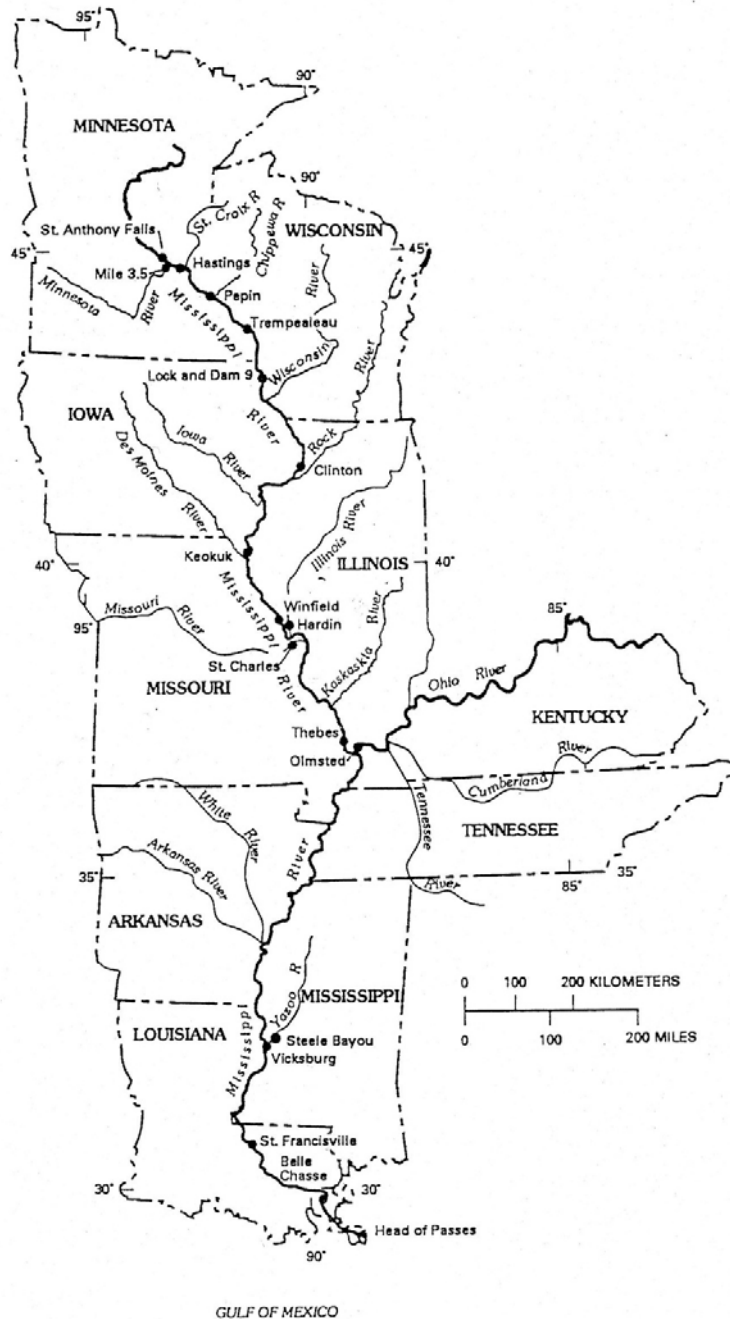


Polar organic compounds of interest: Lower Mississippi River & Gulf of Mexico

Colleen Rostad

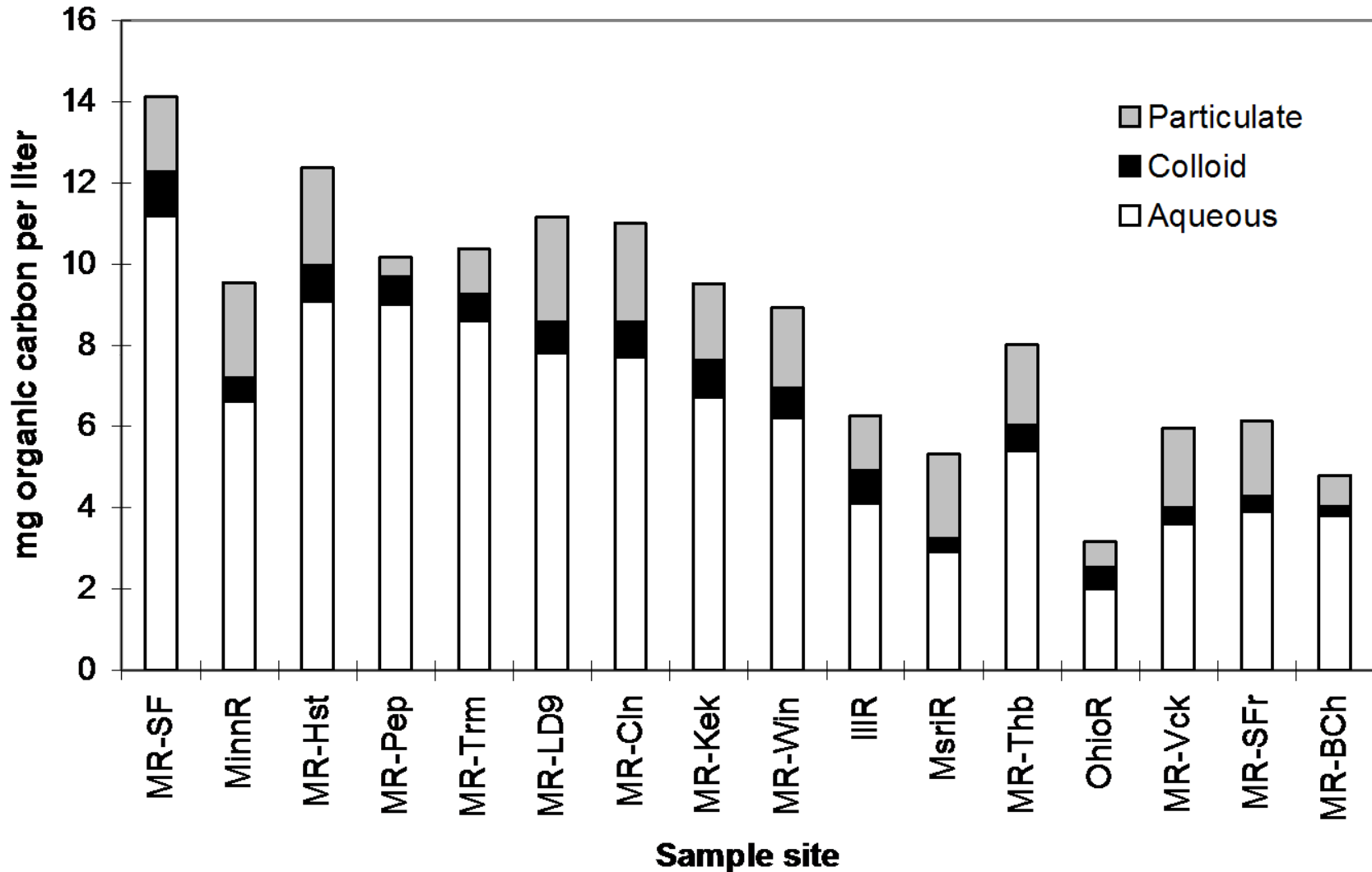
**Research Chemist, US Geological Survey
Branch of Regional Research, Denver, CO**

