Data on Natural Organic Substances in Dissolved, Colloidal, Suspended-Silt and -Clay, and Bed-Sediment Phases in the Mississippi River and some of its Tributaries, 1987-90

by J.A. Leenheer, T.I. Noyes, and P.A. Brown

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Gordon P. Eaton, Director

For additional information write to:

Chief, Branch of Regional Research
U.S. Geological Survey
Box 25046, MS 418
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CONVERSION FACTORS AND RELATED INFORMATION

Multiply	*By*	*To obtain*
liter (L)	1.2642	gallon
micrometer (µm)	0.00003937	inch
metric ton per day	1.102	short ton
centimeter (cm)	0.3937	inch
cubic meter per second (m^3/s)	35.31	cubic foot per second
microsiemen per centimeter at 25 degrees Celsius (µS/cm)	1.000	micromho per centimeter at 25 degrees Celsius

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Degree Celsius may be converted to degree Fahrenheit by using the following equation:

$$°F = 9/5(°C)+32$$

The following terms also are used in this report:

milligrams per liter (mg/L)
millimoles per gram
dalton
parts per million (ppm)

DATA ON NATURAL ORGANIC SUBSTANCES IN DISSOLVED, COLLOIDAL, SUSPENDED-SILT AND -CLAY, AND BED-SEDIMENT PHASES IN THE MISSISSIPPI RIVER AND SOME OF ITS TRIBUTARIES, 1987–90

By J.A. Leenheer, T.I. Noyes, and P.A. Brown

ABSTRACT

The Mississippi River and some of its tributaries were sampled for natural organic substances dissolved in water and in suspended and bed sediments during seven sampling cruises from 1987–90. The sampling cruises were made during different seasons, in the free-flowing reaches of the river from St. Louis, Missouri, to New Orleans, Louisiana. The first three cruises were made during low-water conditions, and the last four cruises during high-water conditions. The purpose for sampling and characterizing natural organic substances in the various phases in the river was to provide an understanding of how these substances facilitate contaminant transport and transformations in the Mississippi River.

Significant conclusions of this study were: (1) Natural organic substances appear to stabilize certain colloids against aggregation; therefore, these colloids remain in suspension and can act as transport agents that are not affected by sedimentation. Bacteria were found to be a significant fraction of organic colloids. (2) A new class of organic contaminants (polyethylene glycols) derived from nonionic surfactant residues was discovered dissolved with natural organic substances in water. These polyethylene glycols have the potential to affect both organic and inorganic contaminant transport in water. (3) The entire dissolved organic-matter component under varying hydrologic and seasonal conditions was characterized. (4) A method was developed to characterize organic matter in sediment by solid-state, ^{13}C-nuclear magnetic resonance spectrometry. (5) The organic matter in suspended sediments was characterized by a variety of spectral and nonspectral methods. The protein component (significant in trace-metal binding) and lipid component (significant in organic-contaminant binding) were found to be major constituents in natural organic matter in suspended sediment. (6) Pools are reservoirs acting as traps of sedimentary organic matter of allochthonous origin and export material of autochthonous origin that is rich in nitrogen. (7) A major portion of the mass of organic colloids in transport consisted of bacterial cells.

INTRODUCTION

Most contaminants in rivers have some degree of association with natural organic substances in the dissolved and particulate phases in the water (Leenheer, 1991, 1994). These associations may either facilitate or retard contaminant transport in rivers, and may transform contaminants into different phases or different compounds, depending on the operative degradative processes.

The broad objectives of the Mississippi River project are to investigate the movement, mixing, and storage processes of sediment-associated pollutants (Moody and Meade, 1993). Some specific objectives are to:

1. Understand the compartmentalization of synthetic organic and inorganic agrochemicals between and water, sediment, and biotic phases.

2. Investigate the mixing, partitioning, and redistribution processes of the various pollutants downstream from major river confluences.
3. Understand the movement, storage, and remobilization of suspended sediment and associated pollutants at seasonal or longer time scales.
4. Predict the location and travel time of water masses and the associated sediment and pollutants; and
5. Examine the geochemistry of the suspended silt, clay, colloidal material, and dissolved phases of river water.

This report summarizes the research on natural organic matter conducted from July 1987 to June 1990 on the Mississippi River and some of its tributaries. Water and sediment samples were collected during seven cruises. Two general objectives of all seven cruises was to quantify the organic substances in dissolved and suspended-sediment phases, and to characterize the organic matter in the various phases through spectrometric and elemental measurements. Each cruise had specific objectives that required slightly different approaches. In order to adequately describe these differences, this report is organized chronologically by cruise and includes a discussion of the objectives and approach, as well as the results, for each cruise.

The location of the sampling sites on the lower Mississippi River and some of its tributaries is shown in figure 1. Integration of the research presented in this report with the research on metal and organic contaminants in the lower Mississippi River will provide an understanding of how natural organic substances affect contaminant transport and transformations.

Acknowledgments

The data presented in this report are the result of a group effort in sampling the Mississippi River and some if its tributaries, processing the samples to fractionate and isolate the various dissolved and sediment phases, and sharing data and assisting in data interpretation.

The authors wish to acknowledge the crew of the research vessel ACADIANA—Lee Black, Wayne Simoneaux, Chuck Guidry, Steve Rabalais, Craig LeBoeuf, Ken Oliver, and Wilton Delaune—who have accommodated our unusual requests and who have ensured the maintenance of proper scientific operations.

We also wish to acknowledge the Mississippi River project chief, Robert Meade, who along with John Moody attempted to teach a boatload of chemists the fundamentals of surface-water hydrology.

We wish to acknowledge our colleagues who assisted in measuring river discharge, collecting and processing large volumes of water for water and sediment sampling, performing field and laboratory measurements, and performing miscellaneous boat operations. These people include Ellen Axtmann, Terry Brinton, Wes Campbell, Phyllis Campbell, Daphne Frilot, John Garbarino, Tom Kraemer, Tom Leiker, Debby Martin, Dick Martin, Brent McKee, Dale Peart, Willie Periera, Jim Ranville, Terry Rees, Colleen Rostad, Jim Seely, Herb Stevens, Bob Stallard, Dick Tagg, and Howard Taylor and Tim Willoughby.

Lastly, we wish to thank Luis Cifuentes of Texas A & M University for determining stable carbon isotope ratio determinations of dissolved humic substances. We also thank Jim Ranville for performing scanning electron microscopy of organic colloids and for reviewing this report. Robert L. Wershaw determined the ^{13}C-NMR spectrum of dissolved humic substances.

SAMPLING CRUISE 1, JULY–AUGUST 1987

The sampling of cruise 1 began on the Missouri River (fig. 1) at Hermann, Missouri, on July 20, 1987, and ended on the Mississippi River below Belle Chasse, Louisiana, on August 9, 1987. Samples were collected in a Lagrangian scheme (Moody, 1993) that tried to follow the same mass of water downriver.

Objectives and Approach

The objectives of sampling cruise 1 were to: (1) Develop a sampling and fractionation procedure for organic substances in the suspended and dissolved phases that also was compatible for trace-metal studies; (2) characterize dissolved organic substances by elemental, spectral, and titrimetric analyses; (3) characterize suspended-sediment fractions by carbon and nitrogen analyses; and (4) determine loads of organic carbon transported in the various phases.

The approach was to obtain 70–100 L of water by depth-integration at 5–40 locations across the river from the research vessel *Acadiana,* (owned and operated by the Louisiana Universities' Marine Consortium) transfer this depth-integrated composite sample to a mobile field laboratory, and fractionate the sediment by a combination of sieving to isolate sand, continuous-flow centrifugation to isolate silt and clay, tangential-flow ultrafiltration to isolate colloids, and resin adsorption to isolate the fulvic-acid fraction of dissolved organic carbon (Leenheer, Meade, and others, 1989). This approach was successfully followed except that the continuous-flow centrifuge broke down after the second sampling was completed at Mississippi River near Winfield, Mo., and gravitational settling in 46-L carboys for 8–12 hours was used to separate the silt and clay from the colloid fractions.

Dissolved Organic Matter

Dissolved organic carbon (DOC) concentrations were determined on the permeate from the ultrafilter by high-temperature oxidation of DOC to CO_2 with a Beckman 915B[1] total organic carbon analyzer (Van Hall and Stenger, 1967). The pore size of the cellulose filters used for ultrafiltration was 0.005 μm. DOC transport was computed using water-discharge measurements reported by Moody and Meade (1992). DOC concentrations and transport at 17 sampling sites are presented in table 1.

DOC concentrations were low in comparison to the National Stream Quality Accounting Network (NASQAN) average (6.0 mg/L in data averaged from 1972–1977) at Belle Chasse, La., (Leenheer, 1982). These low concentrations might result from low terrestrial carbon inputs to the river during this low-water cruise, from ultrafiltration that eliminates colloidal carbon from the data, and from instream biodegradation of DOC. Water temperatures were near 30°C during the entire cruise, and these warm temperatures likely accelerated the biodegradation of DOC.

Only the humic-substance component of dissolved organic matter was isolated from the river for characterization (Leenheer, Brown, and others, 1989). Various characterization data are listed in table 2.

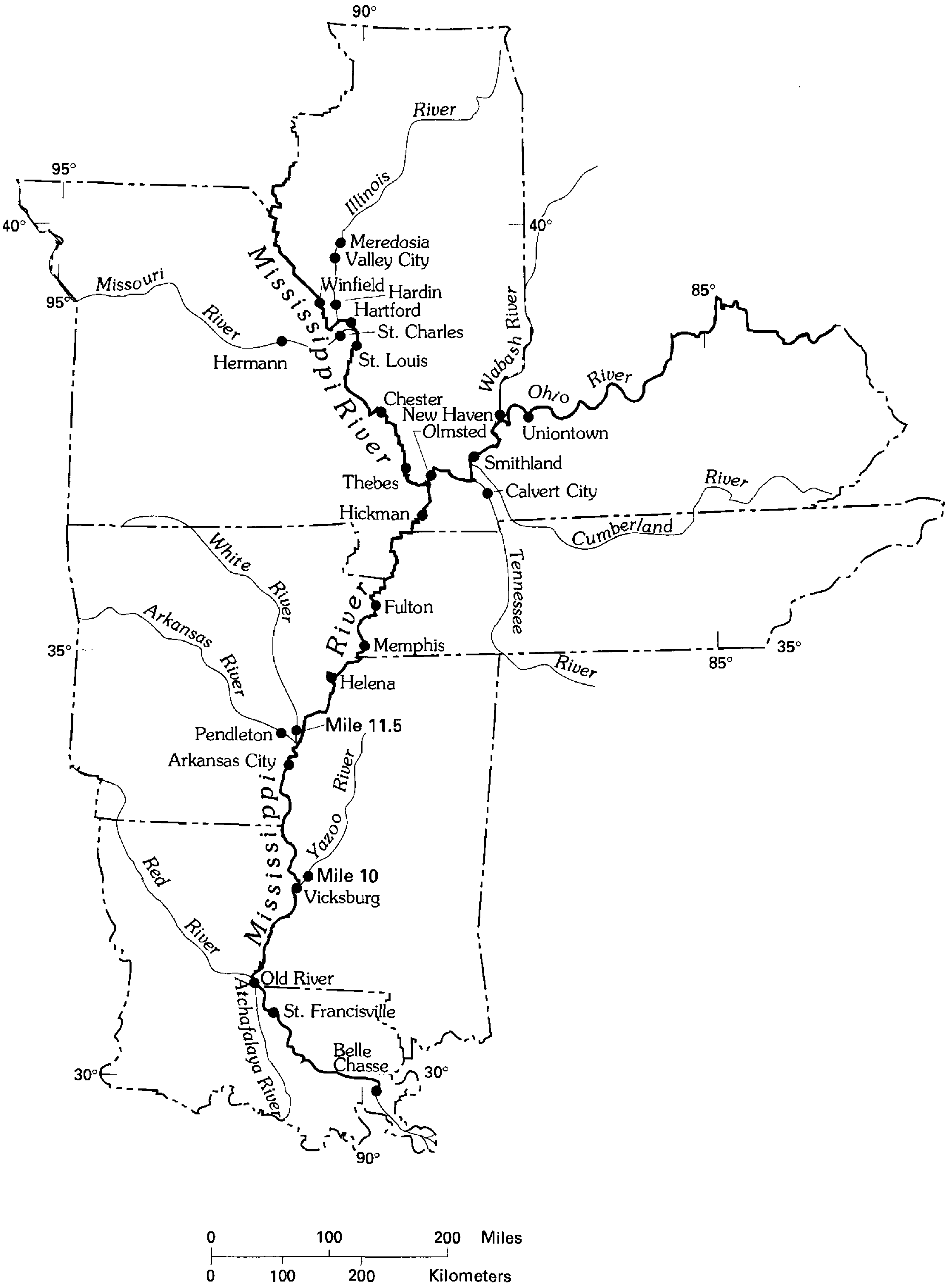

Figure 1.--Sampling locations on the Mississippi River and some of its tributaries.

