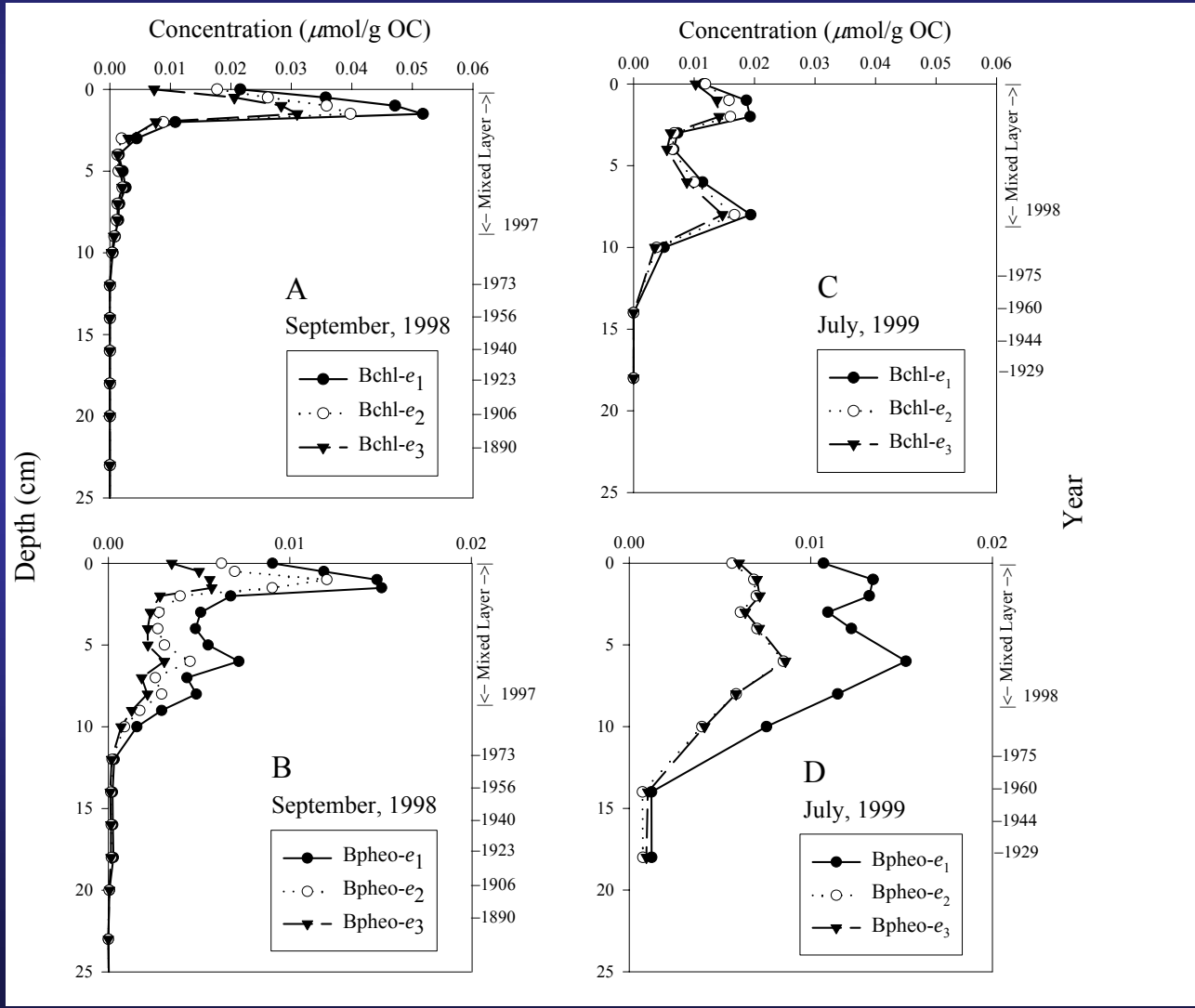
1. Characterized based on UV spectra (HPLC/PAD) and mass spectra (HPLC/MS)

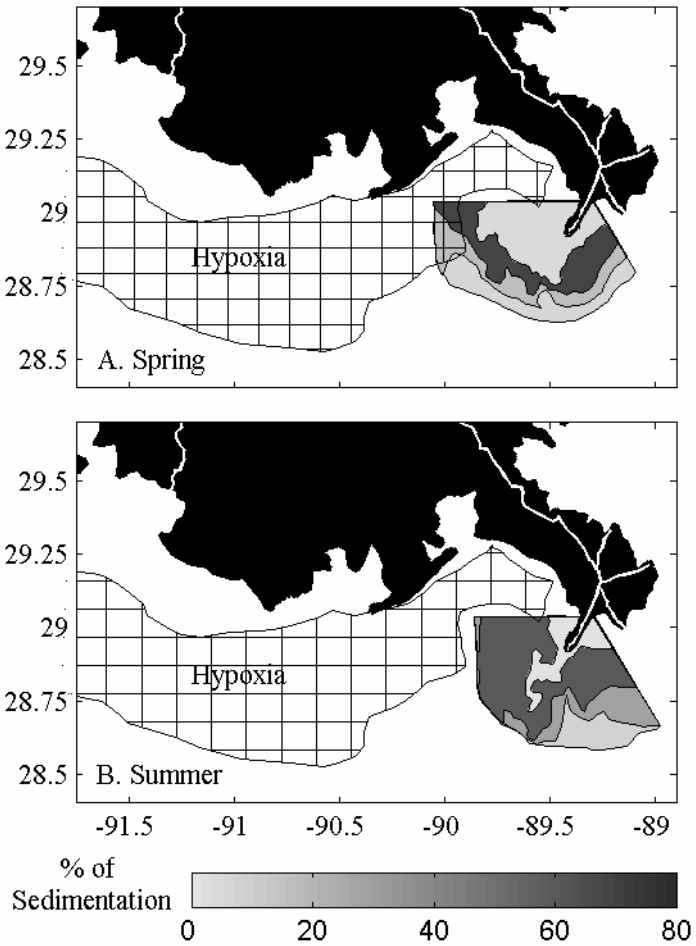
2. Produced by anaerobic photosynthetic green sulfur bacteria, *Chlorobium phaeobacteroides and/or phaeovibroides*