**USGS LEAG Workshop, New Orleans, Louisiana,
April 22-23, 2009**

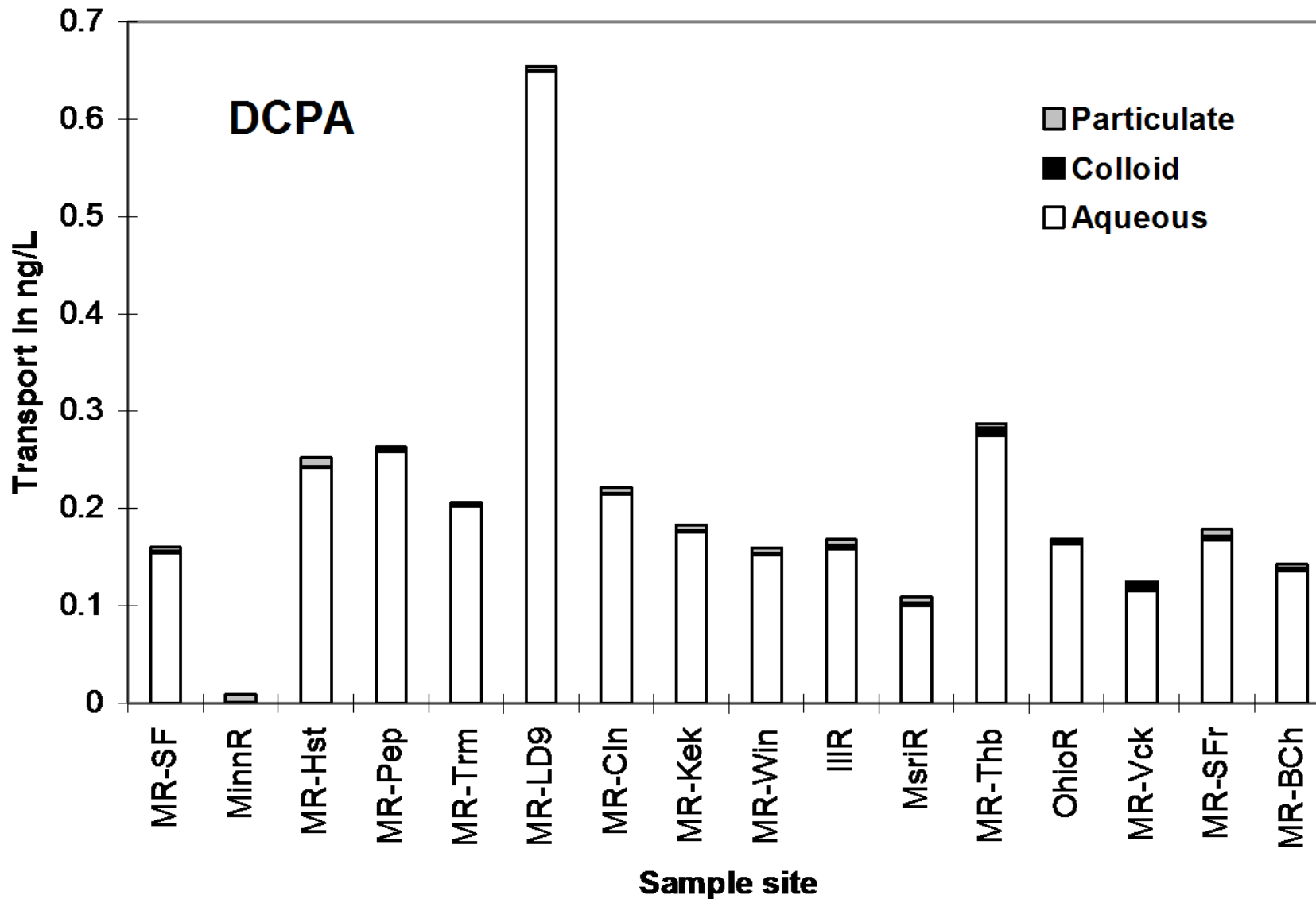


Sample sites on the Mississippi River and major tributaries

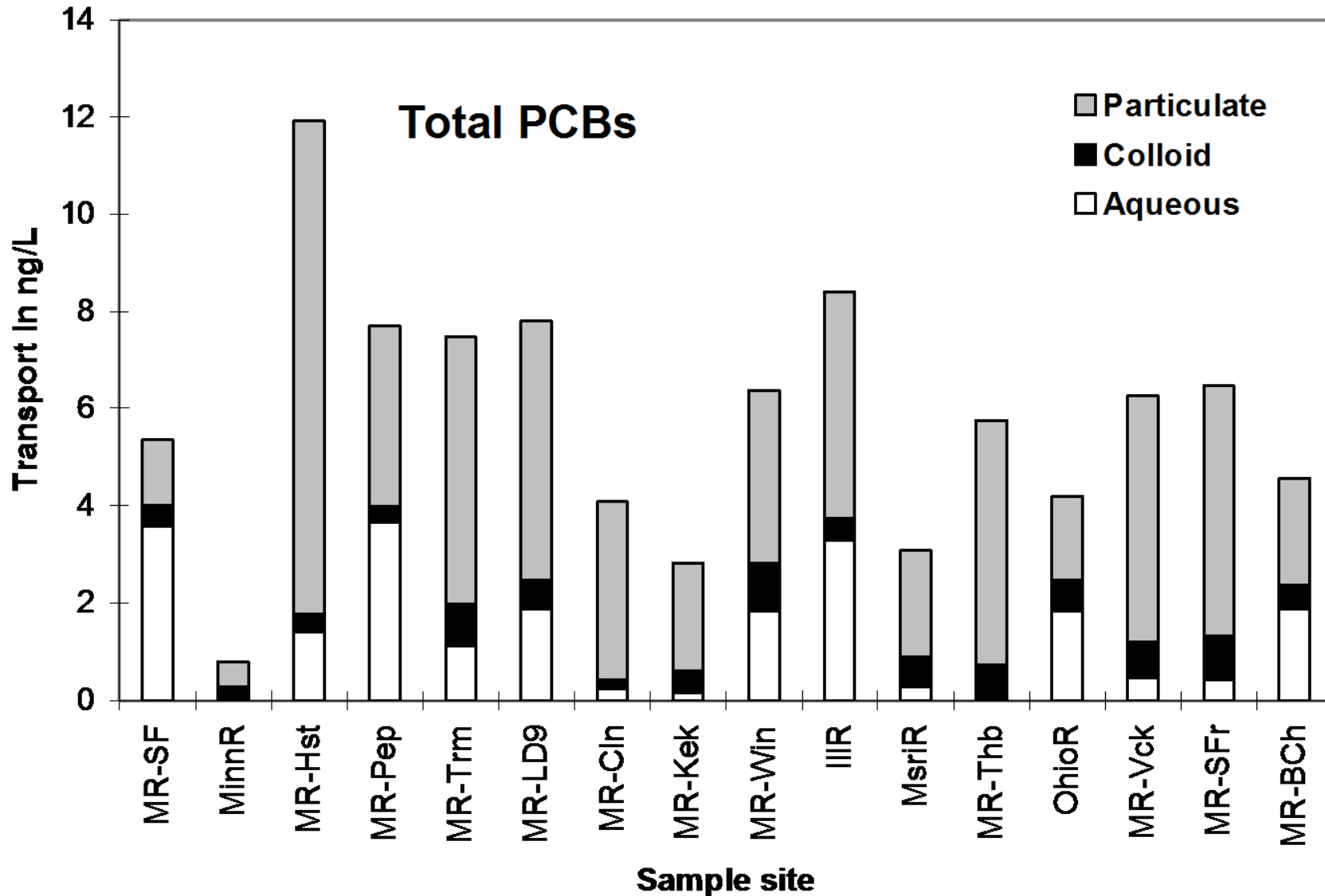
River transport of organic carbon, in milligrams per liter



River transport of polar organic compounds in nanograms per liter

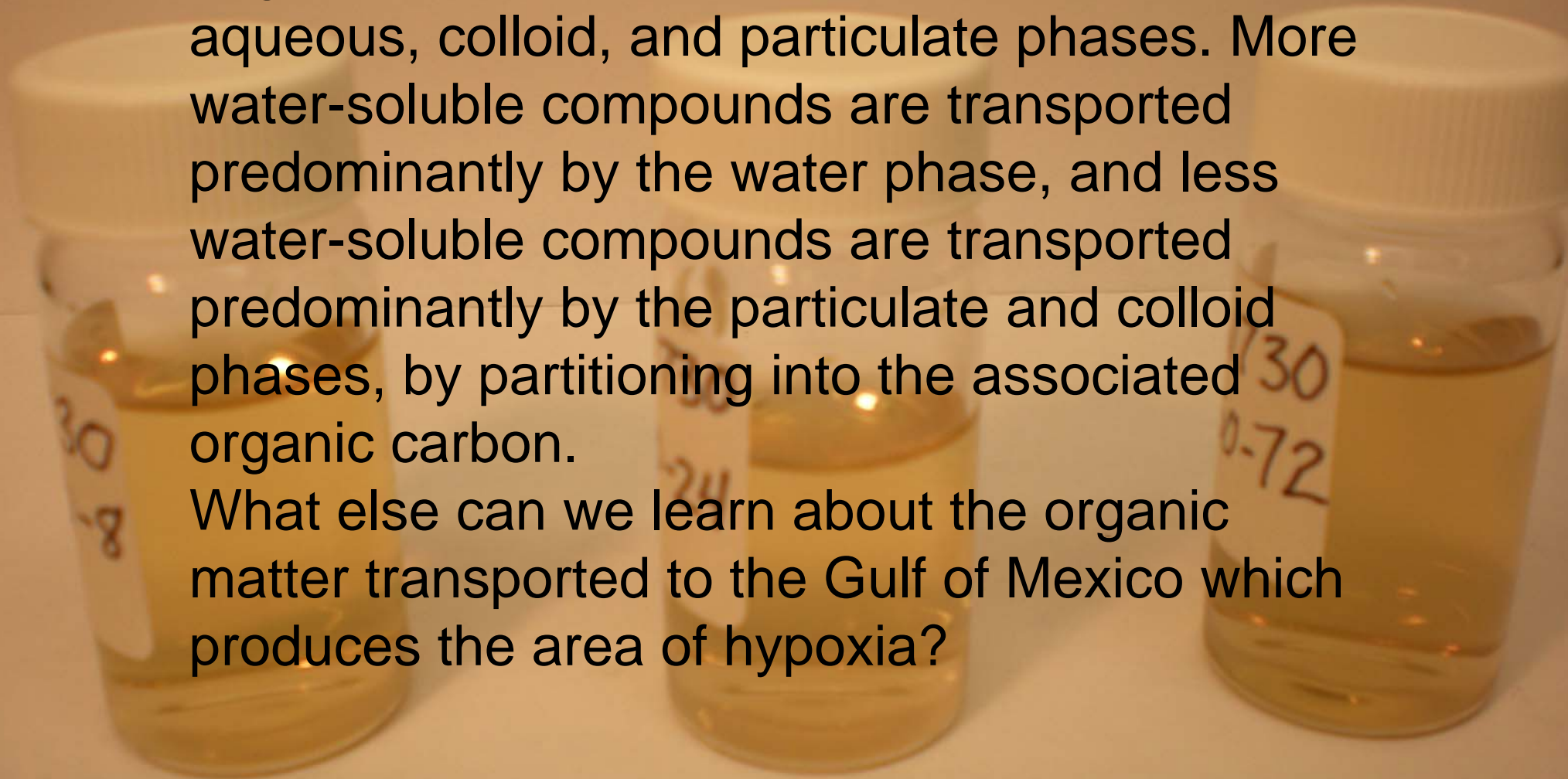


River transport of non-polar organic compounds in nanograms per liter



Organic carbon moves down the river in the aqueous, colloid, and particulate phases. More water-soluble compounds are transported predominantly by the water phase, and less water-soluble compounds are transported predominantly by the particulate and colloid phases, by partitioning into the associated organic carbon.

What else can we learn about the organic matter transported to the Gulf of Mexico which produces the area of hypoxia?



Application of biochar to soil has been proposed as a long-term sink for atmospheric carbon in terrestrial ecosystems while providing improved soil fertility and increased crop production.