Table 1.--Dissolved organic-carbon concentrations and transport for sampling cruise 1, July–August 1987

[Transport was computed using water-discharge data reported by Moody and Meade (1992)]

Sampling site	Water discharge (cubic meters per second)	Dissolved organic-carbon concentration (milligrams per liter)	Transport (metric tons per day)
Mississippi River near Winfield, Mo.	1,370	4.2	498
Illinois River at Naples, Ill.	[1]312	[2]10.5	275
Mississippi River at Hartford, Ill.	1,500	3.2	416
Missouri River at Hermann, Mo.	2,640	3.8	864
Mississippi River at St. Louis, Mo.	3,940	3.7	1,245
Mississippi River at Chester, Ill.	4,250	3.9	1,435
Ohio River below Smithland Locks and Dam, Ill.-Ky.	652	[2]35	No discharge data
Ohio River at Olmsted, Ill.	2,070	1.7	304
Mississippi River below Hickman, Ky.	6,270	1.9	1,030
Mississippi River at Helena, Ark.	6,850	2.0	1,185
White River at Mile 11.5, Ark.	332	1.1	32
Arkansas River at Mile 55.9, Ark.	790	1.0	68
Mississippi River above Arkansas City, Ark.	7,630	1.9	1,254
Mississippi River below Vicksburg, Miss.	7,750	[2]14.6	Dissolved organic-carbon data invalid
Old River Outflow Channel near Knox Landing, La.	2,050	3.1	552
Mississippi River near St. Francisville, La.	6,190	2.3	1,230
Mississippi River below Belle Chasse, La.	No discharge data	1.7	No discharge data

[1] Illinois River water discharge measured below Meredosia, Illinois.

[2] Dissolved organic-carbon data were believed to be contaminated by organic-carbon bleed from ultrafilter membranes.

Table 2.—Acidity, isotopic, molecular-weight, and yield data of dissolved humic substances in the Mississippi River, July–August, 1987

[$\delta^{13}C$, stable carbon isotope ratio, M_n, number average molecular weight; M_w, weight average molecular weight; ND, not determined]

Sampling site	Percent yield of dissolved organic carbon	[1]$\delta^{13}C$ (parts per thousand)	Acidity[2] (milli-moles per gram)	[3]M_n	[3]M_w	Degree of poly-disper-sity (M_w/M_n)
Mississippi River near Winfield, Mo.	44	–26.0	3.2	865	919	1.06
Illinois River at Naples, Ill.	ND	–25.7	4.5	568	992	1.75
Mississippi River at Hartford, Ill.	59	–25.6	5.0	606	919	1.52
Missouri River at Hermann, Mo.	71	–24.9	4.9	506	803	1.59
Mississippi River at St. Louis, Mo.	67	–27.2	5.8	496	805	1.63
Ohio River below Smithland Locks and Dam, Ill—Ky.	ND	–26.5	ND	521	677	1.30
Ohio River at Olmsted, Ill.	83	–26.3	4.9	318	453	1.42
Mississippi River at Helena, Ark.	63	–25.7	5.1	716	907	1.27
White River at Mile 11.5, Ark.	81	–27.0	4.1	409	908	2.22
Arkansas River at Mile 55.9, Ark.	ND	–25.2	5.4	886	1,111	1.25
Mississippi River above Arkansas City, Ark.	75	–25.6	4.9	438	799	1.82
Mississippi River below Vicksburg, Miss.	ND	–24.7	4.8	957	1,154	1.21
Old River Outflow Channel near Knox Landing, La.	53	–25.6	4.7	352	768	2.18
Mississippi River near St. Francisville, La.	60	–26.9	ND	443	681	1.53
Mississippi River below Belle Chasse, La.	86	–25.6	5.1	986	1,041	1.06

[1] $\delta^{13}C$ values were determined by Luis Cifuentes, Department of Oceanography, Texas A & M University.

[2] Acidity determined by base titration to pH 8.5.

[3] Molecular weight determinations were by equilibrium ultracentrifugation in tetrahydrofuran (Leenheer, Meade, and others, 1989).

An average of two-thirds of the DOC was isolated and characterized as humic substances. The relatively low molecular weights and moderately high acidity values typify these dissolved humic substances as predominantly fulvic acids. No discernible trends are apparent in the acidity or molecular weight data to indicate source or instream degradation processes. The isotopic ($\delta^{13}C$) data indicated slightly heavier values than normally are observed for dissolved humic substances in temperate river waters (Malcolm, 1990). Input of humic substances from sewage, known to give heavy $\delta^{13}C$ values, is a possible cause for these sightly heavy values. In freshwater environments, allochthonous sources of humic substances cannot readily be distinguished from autochthonous sources by $\delta^{13}C$ values because the source term signatures are too similar (Mook and Tan, 1991).

Elemental analyses of dissolved humic substances at selected sites are shown in table 3. No significant trends in elemental composition were apparent between sampling sites. The isolated humic substances were exceptionally well separated from inorganic constituents, as shown by the low ash contents. The elemental composition of the Mississippi River isolates differed from humic substances isolated from the black water of the Suwannee River (Averett and others, 1989) in having greater carbon, hydrogen, and nitrogen contents and lower oxygen content. The greater hydrogen and nitrogen contents are especially significant on an atomic basis of comparison. The hydrogen content denotes that humic substances from the Mississippi River have a greater aliphatic character, and the nitrogen content indicates autochthonous sources are more significant in the Mississippi River than in the Suwannee River.

Spectral characterizations of dissolved humic substances were performed with H-nuclear magnetic resonance (NMR) spectrometry, ^{13}C-NMR spectrometry, and infrared spectrometry (IR). Two types of spectral patterns were obtained for the ^{1}H-NMR spectra as shown in figure 2. Most of the spectra were similar to the Mississippi River near St. Francisville, La., sample (fig. 2, spectrum A), however, samples from the Ohio River at Olmsted, Ill., Mississippi River at Helena, Ark.,

Table 3.--Elemental analyses of dissolved humic substances isolated from water samples collected during sampling cruise 1, July–August 1987

[<, less than]

Sampling site	Percent carbon	Percent hydrogen	Percent oxygen	Percent nitrogen	Percent ash
Mississippi River near Winfield, Mo.	55.34	5.07	35.11	2.70	0.74
Missouri River at Hermann, Mo.	54.86	5.05	36.40	2.52	.84
Ohio River at Olmsted, Ill.	56.60	5.48	33.27	2.46	<.1
Mississippi River at Helena, Ark.	57.86	4.60	33.04	2.43	<.1
Arkansas River at Mile 55.9, Ark.	55.92	5.07	34.92	2.37	<.1
Mississippi River near St. Francisville, La.	54.76	5.44	36.44	2.24	.86
Mississippi River below Belle Chasse, La.	55.94	4.92	34.86	2.43	<.1

and the White River gave ^{1}H-NMR spectra similar to spectrum B in figure 2. Spectral intensities at points 2 (methylene protons adjacent to a carboxyl group), 3 (protons associated with carbohydrates), and 4 (aromatic ring protons adjacent to phenolic groups) are diminished in spectrum B compared to spectrum A. The three samples similar to spectrum B also gave lower molecular weights, lower DOC values, and greater carbon and hydrogen contents than the remainder of the samples. All of these data indicate that these three samples are the result of a greater degree of degradation (humification) than the remainder of the samples.

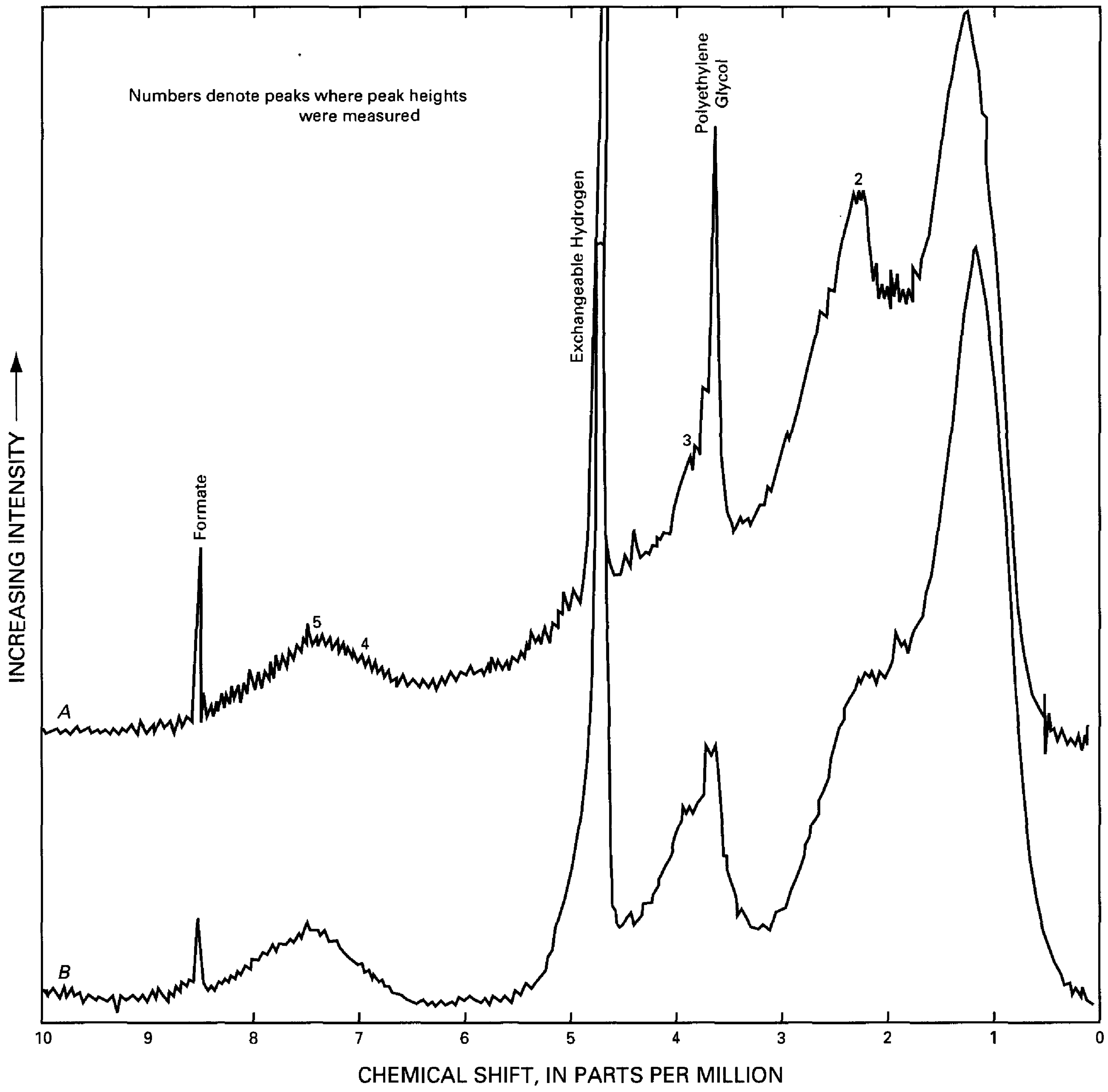

Figure 2.—^{1}H-nuclear magnetic resonance spectra of dissolved humic substances in samples from the (A) Mississippi River near St. Francisville, La., and (B) Ohio River at Olmsted, Ill., sampled July–August 1987.