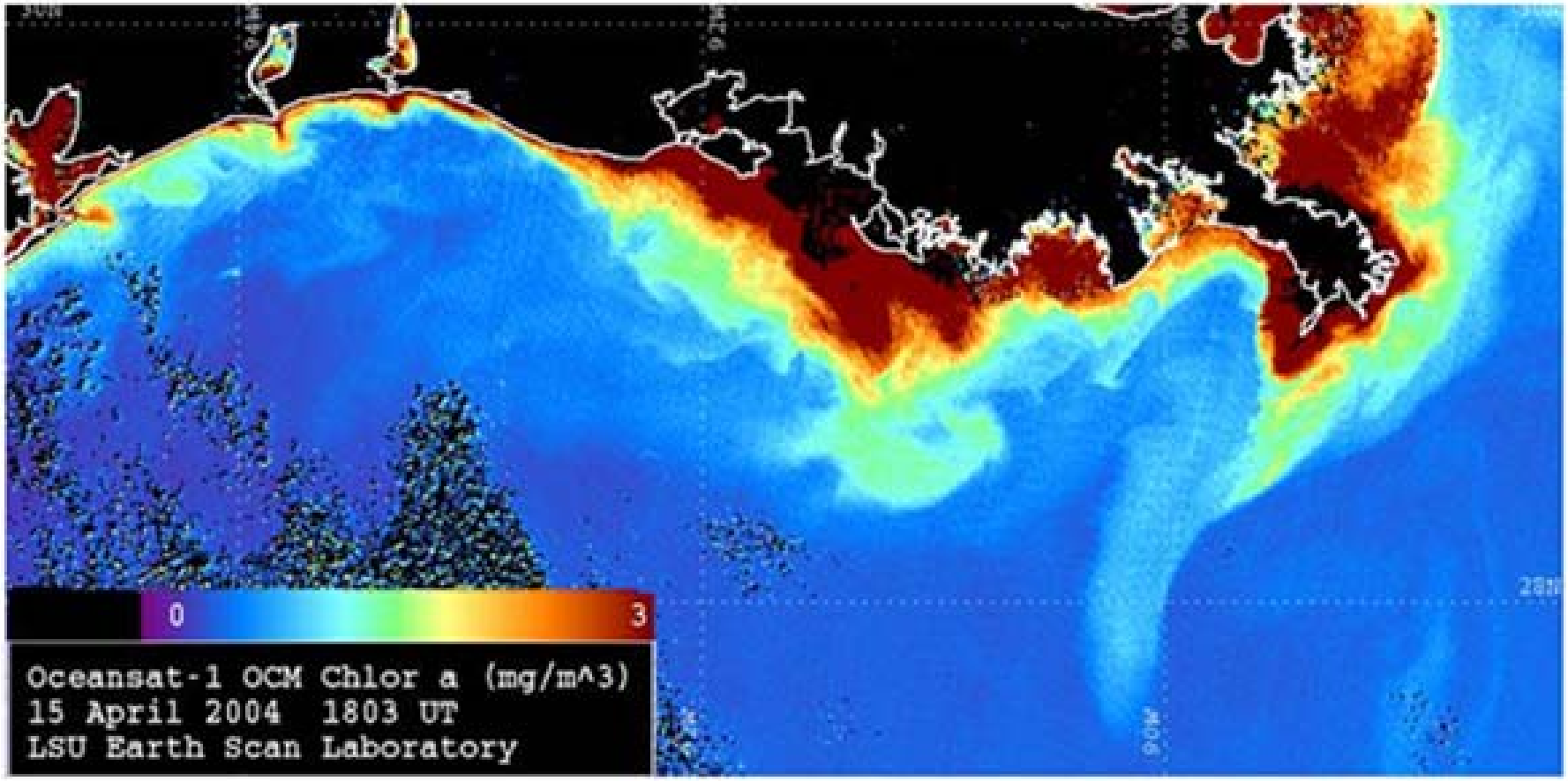
Bacteriochlorophyll-*e*

Down-core Distribution of Bchlorophyll-*e* and Bpheophytin-*e* Homologues





We investigated seasonal variability in organic carbon (OC) budgets using a physical-biological model for the Mississippi River turbidity plume (MRTP). Plume volume was calculated from mixed layer depth and area in each of four salinity subregions based on an extensive set of cruise data and satellite-derived suspended sediment distributions. These physical measurements were coupled with an existing food web model to determine seasonally-dependent budgets for labile (reactive) OC in each salinity subregion.

Our model was also used to calculate O2 demand for the development of regional hypoxia, and our spring and early summer budgets indicated that sedimentation of autochthonous OC from the immediate plume contributed ~23% of the O2 demand necessary for establishment of hypoxia in the region.

Other sources of OC to the Hypoxic Region?