We are investigating the effect of formation conditions on the properties of biochar (from cellulose, lignin, pine, poplar, and switchgrass) and their implications for use of biochar as a soil amendment and for long-term carbon sequestration. Properties related to charring temperature and duration include changes in biochar yield, elemental composition, functional groups by NMR spectroscopy, surface area, and acid functional groups.



As an indication of impacts of large-scale biochar incorporation into agricultural soils to surface waters downstream, we are investigating effects of charring temperature and duration on water extracts of biochars, as determined by pH, dissolved organic carbon, and analysis of polar and non-polar organic compounds.

Black Carbon from the Mississippi River: Quantities, Sources, and Potential Implications for the Global Carbon Cycle

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Black carbon (BC) may be a major component of riverine carbon exported to the ocean, but its flux from large

as an indicator of historic vegetation fires, and the igneous processes in the global other fossil fuel combustion found in deeper Atlantic and in some cases, it constitutes organic carbon (OC) (7, 8) has been studied for the and sources of large rivers not been accurately cons

Upon entering the atmosphere reaches rivers and stream deposition or indirectly also and soil erosion (4). In shall may also introduce sediment Annual global BC formation 0.02 Pg (5). Similarly, an estimate BC has been estimated to be ocean sediments via both

Fate of black carbon in the hypoxic area, characterization expanded using BPCA analysis

GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 23, GB1015, doi:10.1029/2008GB003253, 2009



before and after widespread biochar use

Fluxes of soot black carbon to South Atlantic sediments

Rainer Lohmann,¹ Kevyn Bollinger,¹ Mark Cantwell,² Johann Feichter,³
Irene Fischer-Bruns,³ and Matthias Zabel⁴

Received 7 May 2008; revised 15 December 2008; accepted 22 December 2008; published 24 March 2009.

[1] Deep sea sediment samples from the South Atlantic Ocean were analyzed for soot black carbon (BC), total organic carbon (TOC), stable carbon isotope ratios ($\delta^{13}\text{C}$), and polycyclic aromatic hydrocarbons (PAHs). Soot BC was present at low concentrations

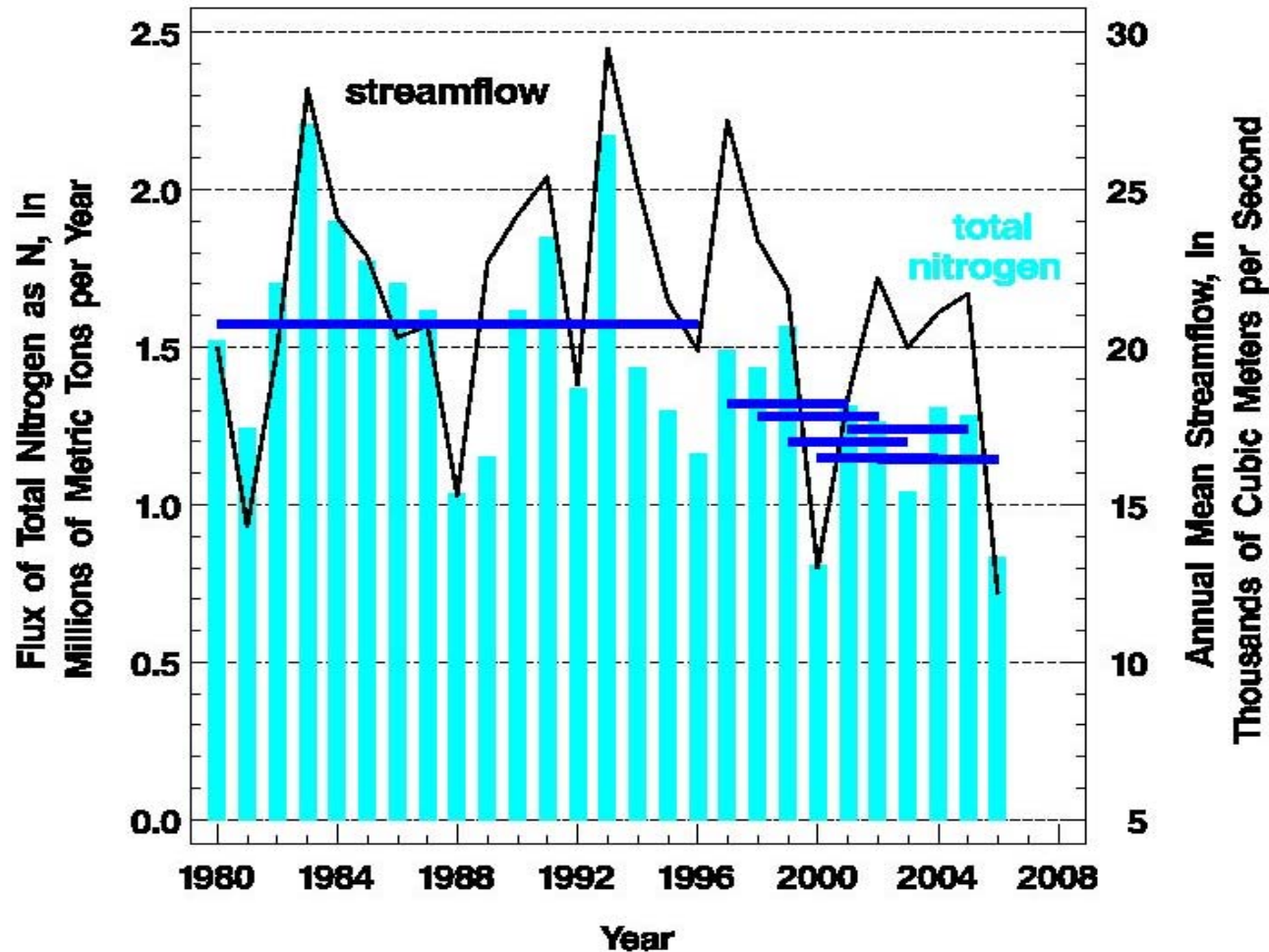
Dissolved Organic Nitrogen in Surface Waters

- Increasing Concern
- Sources
- Complicated chemistry

Fate, transport, and reactivity of dissolved organic nitrogen have been overshadowed by nitrogen cycling studies that focus on inorganic nitrogen

Annual Flux to Gulf of Mexico: Total Nitrogen

- 1980-96 average
 - 1,575,000 MT
- 2002-2006 average
 - 1,146,000 MT
 - 27.2% decrease
- 2001-2005 average
 - 1,243,000 MT
 - 21.1% decrease
- Six 5-year windows
 - average of 22.4% decrease
- Medians are significantly different
 - $P = 0.05$