The sharp peak at 3.6 ppm was found to be related to polyethylene glycol contaminants from nonionic surfactants (Leenheer and others, 1991). Polyethylene glycols cannot be analyzed by conventional solvent extraction, gas chromatographic, or mass spectrometric analyses. These contaminants were found in nearly all the samples from the first two sampling cruises, and they probably represent the most abundant organic contaminant found in the river during sampling cruise 1.

A ^{13}C-NMR spectrum acquired under quantitative conditions for dissolved humic substances isolated from a sample from the Mississippi River near St. Francisville, La., is shown in figure 3. The spectrum is typical of an aquatic fulvic-acid sample with the exception that in spectral regions near 115 ppm and from 140 to 160 ppm, both of which are indicative of phenolic substituents, are depleted relative to these spectral regions for fulvic acid isolated from the Suwannee River (Thorn, 1989). A second ^{13}C-NMR spectrum for humic substances isolated from a sample from the Mississippi River at St. Louis, Mo., gave nearly identical results.

An infrared spectrum of dissolved humic substances isolated from a sample from the Mississippi River at St. Louis is shown in figure 4. The spectrum is dominated by hydroxyl (3,600–2,500 cm^{-1}) and carboxyl (1,720 cm^{-1}) group absorbances. Infrared spectra were run on all of the humic-substance isolates, but no trends or information of particular geochemical significance were found.

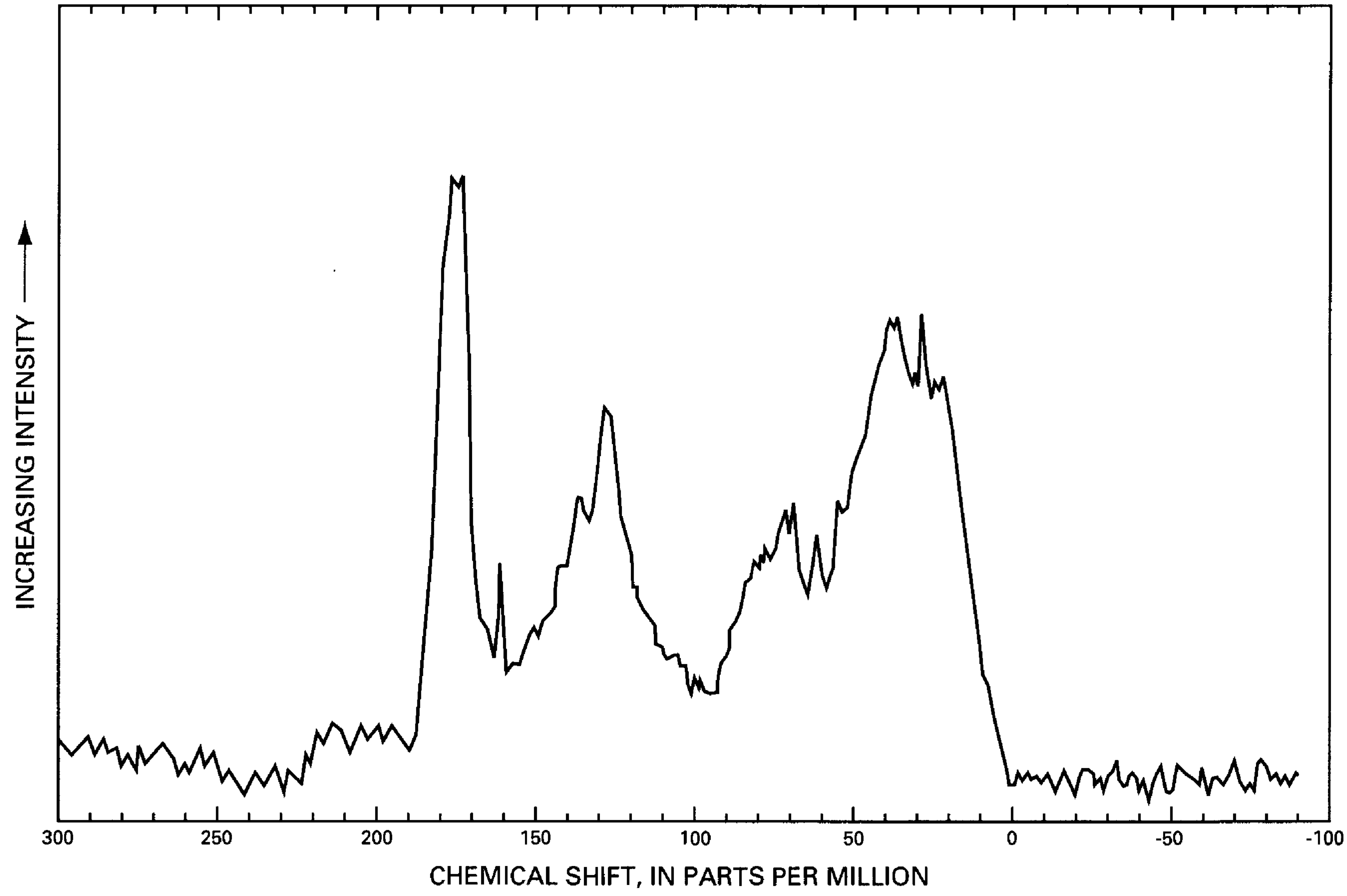

Figure 3.—^{13}**C-nuclear magnetic resonance spectrum of dissolved humic substances isolated from the Mississippi River near St. Francisville, La., sampled July–August 1987.**

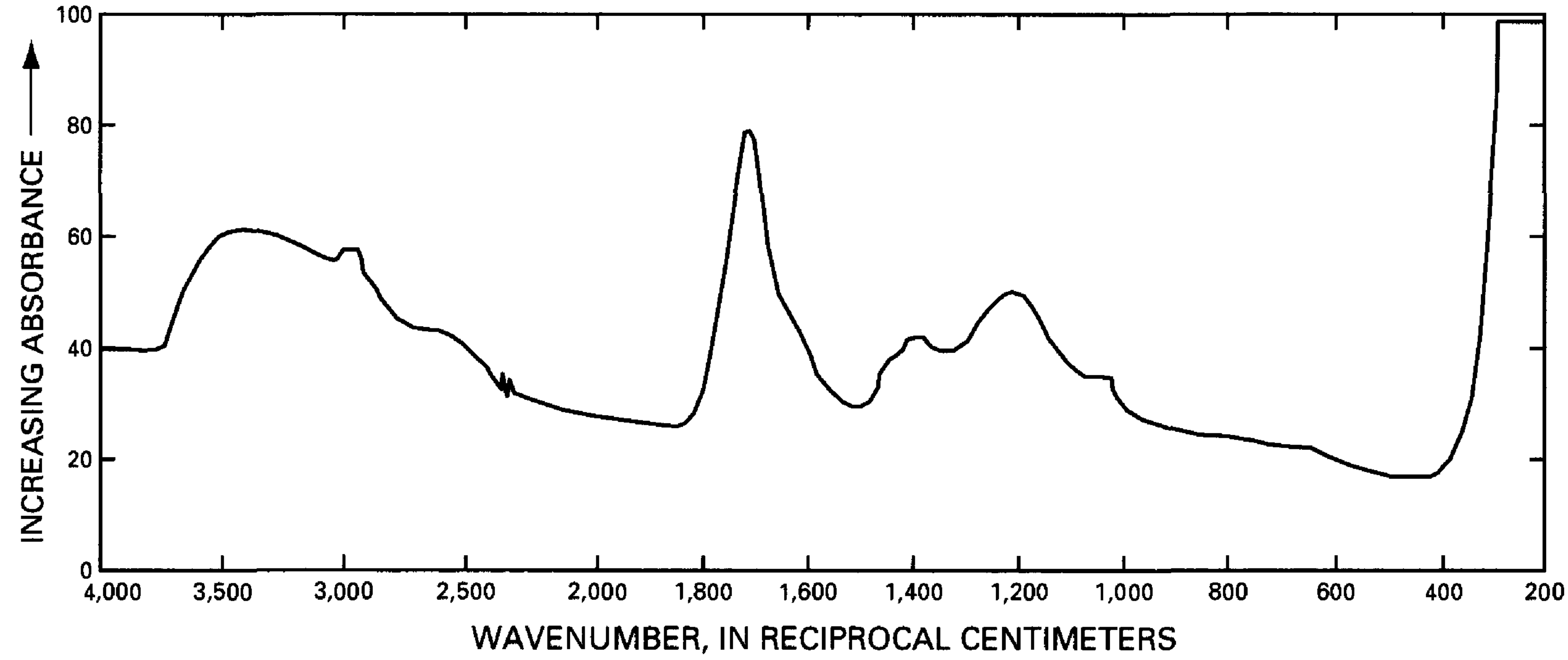

Figure 4.--Infared spectrum of dissolved humic substances isolated from a sample from the Mississippi River at St. Louis, Mo., sampled July-August 1987.

Organic Matter in Suspended-Sediment Fractions

Differences in organic composition between colloid and silt and clay fractions were published in the report by Leenheer, Brown, and others (1989). Organic carbon percentages were consistently greater in the colloid fraction than in the silt fraction. Atomic carbon-nitrogen (C:N) ratios were consistently less in the colloid fraction than in the silt and clay fraction. These consistent differences occurred throughout a wide range of organic-carbon compositions from 1.5 to 20.1 percent and organic-nitrogen compositions from 0.2 to 3.7 percent. The small C:N ratios in the colloid fraction were caused by large amounts of phytoplankton and related low-density organic matter that coisolate with colloid-size material.

Organic-carbon and nitrogen transport in the silt and clay and colloid fractions are listed in table 4. The transport in the Mississippi River was dominated by input from the silt and clay fraction in the Missouri River. The Mississippi River at Hartford, Ill., and the Ohio, White, and Arkansas Rivers were at low stages and had greater transport on the colloid fractions than on the silt and clay fractions. The organic-carbon transport on the colloid fraction was slightly less than the dissolved organic carbon (table 1), but the organic-carbon transport on the silt and clay greatly exceeded the dissolved organic-carbon transport for sampling sites containing silt and clay derived from the Missouri River. The reason for the significant transport in the colloid fraction is that the settling procedure did not remove suspended-mineral colloids greater than 1–2 µm in diameter or low-density phytoplankton. Therefore, material that normally is removed by filtration or centrifugation was included in the colloid fraction.

Organic materials in the colloid fraction were characterized by solid-state ^{13}C-NMR spectrometry by Professor Gary Maciel of the Regional NMR Center at Colorado State University, Ft. Collins, Colo. These were the first spectra of aquatic colloids characterized in this manner, and the relatively low carbon content of the colloids resulted in the spectra being of low intensity and poor quality. Only general qualitative significance should be attached to the spectra. Three of the spectra are shown in figure 5.

Table 4.–Organic-carbon and nitrogen transport on the silt and clay and colloid fractions for sampling cruise 1, July–August 1987

[Water-discharge and suspended-sediment concentration data used for computing transport reported by Moody and Meade (1992)]

Sampling site	Organic-carbon transport on silt and clay (metric tons per day)	Nitrogen transport on silt and clay (metric tons per day)	Organic-carbon transport on colloids (metric tons per day)	Nitrogen transport on colloids (metric tons per day)
Mississippi River at Hartford, Ill.	92	12	129	25
Missouri River at Hermann, Mo.	7,145	693	829	107
Mississippi River at St. Louis, Mo.	4,019	408	867	124
Mississippi River at Chester, Ill.	4,454	456	1,107	167
Ohio River below Smithland Locks and Dam, Ill.—Ky.	20	3	44	6
Ohio River at Olmsted, Ill.	96	10	151	24
Mississippi River below Hickman, Ky.	1,625	160	789	121
Mississippi River at Helena, Ark.	2,975	298	985	153
White River at Mile 11.5, Ark.	44	8	23	4
Arkansas River at Mile 55.9, Ark.	71	10	82	15
Mississippi River above Arkansas City, Ark.	2,018	191	1,114	164
Mississippi River below Vicksburg, Miss.	2,585	296	1,033	166
Old River Outflow Channel near Knox Landing, La.	508	49	276	40
Mississippi River near St. Francisville, La.	2,086	170	671	113

The best spectrum, which had 20.1 percent carbon, was obtained on the colloid fraction from the Arkansas River (fig. 5A). The lipid/hydrocarbon peak near 25 ppm and the carbohydrate peak near 70 ppm are of equal intensity, and the carbonyl peak associated with proteins, esters, and acids is near 170 ppm. A small aromatic carbon peak exists near 130 ppm. Most of the Mississippi River and tributary sites gave spectra similar to spectrum B (fig. 5) in which the lipid/hydrocarbon peak seemed to be diminished in intensity relative to the Arkansas River sample. Two exceptions were the colloids from samples from the Mississippi River at St. Louis, Mo., (spectrum C, fig. 5) and from the Mississippi River at Chester, Ill., immediately downriver. The lipid/hydrocarbon peak is enriched in these colloid fractions and might represent hydrocarbon contamination from the St. Louis area. The ^{13}C-NMR spectra of the colloid fraction (fig. 5) is markedly different than the dissolved humic-substance fraction (fig. 3) in which the carbonyl and aromatic carbon are greater and the carbohydrate carbon is much less. The enhanced lipid/hydrocarbon component on the colloid fraction relative to the dissolved humic-substance fraction should make the colloids better carriers of nonionic, nonpolar, organic contaminants.

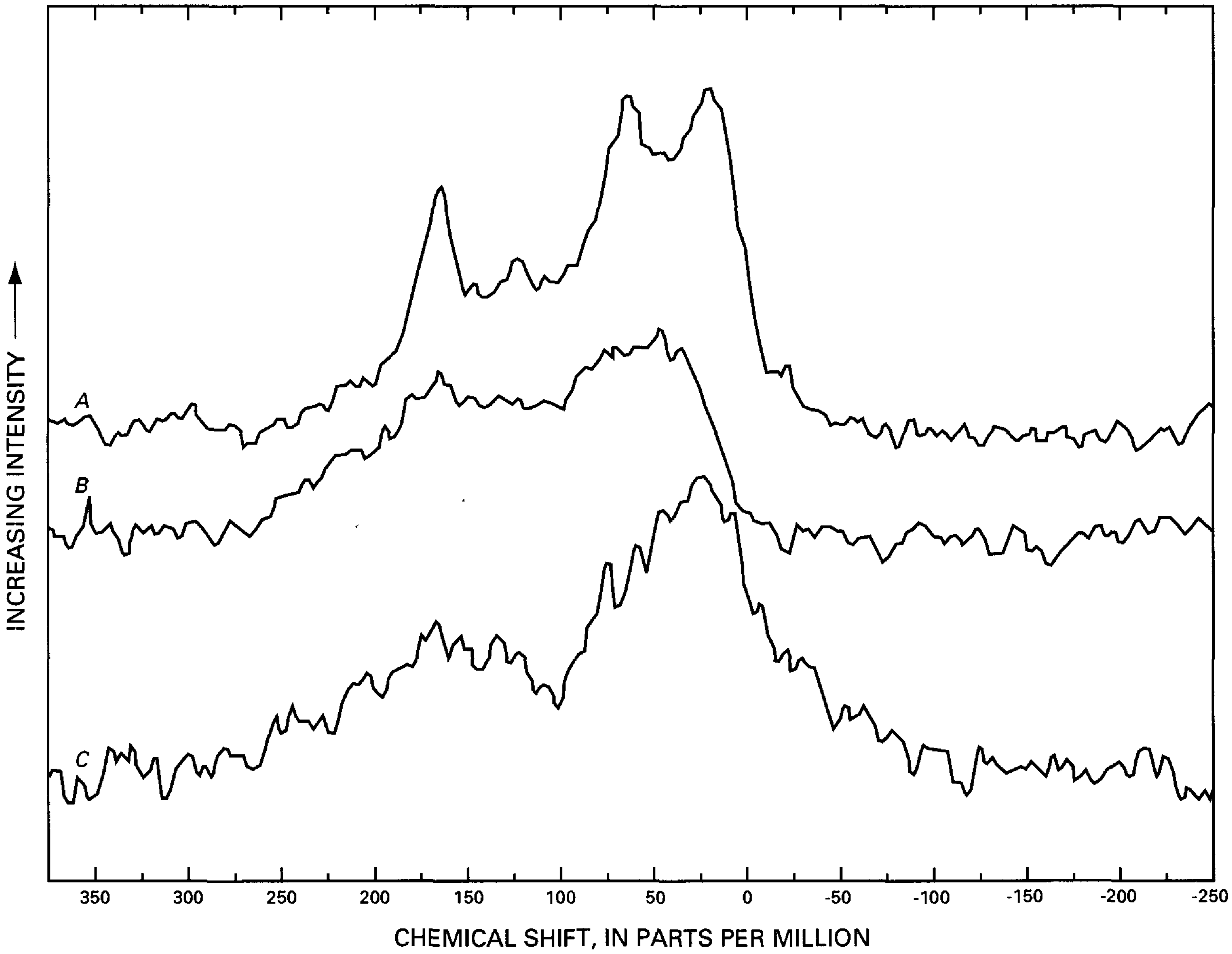

Figure 5.--Solid-state ^{13}C-nuclear magnetic resonance spectra of colloids isolated from the: (A) Arkansas River at Mile 55.9, (B) Mississippi River below Vicksburg, Miss., and (C) Mississippi River at St. Louis, Mo., sampled July–August 1987.

SAMPLING CRUISE 2, NOVEMBER–DECEMBER 1987

The sampling of cruise 2 began on the Illinois River below Meredosia, Illinois, on November 29, 1989, and ended on the Mississippi River below Belle Chasse, Louisiana, on December 20, 1987. Sampling site changes from the first cruise were: (1) Sites on the Mississippi River at Hartford, Illinois, the Ohio River below Smithland Lock and Dam, and the Arkansas River at Mile 55.9 were eliminated. (2) The site on the Mississippi River at Chester, Illinois, was changed to Mississippi River at Thebes, Illinois, the site on the Missouri River was changed from Hermann, Missouri, to St. Charles, Missouri, and the site on the Illinois River at Naples, Illinois, was changed to below Meredosia, Illinois. (3) New sites were added on the Mississippi River at Fulton, Tennessee, and the Yazoo River at Mile 10, Mississippi.

Objectives and Approach

The major objective of sampling cruise 2 was to repeat the research investigations of the first cruise during the late fall, when water temperatures that affect the biological production and degradation processes are much lower. The nature of dissolved and suspended organic matter in the Mississippi River should be altered compared to the summer conditions of the first trip. Secondary objectives were to move the sample processing and sediment fractionation procedures to a laboratory mounted on the stern of the boat and to evaluate continuous-flow centrifugation and gravitational settling as a means of separating the silt and colloid fractions.

A flow chart of procedures for water and suspended-sediment fractionation of the depth-integrated composite sample is shown in figure 6 (Leenheer, Meade, and others, 1989). A Sharples Model AS-12 continuous-flow supercentrifuge was borrowed from the Great Lakes Research Institute of the University of Wisconsin and was installed on the *Acadiana* at Alton, Ill. For the gravitational settling procedure, the silt and clay in the composite B fraction (fig. 6) was settled in a carboy suspended in a custom-made gimbal on the boat. The gimbal minimized the rocking motion of the boat; an air-filled plenum on which the carboy was placed also minimized vibrations from the boat.

Dissolved Organic Matter

DOC concentrations and transport are listed in table 5. DOC transport for sampling site on the Mississippi River downriver from Helena, Arkansas, are approximately double the transport measured for the first sampling cruise (table 1). This transport increase is due to the combined effect of a discharge increase (38-percent average increase for Mississippi River sites upstream from the Old River Outflow) and a 24-percent DOC increase (all sites averaged on the Mississippi River) over equivalent data for sampling cruise 1. The Ohio River had a DOC transport increase of 3.8 times the DOC transport for the first sampling cruise, and DOC transport in the Mississippi River downriver from the Ohio River is proportionately increased. Water temperatures were much cooler for the second cruise—near 5°C for sites near St. Louis and increasing to 10°C for sites near New Orleans. The most likely explanation for the greater DOC concentrations in the Lower Mississippi River during sampling cruise 2 is that there is less biodegradation when water temperatures are cooler in late fall. During both sampling cruises, DOC concentrations generally decreased in the downstream direction; this observation supports the biodegradation hypothesis.