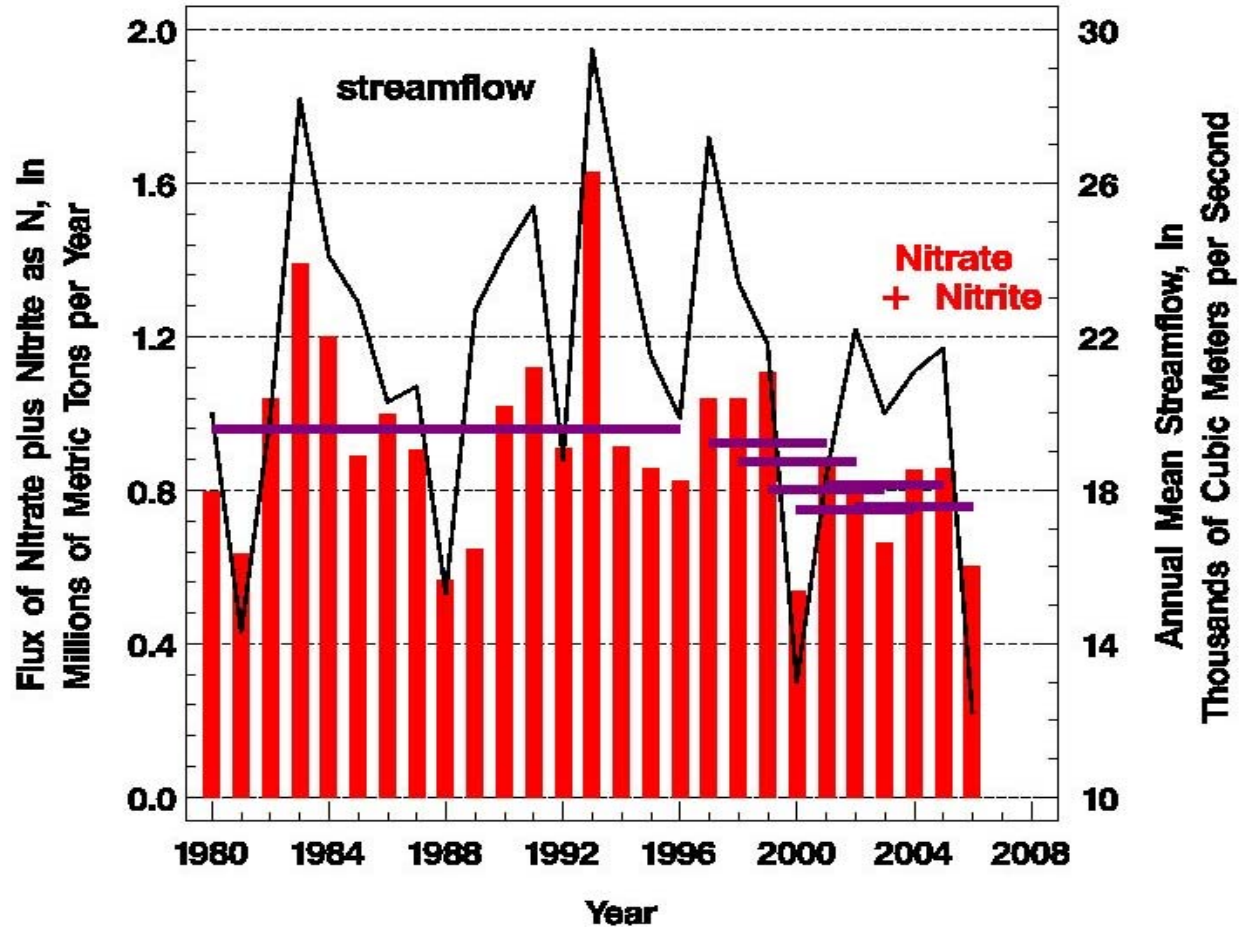


All flux and flow estimates are for water years (October 1 through September 30)

Courtesy of Bill Battaglin, CO WSC

Annual Flux to Gulf of Mexico: Nitrate

- 1980-96 Average
 - 961,470 MT
- 2002-2006 average
 - 757,000 MT
 - 21.3% decrease
- 2001-2005 average
 - 813,400 MT
 - 15.4% decrease
- Six 5-year windows
 - average of 14.7% decrease
- Medians not significantly different
 - $P = 0.23$