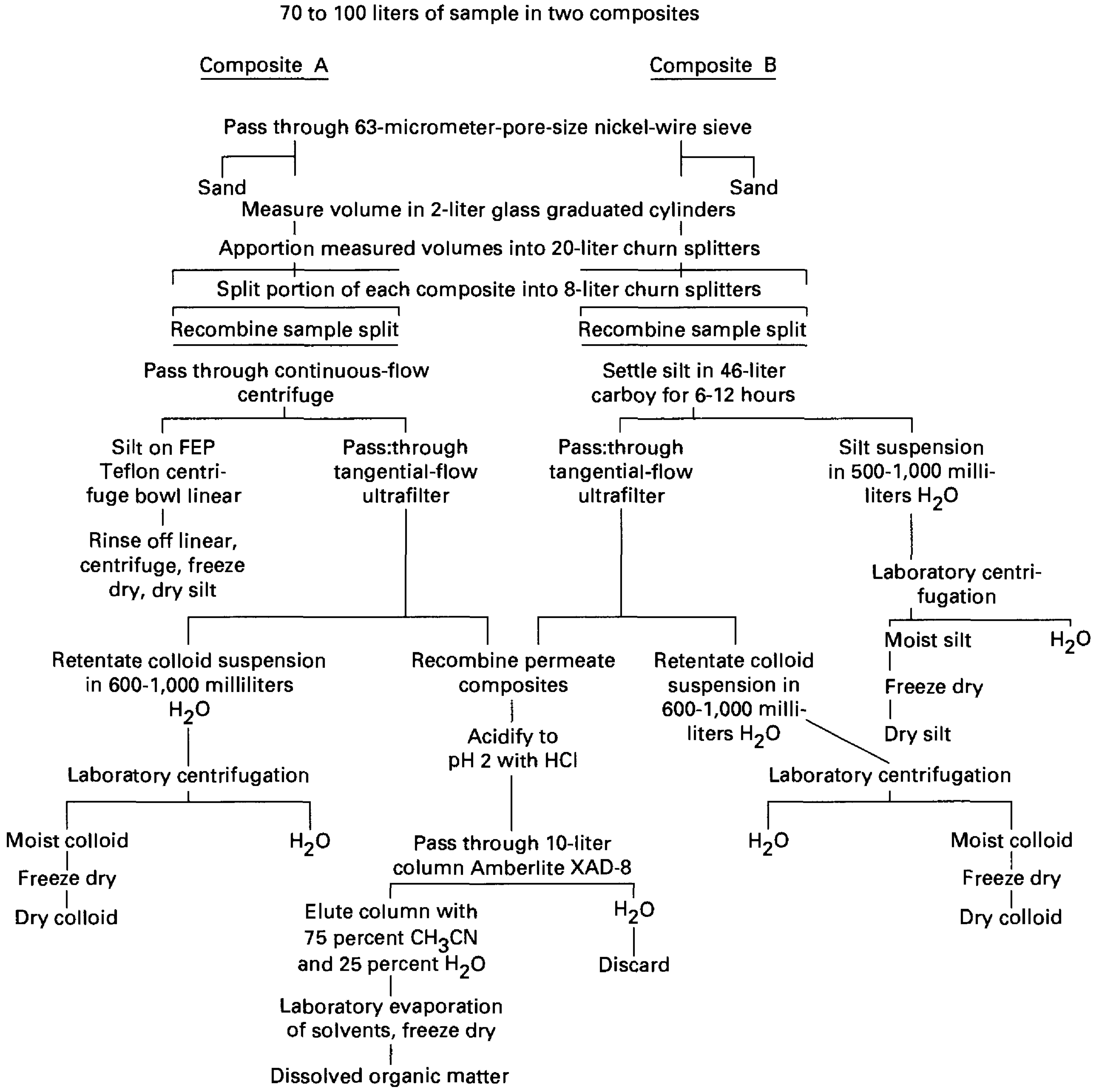

Figure 6.—Flow chart of procedures for water and suspended-sediment sampling, sampling cruise 2, November–December 1987.

Table 5.--Dissolved organic-carbon concentrations and transport for sampling cruise 2, November-December 1987

[Transport was computed using water-discharge data reported by Moody and Meade (1992)]

Sampling site	Water discharge (cubic meters per second)	Dissolved organic-carbon concentration (milligrams per liter)	Transport (metric tons per day)
Mississippi River near Winfield, Mo.	2,040	3.8	670
Illinois River below Meredosia, Ill.	262	4.3	97
Missouri River at St. Charles, Mo.	2,810	3.4	822
Mississippi River at St. Louis, Mo.	5,440	3.9	1,833
Mississippi River at Thebes, Ill.	5,190	5.8	2,598
Ohio River at Olmsted, Ill.	4,200	3.2	1,160
Mississippi River at Helena, Ark.	8,770	3.1	2,349
White River at Mile 11.5, Ark.	519	3.2	143
Mississippi River above Arkansas City, Ark.	9,920	4.4	3,683
Yazoo River at Mile 10, Miss.	177	2.7	41
Mississippi River below Vicksburg, Miss.	10,410	2.4	2,159
Old River Outflow Channel near Knox Landing, La.	1,830	2.5	359
Mississippi River near St. Francisville, La.	8,180	2.7	1,908
Mississippi River below Belle Chasse, La.	9,560	2.7	1,982

Acidity, molecular-weight, and yield data of dissolved humic substances in the Mississippi River sampled during sampling cruise 2 are shown in table 6. Dissolved humic substances constituted an average of 63 percent of the DOC for all the sites. This average was very similar to the data from sampling cruise 1 (table 2).

Elemental analyses of dissolved humic substances isolated from samples obtained during sampling cruise 2 are shown in table 7. The only significant difference from humic-substance samples obtained during the first cruise (table 3) is the lower nitrogen content of the samples obtained from the river during the late fall season. The lower nitrogen content is hypothesized to result from greater allochthonous (terrestrial) inputs to stream humic substances during the fall when instream (autochthonous) productivity is decreased relative to the summer. Elemental analyses during both sampling cruises indicated the samples from the Mississippi River near Winfield, Mo., gave the greatest nitrogen content. The Winfield samples represent water discharged from the Upper Mississippi River where instream productivity should be the greatest because of the extensive series of pools above the locks and dams in this reach of the river.

Table 6.–Acidity, molecular-weight, and yield data of dissolved humic substances in the Mississippi River sampled November–December 1987

[M_n, number average molecular weight; M_w, weight average molecular weight; ND, not determined]

Sampling site	Percent yield of dissolved organic carbon	Acidity[1] (milli-moles per gram)	[2]M_n	[2]M_w	Degree of poly-dispersity (M_w/M_n)
Mississippi River near Winfield, Mo.	63	5.4	823	1,066	1.30
Illinois River below Meredosia, Ill.	59	5.7	596	1,003	1.68
Missouri River at St. Charles, Mo.	62	5.2	580	713	1.23
Mississippi River at St. Louis, Mo.	57	ND	ND	ND	ND
Mississippi River at Thebes, Ill.	38	5.3	262	593	2.26
Ohio River at Olmsted, Ill.	44	4.8	876	1,003	1.14
Mississippi River below Hickman, Ky.	ND	5.9	378	528	1.40
Mississippi River at Fulton, Tenn.	ND	4.7	404	948	2.34
Mississippi River at Helena, Ark.	47	5.5	439	829	1.89
White River at Mile 11.5, Ark.	63	4.8	734	1,142	1.56
Mississippi River above Arkansas City, Ark.	50	5.2	721	1,091	1.51
Yazoo River at Mile 10, Miss.	91	4.5	909	1,126	1.23
Mississippi River below Vicksburg, Miss.	84	5.0	586	992	1.69
Old River Outflow Channel near Knox Landing, La.	82	4.4	679	951	1.40
Mississippi River near St. Francisville, La.	71	4.7	361	455	1.26
Mississippi River below Belle Chasse, La.	68	4.2	664	856	1.29

[1] Acidity determined by base titration to pH 8.5.

[2] Molecular-weight determinations were by equilibrium ultracentrifugation in tetrahydrofuran (Leenheer, Meade, and others, 1989).

Table 7.–Elemental analyses of dissolved humic substances isolated from water samples collected during sampling cruise 2, November–December 1987

[<, less than]

Sampling site	Percent carbon	Percent hydrogen	Percent oxygen	Percent nitrogen	Percent ash
Mississippi River near Winfield, Mo.	55.03	5.04	36.18	2.27	0.17
Missouri River at St. Charles, Mo.	56.44	5.22	35.07	2.07	.14
Ohio River at Olmsted, Ill.	55.86	5.12	34.86	2.05	<.1
White River at Mile 11.5, Ark.	55.48	4.90	35.87	1.81	<.1
Mississippi River below Belle Chasse, La.	50.97	5.00	33.17	1.83	7.33

Proton NMR spectra of dissolved humic substances isolated from water at three sites during the late fall cruise are shown in figure 7. Humic substances isolated from the Illinois River (fig. 6, spectrum A) appear to be extensively contaminated with petroleum hydrocarbons as indicated by sharp peaks at 0.9, 1.1, 1.4, 1.8, and 2.2 ppm. Lesser amounts of these contaminants were found in the Mississippi River near Winfield, Mo. Perhaps the cool water temperatures (4–6°C), which retard hydrocarbon volatilization losses, low suspended-sediment concentrations (Illinois River, 79 mg/L; Mississippi River near Winfield, Mo., 31 mg/L), which limit hydrocarbon sorption losses, and decreased biologic activity in cold water may lead to a buildup of hydrocarbon contaminants in the dissolved phase at certain times of the year. Most of the ^{1}H-NMR spectra also contained indications of polyethylene glycol contaminants (Leenheer and others, 1991).

Humic substances isolated during the late fall cruise (fig. 7, spectra B and C) differed from humic substances isolated during the summer cruise (fig. 2) in having higher peak height ratios of peaks 2, 3, and 4 to peak 1. Because these peaks represent the structural moieties that are the most likely to be biodegraded or sorbed onto sediment constituents, it is not surprising that these peaks are greater during the fall cruise than during the summer cruise. The dissolved humic substances isolated from the White River had the greatest increase in peaks 2, 3, and 4 (fig. 7, spectrum B). Humic substances from the White River site also had the lowest nitrogen content (table 7), so spectrum B represents the allochthonous "end member" for dissolved humic-substances studies for the fall 1987 sampling cruise.

Organic Matter on Suspended-Sediment Fractions

Recoveries of silt and clay and colloids comparing the gravitational settling and continuous-flow centrifugation methods are presented in the report by Leenheer, Meade, and others (1989). The centrifuge recovered material about one order of magnitude (down to 0.3 µm in diameter) smaller than did the gravitational settling technique, and there was an average 20-percent shift of colloids into the silt and clay fraction with centrifugation, based on the percentage of colloids recovered after centrifugation.

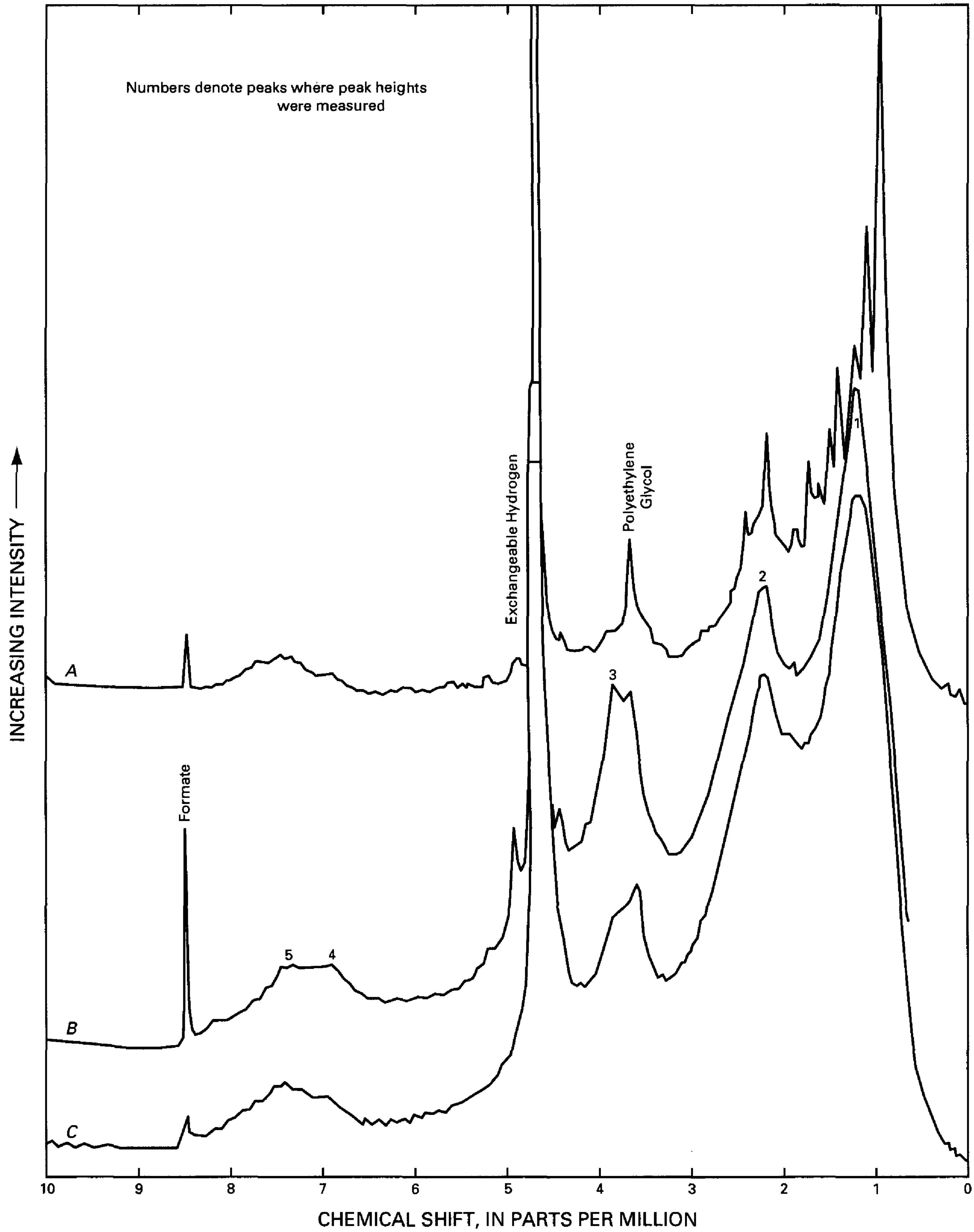

Figure 7.--^{1}H-nuclear magnetic resonance spectra of dissolved humic substances from samples from the: (A) Illinois River below Meredosia, Ill., (B) White River at Mile 11.5, Ark., and (C) Mississippi River below Belle Chasse, La., sampled November–December 1987.

Percentages of carbon and nitrogen measured on the silt and clay and colloid fractions are given in table 8. The carbon and nitrogen percentages on the silt and clay and colloid fractions on which the centrifuge was used were generally greater than for the fractions that were separated by gravitational settling. Apparently, inclusion of smaller particles into the operationally defined "silt and clay" fraction separated by centrifugion resulted in greater carbon percentages than for silt and clay separated by gravitational settling. The samples highest in organic-matter content were from the Mississippi River near Winfield, Mo., and the organic-matter content of the settled silt and clay fraction generally decreased in the downriver direction.

Table 8.–Organic-carbon and nitrogen contents of silt and clay and colloid fractions of suspended sediment from sampling cruise 2, November–December 1987

[ND, not determined]

Sampling site	Percent carbon on silt and clay		Percent nitrogen on silt and clay		Percent carbon on colloid		Percent nitrogen on colloid	
	Settled	Centrifuged	Settled	Centrifuged	Settled	Centrifuged	Settled	Centrifuged
Mississippi River near Winfield, Mo.	5.86	ND	0.84	ND	14.99	ND	2.21	ND
Illinois River below Meredosia, Ill.	2.86	ND	.31	ND	6.71	ND	.94	ND
Missouri River at St. Charles, Mo.	1.44	ND	.15	ND	2.75	7.25	.29	0.60
Mississippi River at St. Louis, Mo.	ND	ND	ND	ND	4.72	7.28	.53	.53
Mississippi River at Thebes, Ill.	1.86	2.01	.22	0.22	4.13	7.26	.46	.70
Ohio River at Olmsted, Ill.	1.83	2.40	.23	.26	6.67	8.09	.64	.81
Mississippi River below Hickman, Ky.	1.87	2.15	.22	.24	5.21	7.25	.45	.47
Mississippi River at Fulton, Tenn.	1.66	2.10	.20	.25	4.32	8.75	.50	.90
Mississippi River at Helena, Ark.	1.88	2.24	.21	.25	4.58	4.67	.35	.43
White River at Mile 11.5, Ark.	1.18	1.61	.13	.19	3.07	4.47	.35	.43
Mississippi River above Arkansas City, Ark.	1.75	2.42	.21	.28	3.54	5.63	.45	.56
Yazoo River at Mile 10, Miss.	1.05	1.58	.13	.24	2.56	4.01	.33	.37
Mississippi River below Vicksburg, Miss.	1.64	3.03	.17	.41	4.01	8.72	.52	.65
Old River Outflow Channel near Knox Landing, La.	1.44	2.21	.17	.24	3.66	7.77	.41	.73
Mississippi River near St. Francisville, La.	1.83	1.99	.21	.25	3.99	8.33	.44	.63
Mississippi River below Belle Chasse, La.	ND	ND	ND	ND	ND	6.52	ND	.68

Organic-carbon and nitrogen transport for the November–December 1987 sampling are presented in table 9. Only the data for the gravitational settling experiment were computed as this data set is more complete, and it allows direct comparison with the data in table 4. The major input to the organic-carbon and nitrogen transport on the silt and clay fraction was again the Missouri River, but this input is not nearly as substantial as for the July–August 1987 sampling (table 4).

Table 9.–Organic-carbon and nitrogen transport on the silt and clay and colloid fractions for sampling cruise 2, November–December 1987

[Water-discharge and suspended-sediment concentration data used to compute transport are reported by Moody and Meade (1992); ND, not determined]

Sampling site	Organic-carbon transport on silt and clay (metric tons per day)	Nitrogen transport on silt and clay (metric tons per day)	Organic-carbon transport on colloids (metric tons per day)	Nitrogen transport on colloids (metric tons per day)
Mississippi River near Winfield, Mo.	223	32	225	33
Illinois River below Meredosia, Ill.	35	4	38	5
Missouri River at St. Charles, Mo.	761	79	306	32
Mississippi River at St. Louis, Mo.	ND	ND	561	63
Mississippi River at Thebes, Ill.	1,299	154	708	79
Ohio River at Olmsted, Ill.	155	19	308	30
Mississippi River below Hickman, Ky.	1,388	163	1,289	111
Mississippi River at Fulton, Tenn.	1,004	121	843	98
Mississippi River at Helena, Ark.	1,108	124	1,009	77
White River at Mile 11.5, Ark.	28	3	57	6
Mississippi River above Arkansas City, Ark.	1,051	126	1,024	130
Yazoo River at Mile 10, Miss.	12	1	37	5
Mississippi River below Vicksburg, Miss.	1,072	111	783	159
Old River Outflow Channel near Knox Landing, La.	173	20	184	21
Mississippi River near St. Francisville, La.	1,078	123	882	97
Mississippi River below Belle Chasse, La.	ND	ND	[1]401	[1]42

[1] Colloid recovered from centrifuge effluent.

Organic-carbon and nitrogen transport on the colloid fraction (table 9) exceeded the silt and clay transport for the tributary rivers (Missouri River excepted) and the Mississippi River near Winfield, Mo., and the colloid carbon and nitrogen transport were within a factor of 2 of the silt and clay carbon and nitrogen transport for the Mississippi River sites. These data show the importance of colloids as a transport medium for contaminants that are associated with natural organic substances in water.

Concentrations of particulate organic carbon for the November–December 1987 sampling are shown in table 10. The concentrations were determined in two independent manners: (1) Computed as the difference between total organic-carbon and DOC concentrations on whole and filtered water samples injected into a high-temperature combustion furnace of the Beckman 915B carbon analyzer, and (2) computed from the organic-carbon transport (table 9) divided by the discharge volume reported by Moody and Meade (1992). The two sets of concentrations are similar, but the set derived from the transport is much less variable than the set from the difference determination. Additivity of errors associated from the difference determination is believed to be the cause of the greater variability.

Table 10.--Concentrations of particulate organic carbon for sampling cruise 2, November–December 1987

Sampling site	Particulate organic carbon determined by total organic carbon minus dissolved organic carbon (milligrams per liter)	Particulate organic carbon determined form carbon analysis of isolated suspended-sediment fractions (milligrams per liter)
Mississippi River near Winfield, Mo.	3.5	2.5
Illinois River below Meredosia, Ill.	4.2	3.2
Missouri River at St. Charles, Mo.	4.4	4.4
Mississippi River at Thebes, Ill.	1.6	4.4
Mississippi River at Helena, Ark.	1.3	2.7
White River at Mile 11.5, Ark.	1.3	1.9
Mississippi River above Arkansas City, Ark.	1.7	2.5
Yazoo River at Mile 10, Miss.	3.4	3.2
Mississippi River below Vicksburg, Miss.	2.3	2.1
Old River Outflow Channel near Knox Landing, La.	3.1	2.4
Mississippi River near St. Francisville, La.	3.1	2.8

SAMPLING CRUISE 3, MAY–JUNE 1988

The sampling of cruise 3 began on the Illinois River below Meredosia, Illinois, on May 16, 1988, and ended on the Mississippi River below Belle Chasse, Louisiana, on June 7, 1988. The one sampling site change from cruise 2 was that the Missouri River was sampled at Hermann, Missouri instead of St. Charles, Missouri.

Objectives and Approach

The major objective of sampling cruise 3 was to repeat the research investigations of the first two cruises during a high-flow period during the spring; unfortunately, flow was at record low levels during this cruise. Another objective was to obtain a more complete characterization of the dissolved and colloidal fractions that were not recovered for analysis during the previous two cruises. The hydrophilic fraction (dissolved organic matter that does not adsorb on Amberlite XAD-8 resins) was studied, and an organic colloid fraction that was not recovered by laboratory supercentrifugation was also characterized.

The approach to isolating and characterizing the dissolved organic-matter fractions was modified significantly. The large 10-L column of Amberlite XAD-8 resin was removed from the boat, and 20-L samples of ultrafilter permeates were collected in cubitainers, preserved with chloroform, and shipped back to the laboratory. In the laboratory, the samples were acidified to pH 4 with HCl and vacuum evaporated to 500 mL to 1 L (the point of salt saturation), the pH adjusted to 2 with HCl, and the sample concentrates passed through a 500-mL column of Amberlite XAD-8. Dissolved organic matter that adsorbed on the resin was eluted with 75 percent acetonitrile and 25 percent water acidified to pH 2. This modification of the procedure increased the recovery of dissolved organic matter that adsorbed on the resin. The procedure used in the first two sampling cruises recovered solutes whose column capacity factor (k') was 10 or greater (Leenheer, 1981); the modified procedure recovered solutes of k' equal to 1 or greater.