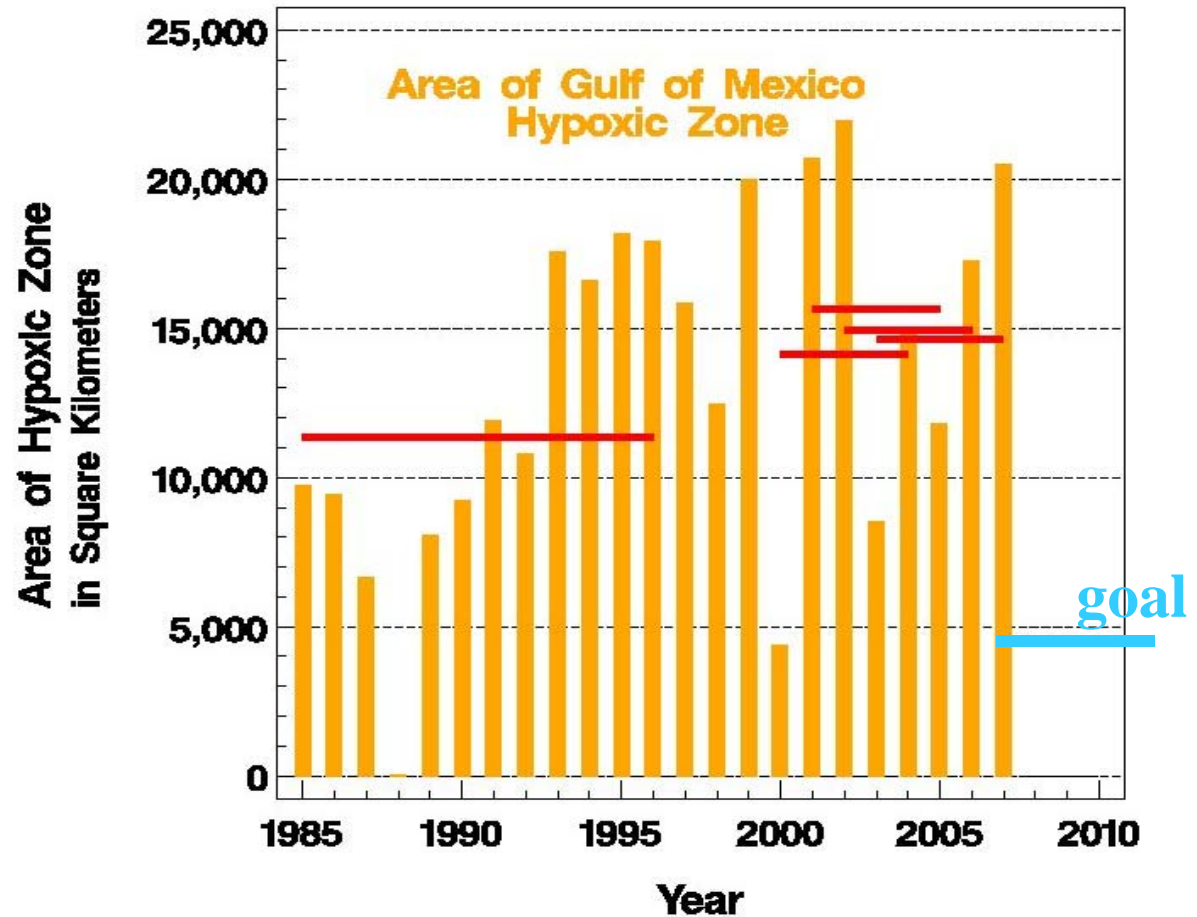


All flux and flow estimates are for water years (October 1 through September 30)

Courtesy of Bill Battaglin, CO WSC

Why is the size of the Hypoxic Zone Increasing?

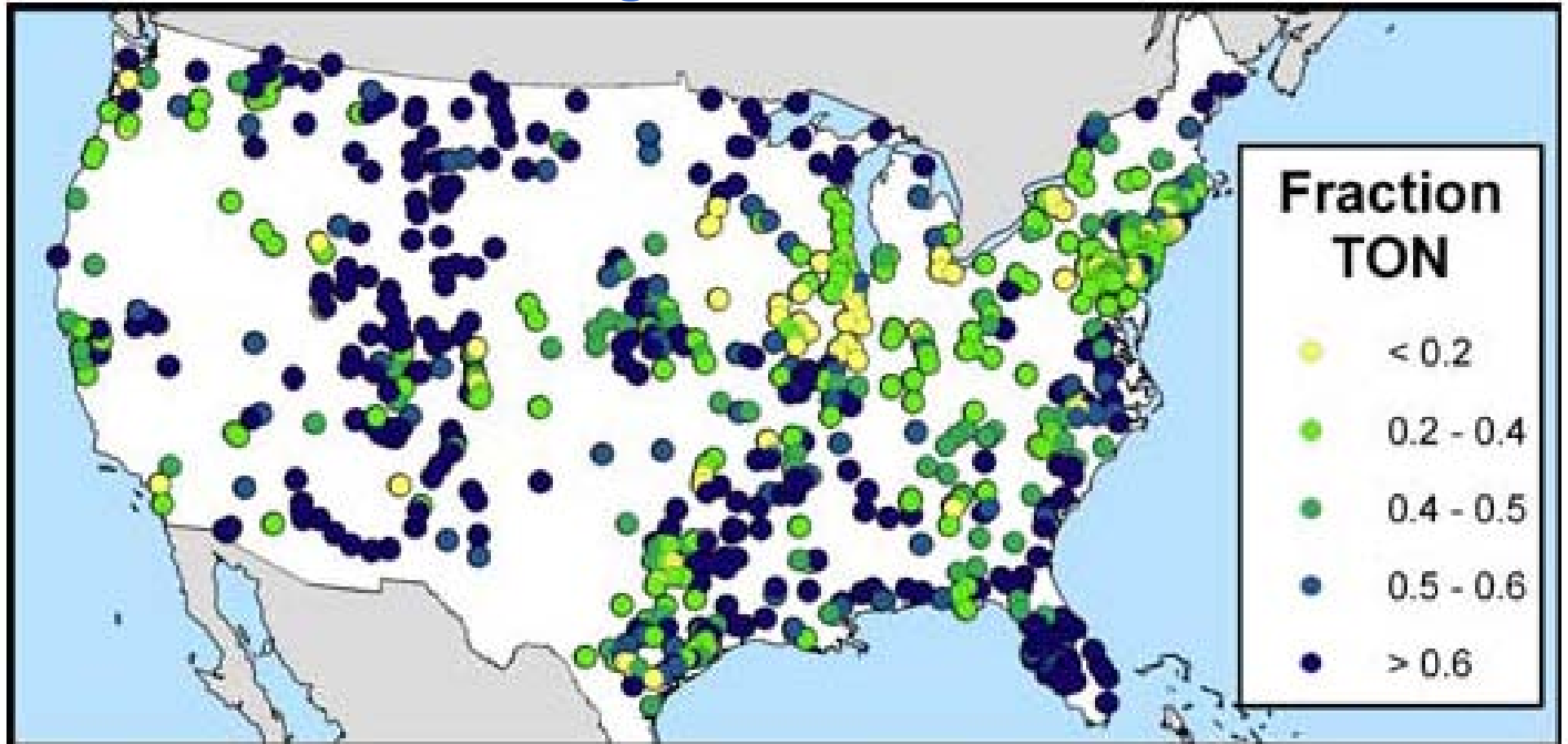
- 1985-1996 average
 - 11,360 Km²
- 2003-2007 average
 - 14,640 Km²
 - 28.9% increase
- 2002-2006 average
 - 14,940 Km²
 - 31.5% increase
- 2001-2005 average
 - 15,630 Km²
 - 37.6% increase
- Seven 5-year windows
 - 32% increase
- Medians not significant| different
 - P = 0.82