Hydrophilic organic solutes that did not adsorb on the resins were collected in the eluent from the XAD-8 column, the eluent was vacuum evaporated to the point of salt crystallization, then glacial acetic acid was added to double the volume of the concentrate. Successive additions of acetic acid and separation of inorganic salts by centrifugation served to separate hydrophilic organic solutes from water and inorganic salts. After no more inorganic salts could be separated, the residue was dissolved in water and passed through a cation-exchange column in the hydrogen form to convert hydrophilic organic salts to acids.

Organic colloids that were not recoverable by centrifugation of the colloid fraction were recovered by placing the supernatant from the centrifugation in a 10,000-dalton pore-size dialysis bag, removing the salts by dialysis against distilled water, and freeze-drying the colloids remaining inside the dialysis bag.

A Sharples Model AS-12 continuous-flow centrifuge was acquired by the project for use during this and subsequent sampling cruises. It was decided to use centrifugation to separate the silt and clay and colloid fractions rather than gravitational settling because centrifugation was much more time efficient with regard to the amount of water processed and the amount of silt and clay recovered. A pumped composite sample (see Moody and Meade, 1993) consisting of 300 to 700 liters was collected in addition to the depth-integrated composite sample.

Dissolved Organic Matter

DOC concentrations and transport for sampling cruise 3 are listed in table 11. Organic-carbon concentrations and transport are similar in the Mississippi River and tributary sites upstream from the Ohio River compared to the first cruise (table 1), where similar low-flow conditions existed; but concentrations and transport for sites downstream from the Ohio River are 50–80 percent greater than the values for sampling cruise 1. The only significant difference between these cruises is water temperature—near 30°C for the first cruise and 20–25°C for the third cruise. There may have been less instream degradation of DOC during the moderate temperatures of the third cruise than during the first cruise.

Table 11.--Dissolved organic-carbon concentrations and transport for sampling cruise 3, May–June 1988

[Transport was computed using water-discharge data reported by Moody and Meade (1992)]

Sampling site	Water discharge (cubic meters per second)	Dissolved organic-carbon concentration (milligrams per liter)	Transport (metric tons per day)
Mississippi River near Winfield, Ill.	1,740	4.8	699
Illinois River below Meredosia, Ill.	332	4.4	126
Missouri River at Hermann, Mo.	1,480	3.5	456
Mississippi River at St. Louis, Mo.	3,350	4.1	1,004
Mississippi River at Thebes, Ill.	3,590	3.9	1,260
Ohio River at Olmsted, Ill.	3,230	2.3	639
Mississippi River below Hickman, Ky.	6,790	3.1	1,827
Mississippi River at Fulton, Tenn.	7,170	3.2	1,997
Mississippi River at Helena, Ark.	7,050	3.1	1,883
White River at Mile 11.5, Ark.	438	2.0	76
Mississippi River above Arkansas City, Ark.	8,160	2.9	2,083
Yazoo River at Mile 10, Miss.	73	3.5	21
Mississippi River below Vicksburg, Miss.	7,950	3.5	2,412
Old River Outflow Channel near Knox Landing, La.	2,150	3.5	663
Mississippi River near St. Francisville, La.	5,700	3.7	1,802
Mississippi River below Belle Chasse, La.	5,570	3.2	1,543

Organic elemental analyses and yields of dissolved and colloidal organic substances isolated from water samples collected on the May–June 1988 sampling cruise are tabulated in table 12. Yields of the humic-substance fraction did not appreciably improve compared to data from the previous two cruises. The humic-substance fraction constitutes an average of about two-thirds of the DOC, and this fraction was quantitatively isolated in all three procedures. However, the ash content of the humic-substance fraction was much greater with this modified procedure because

Table 12.--Elemental analyses of dissolved and colloidal organic substances isolated from water samples collected during sampling cruise 3, May–June 1988

[--, no data]

Sampling site	Fraction	Percent yield of dissolved organic carbon	Percent carbon (ash-free)	Percent hydrogen (ash-free)	Percent oxygen (ash-free)	Percent nitrogen (ash-free)	Percent ash
Illinois River below Meredosia, Ill.	Dissolved humic substances	75.8	42.06 (49.9)	4.10 (4.9)	29.29 (34.8)	2.44 (2.9)	15.78
	Dissolved hydrophilic substances	7.1	20.31 (30.4)	2.54 (3.8)	41.03 (61.4)	6.56 (9.8)	33.17
	Organic colloids	--	45.51 (47.4)	6.13 (6.4)	38.21 (39.8)	3.77 (3.9)	3.94
Mississippi River below Hickman, Ky.	Dissolved humic substances	61.1	38.33 (50.7)	3.49 (4.6)	29.32 (38.8)	2.26 (2.9)	24.46
	Dissolved hydrophilic substances	12.4	31.73 (39.1)	3.37 (4.2)	32.09 (39.6)	4.02 (5.0)	18.94
	Organic colloids	--	40.64 (45.8)	5.54 (6.2)	35.04 (39.5)	3.66 (4.1)	11.33
Mississippi River at Helena, Ark.	Dissolved humic substances	69.5	47.81 (51.3)	4.34 (4.7)	33.53 (36.0)	2.68 (2.9)	6.85
	Dissolved hydrophilic substances	12.7	34.09 (39.4)	3.58 (4.1)	38.39 (44.6)	4.11 (4.8)	13.55
	Organic colloids	--	42.89 (46.5)	5.96 (6.5)	34.32 (37.2)	3.59 (3.9)	7.83
Mississippi River below Vicksburg, Miss.	Dissolved humic substances	58.4	43.67 (50.3)	4.01 (4.6)	32.38 (37.3)	2.60 (3.0)	13.22
	Dissolved hydrophilic substances	9.1	31.44 (38.1)	3.26 (4.0)	31.97 (38.7)	3.26 (4.0)	17.49
	Organic colloids	--	25.16 (40.4)	2.94 (4.7)	33.58 (53.9)	2.60 (4.2)	37.75

of incomplete removal of dissolved inorganic salts. This high ash content obviated the molecular weight and acidity determinations. The humic-substance fraction (ash-free data) has small shifts toward lower carbon, greater oxygen, and greater nitrogen percentages than for humic isolates from the previous two cruises. These elemental shifts indicate the modified procedure added small quantities of more hydrophilic substances to the dissolved humic-substance fraction.

The hydrophilic-substance fraction yields average only 10.3 percent, but it is likely the procedural yields are only 50 percent because of losses during precipitation, centrifugation, washing, drying, and weighing steps in the procedure. Therefore, the actual percentage of this fraction probably is closer to 20 percent or greater. The hydrophilic-substance fraction has lower carbon and hydrogen percentages and greater oxygen and nitrogen percentages than the dissolved humic-substance fraction. The ratio of carbon to oxygen is similar to carbohydrate substances. The high percentage of nitrogen suggests amino and amide substituents in the mixture. Nitrate ion also was not completely separated by the desalting process.

The organic-colloid fraction has a unique elemental signature compared to the dissolved-substance fraction. The high hydrogen percentage is unusual for a degraded fraction; therefore, the colloidal organic material may not be appreciably degraded.

Spectrometric characterizations of the dissolved and organic colloid fractions isolated from the Mississippi River during sampling cruise 3 are shown in figure 8 (^{1}H-NMR) and figure 9 (IR). Dissolved hydrophilic substances are very different from dissolved humic substances, as shown in figure 8 and 9. Dissolved hydrophilic substances are predominantly carbohydrates (peak 3 in spectrum B, fig. 8). In the IR spectrum of the dissolved hydrophilic-substance fraction (spectrum B, fig. 9), the presence of a carboxylic acid peak near 1,720 cm^{-1}, and the shape of the carbohydrate peak near 1,100 cm^{-1} indicate that the hemiacetal linkage in carbohydrates has been partially oxidized to acid carboxyl groups. The small peak at 2.8 ppm in the ^{1}H-NMR spectrum and the peak at 1,650 in the IR spectrum are probable indicators of amide structures in the dissolved hydrophilic-substance fraction.

The dissolved humic-substance fraction is similar to humic-substance fractions isolated from the Mississippi River during the previous two sampling cruises. The alteration of the isolation procedure in which the column capacity factor (k') of recovered solutes was lowered by a factor of 10 caused a small increase in peaks 2 and 3 (fig. 8, spectrum A) that is related to more hydrophilic structures, but the changes in overall character of the spectrum were relatively minor. The character of the fulvic acid, determined by calculating the peak height ratio of peaks 2, 3, 4, and 5 to peak 1 (spectrum A, fig. 8) is more similar to the fulvic acids characterized for sampling cruise 2 than sampling cruise 1. The high water temperatures of cruise 1 may have resulted in exceptionally degraded humic substances with unique ^{1}H-NHR spectral features.

The infrared spectra of organic-colloid fraction indicate a material composed of undegraded carbohydrates (peaks at 3,400 and 1,040 cm^{-1}), hydrocarbons (peak at 2,930 cm^{-1}), and proteins (peaks at 1,650 and 1,550 cm^{-1}) (fig. 9). Chemically, the colloid can be described as a glycolipoprotein. A scanning electron micrograph of the organic-colloid fraction (fig. 10) shows that the material consists predominantly of bacteria cells. Therefore, the interpretation of the spectral data of the colloid as being an undegraded glycolipoprotein is correct, as bacteria are glycolipoproteins.