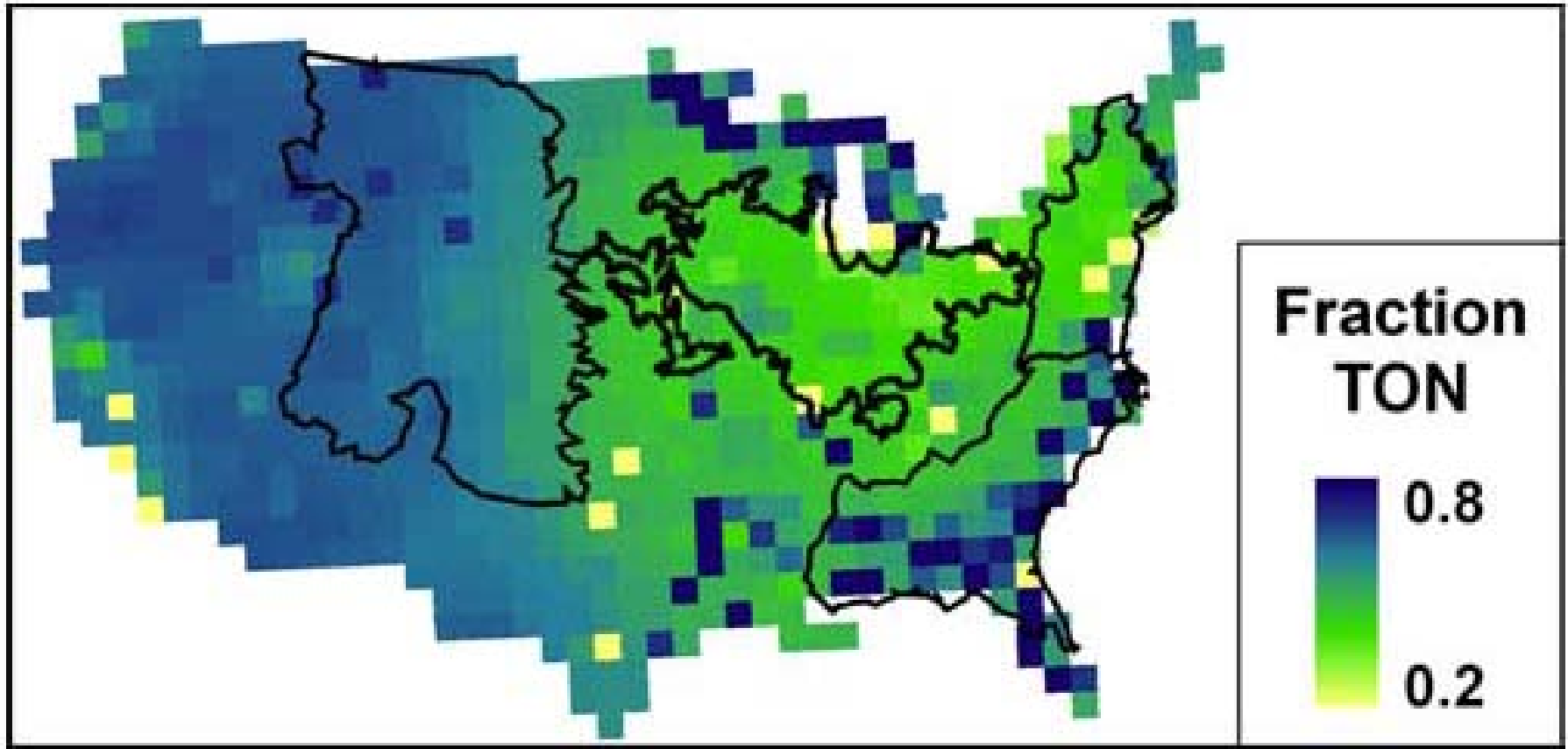
Source: Rabalais

Courtesy of Bill Battaglin, CO WSC

Across the conterminous US, organic nitrogen is the dominant nitrogen fraction of river N loads



Important for ecosystem functioning and trophic dynamics





DON can account for 20 to 90% of the total nitrogen loading to estuaries, and plays vital role in oceanic biogeochemical cycles



Gulf of Mexico Tidal Wetlands
healthy mangroves on the Big Bend coast

A yellow and white tractor is pulling a large agricultural sprayer in a field. The sprayer has a long, low-profile boom with multiple nozzles. The tractor is moving from right to left, and a fine mist of spray is visible behind the boom. The background consists of a line of green trees under a blue sky with light clouds. The foreground is a field of green grass.

**Most nitrogen export by Mississippi River,
initially attributed to agricultural fertilizer
and runoff**

A young girl with blonde hair is shown in profile, drinking water from a clear glass. She is wearing a white sleeveless top. The setting is a kitchen with wooden cabinets and a white countertop. In the background, there is a window with white curtains and a sink area with a faucet, a yellow sponge, and a bottle of dish soap. The text "Drinking water treatment changing from chlorination to chloramination" is overlaid on the bottom half of the image.

**Drinking water treatment changing from
chlorination to chloramination**

DON: 65 percent of DN in wastewater effluents, 80 percent in nitrification-denitrification systems.

- **secondary treated wastewater
5-25 mg DON/L**
- **tertiary treated wastewater
less than 4 mg DON/L**

Most wastewater is disinfected with chlorine - high DON produces organic chloramines

C/N ratios

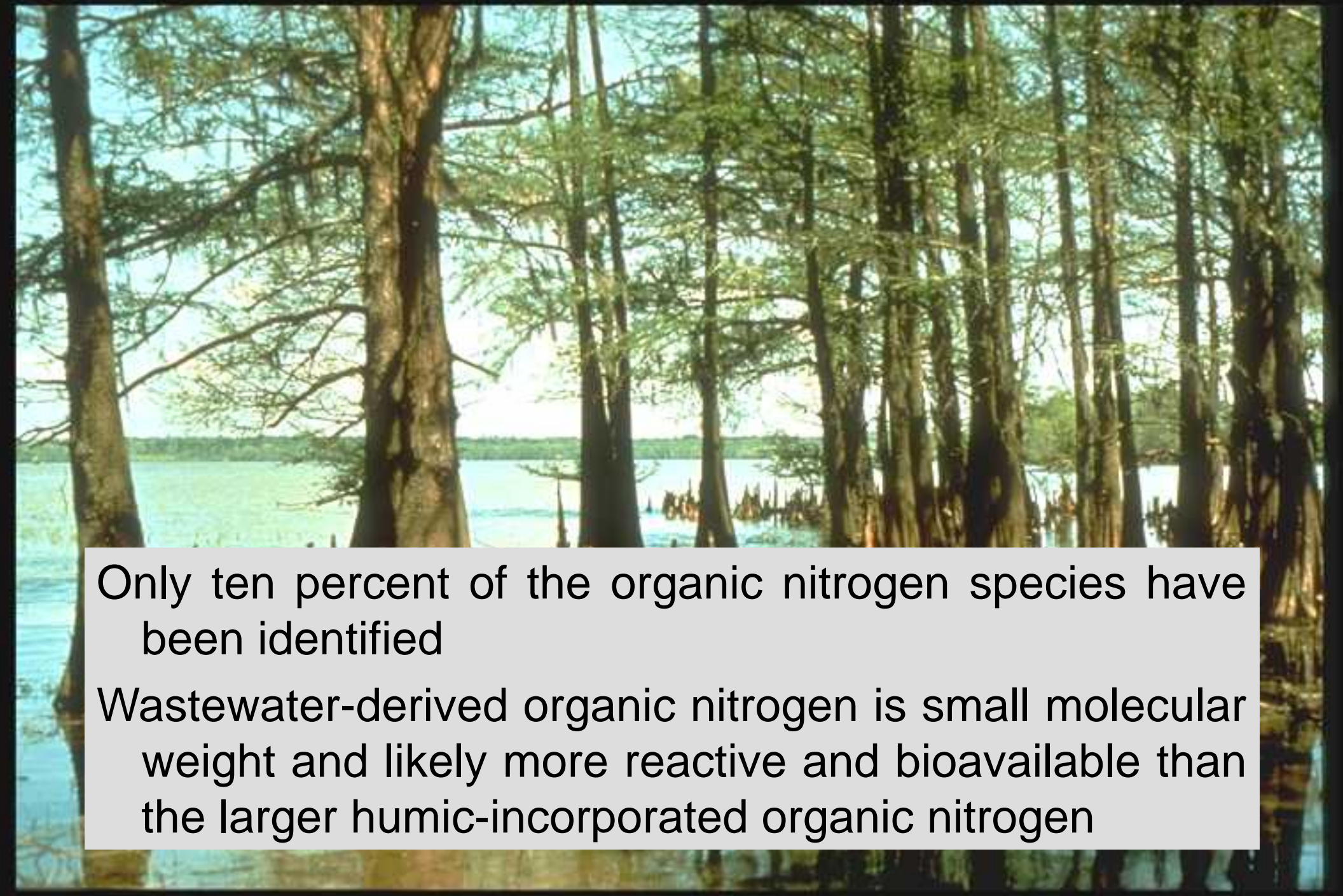
400	cellulose
80	wheat straw
40	coal
25	ferns
21	mosses
20	legumes
18	flowering plants with seeds
16	cycads and conifers
30	horse manure
19	cattle manure
16	sheep manure
9-19	pigs manure
2	proteins
3-5	bacteria
6	algae
4.5-15	fungi
5-8	soil orgasms
6	microbial cells
5-15	soil biomass

- Lower C/N ratio is indicative of more autochthonous NOM sources
- Higher C/N ratio represents allochthonous NOM sources



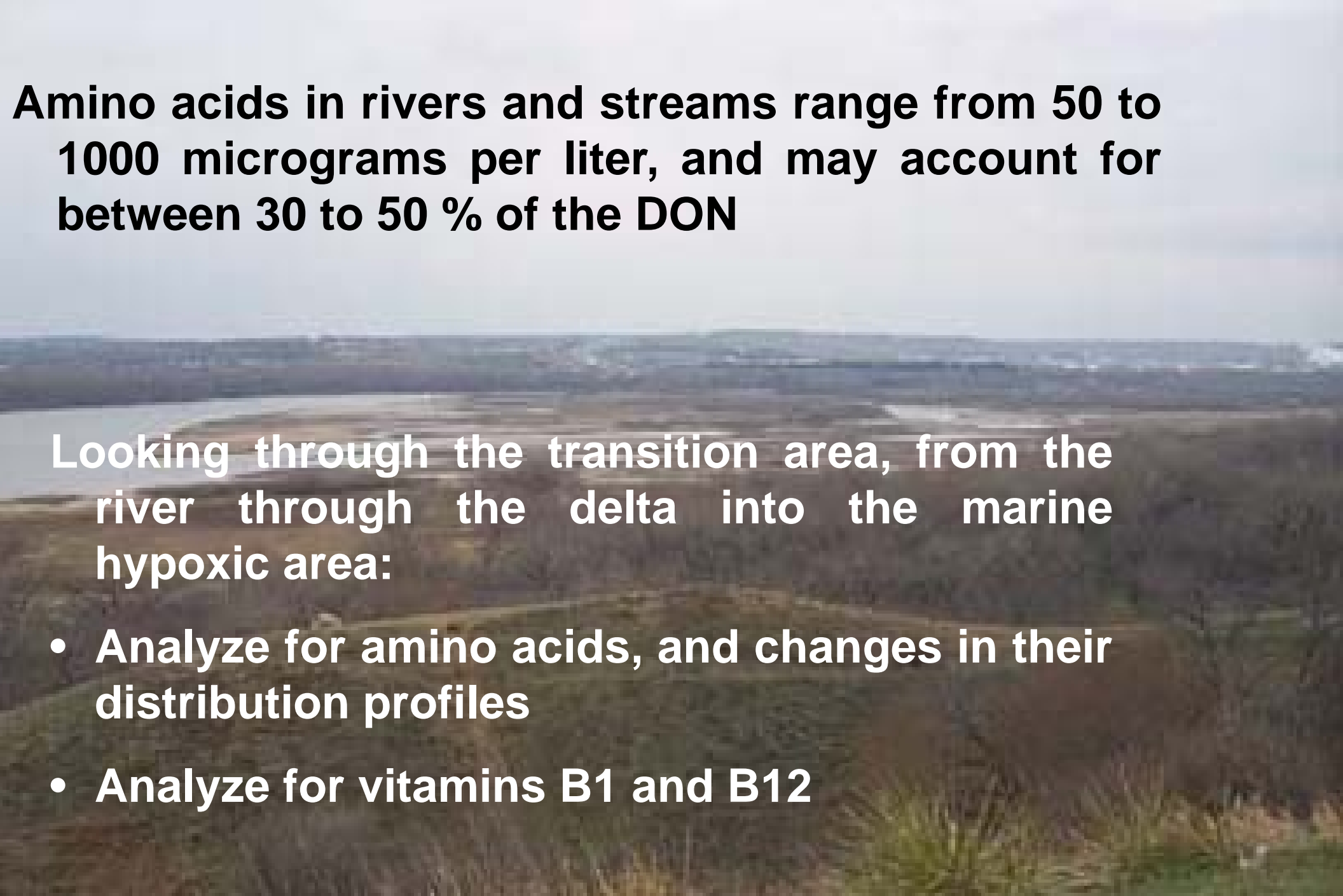
Major soil organic nitrogen components:

- 40 % Proteinaceous material
(proteins, peptides and amino acids)
- 35% Heterocyclic organic nitrogen compounds
(purines, pyrimidines)
- 20% Ammonia
- 5% Amino sugars



Only ten percent of the organic nitrogen species have been identified

Wastewater-derived organic nitrogen is small molecular weight and likely more reactive and bioavailable than the larger humic-incorporated organic nitrogen



Amino acids in rivers and streams range from 50 to 1000 micrograms per liter, and may account for between 30 to 50 % of the DON

Looking through the transition area, from the river through the delta into the marine hypoxic area:

- Analyze for amino acids, and changes in their distribution profiles**
- Analyze for vitamins B1 and B12**

Also, analyzing the organic matter in the hypoxic zone to determine if organic nitrogen (dissolved and particulate) is responsible for the hysteresis of the hypoxic zone in the Gulf.