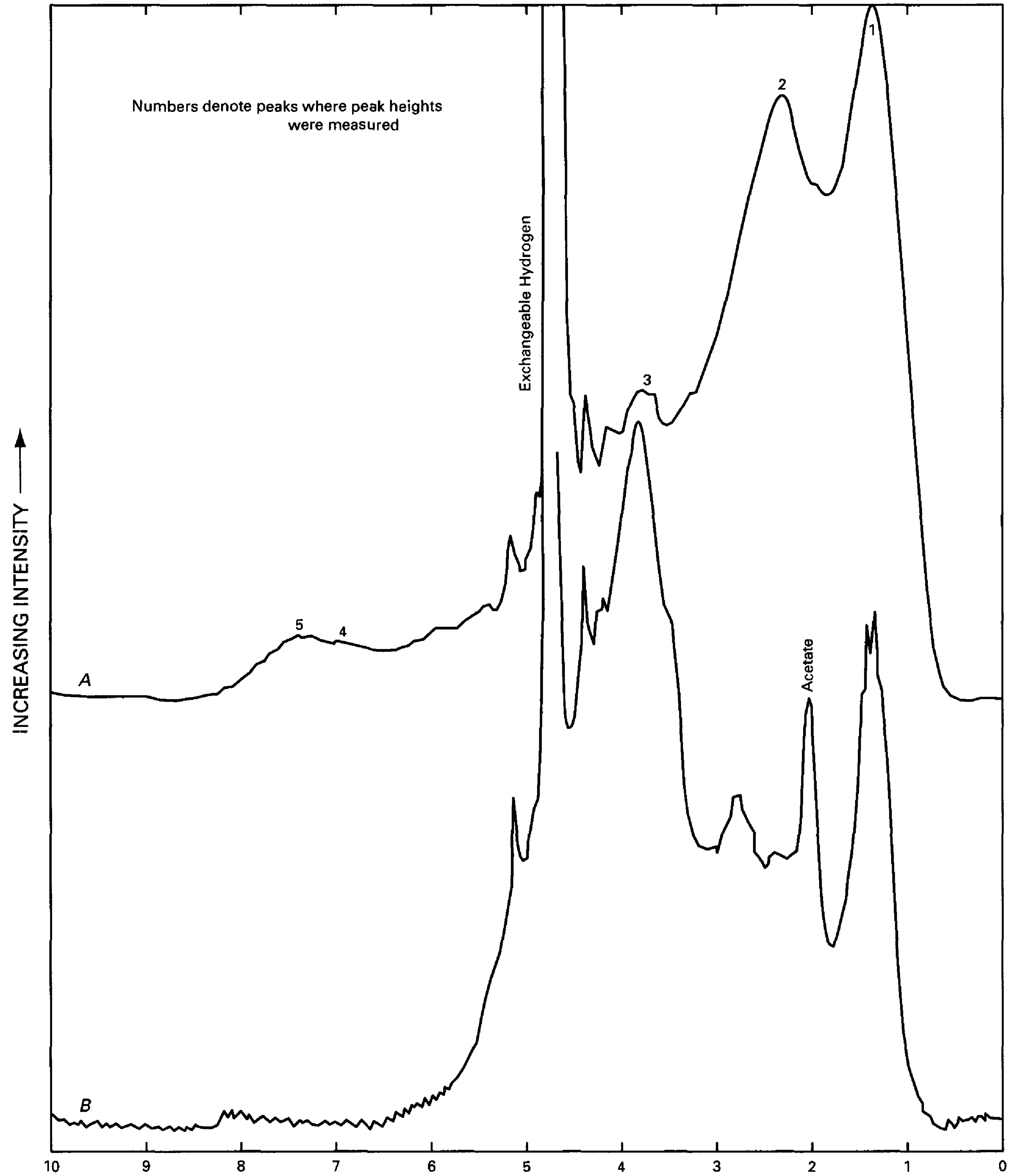

Figure 8.--^{1}H-nuclear magnetic resonance spectra of (A) dissolved humic substances and (B) dissolved hydrophilic substances from the Mississippi River near St. Francisville, La., June 1988.

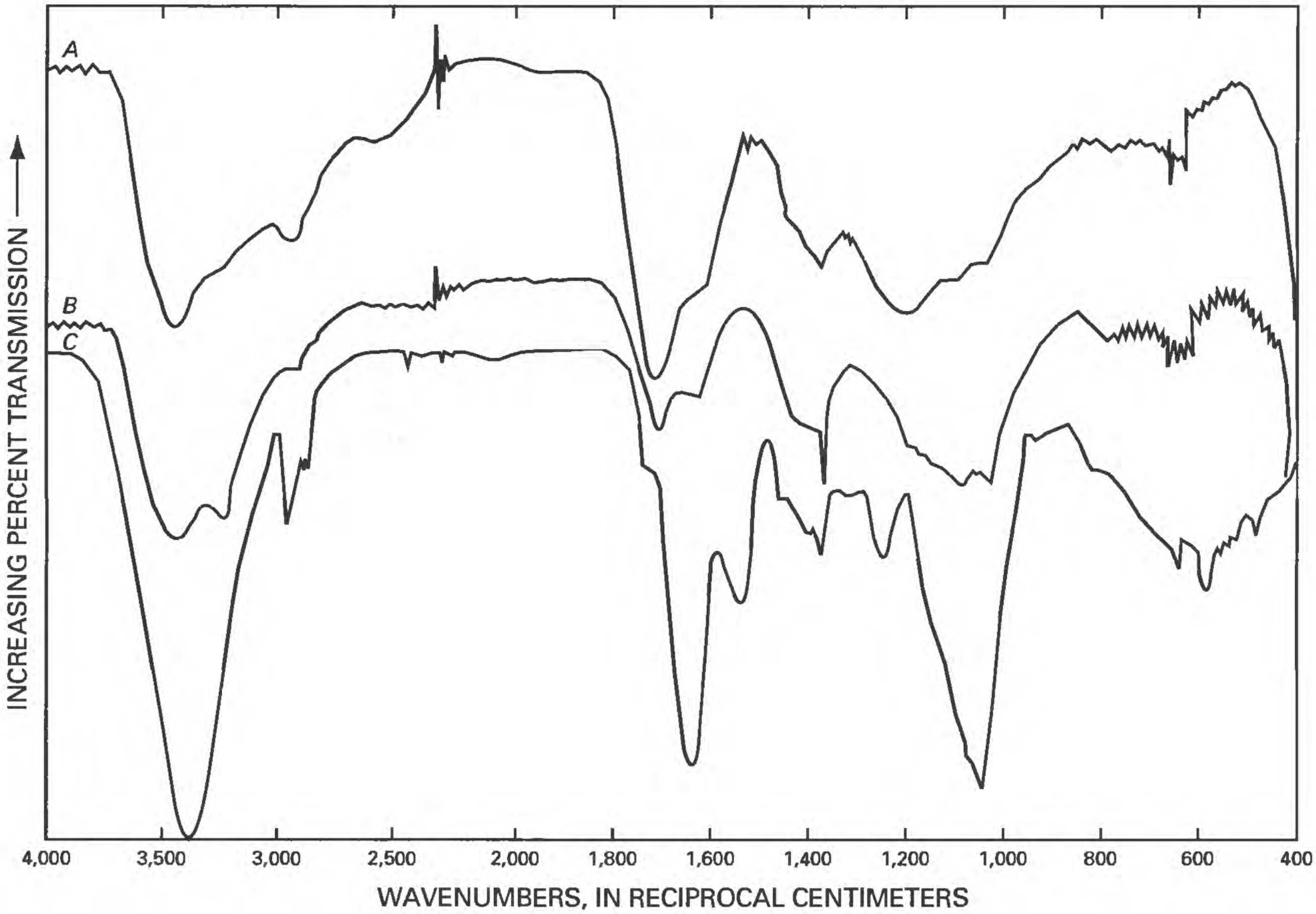

Figure 9.--Infared spectra of (A) dissolved humic substances and (B) dissolved hydrophilic substances from the Mississippi River near St. Francisville, La., and (C) infrared spectrum of organic colloids from the Mississippi River at Fulton, Tenn., June 1988.

The significance of the comparative spectra of figures 8 and 9 and the comparative elemental analyses of table 12 is that these data show there are two distinct components of the dissolved organic-substance phase and a distinct organic-colloid phase that has properties intermediate between dissolved and particulate materials. Each of these components and phases should have unique contaminant interactions that affect contaminant fate and transport.

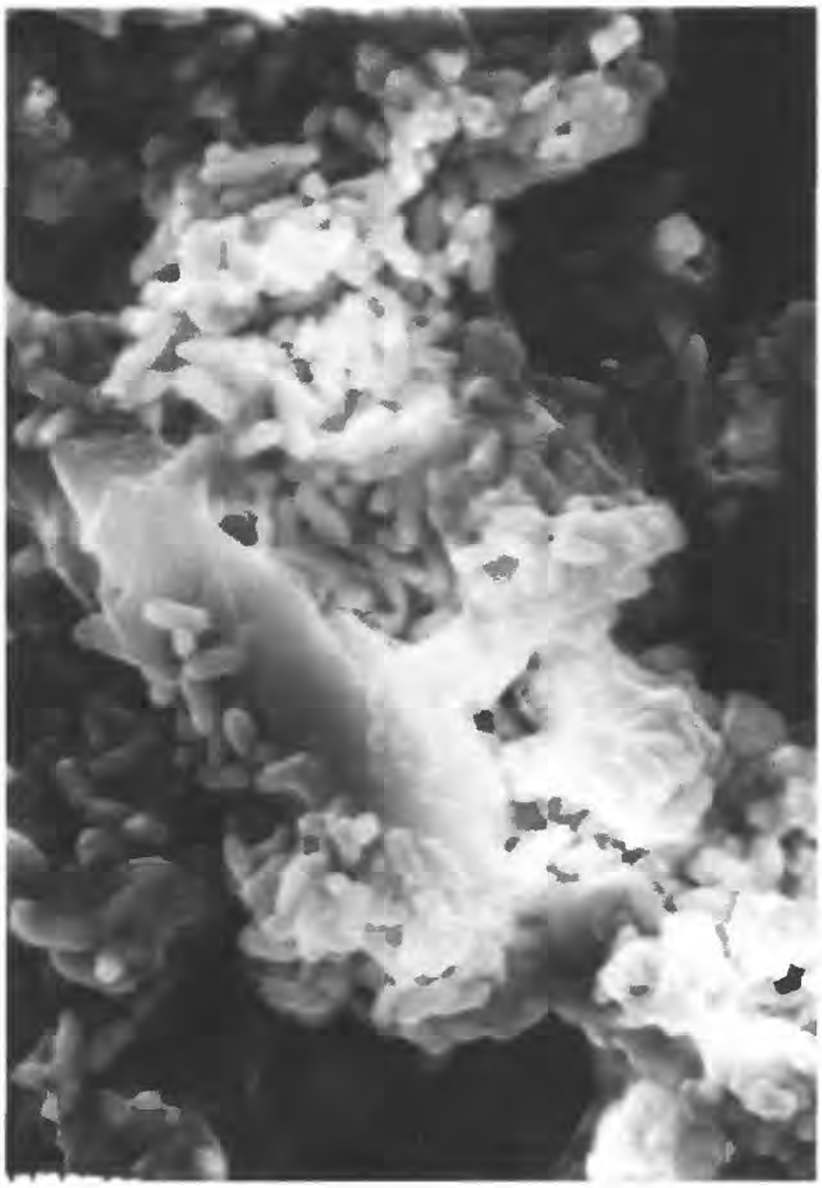

Figure 10.--Scanning electron micrograph of organic colloids isolated from the Mississippi River at Thebes, Ill., May 1988. The micrograph was taken by James F. Ranville (U.S. Geological Survey).

Organic Matter in Suspended-Sediment Fractions

The relative percentages of silt and clay, mineral colloids, and organic colloids in water samples collected during the May–June 1988 sampling cruise are given in table 13. As mentioned previously, use of the centrifuge rather than gravitational settling shifted the relative percentage of silt to 90 percent or greater for most samples. The Yazoo River, in which most of the colloids are disaggregated, contained a lower percentage of silt and clay, and the Mississippi River below Belle Chasse, La., contained a lower percentage of silt and clay because of sedimentation loss of the silt and clay fraction, which occurred during this low-flow period. The mineral-colloid fraction ranged between 1.6 to 9.2 percent of the total suspended-sediment weight, and the organic-colloid fraction ranged from 0.3 to 3.6 percent.

Table 13.--Relative percentages[1] of silt and clay, mineral colloids, and organic colloids in the Mississippi River and some of its tributaries for the May–June 1988 sampling cruise

[ND, not determined]

Sampling site	Percent silt and clay (centrifuged)	Percent mineral colloids (ultrafiltered and centrifuged)	Percent organic colloids (ultrafiltered and dialyzed)
Mississippi River near Winfield, Mo.	91.3	ND	ND
Illinois River below Meredosia, Ill.	97.3	2.1	0.5
Missouri River at Hermann, Mo.	96.4	3.3	.3
Mississippi River at St. Louis, Mo.	95.0	3.5	1.5
Mississippi River at Thebes, Ill.	94.7	3.4	1.9
Ohio River at Olmsted, Ill.	93.0	4.6	2.4
Mississippi River below Hickman, Ky.	96.3	2.9	.8
Mississippi River at Fulton, Tenn.	97.3	1.6	1.1
Mississippi River at Helena, Ark.	95.3	4.0	.7
White River at Mile 11.5, Ark.	91.2	7.7	1.1
Mississippi River above Arkansas City, Ark.	94.3	4.2	1.5
Yazoo River at Mile 10, Miss.	87.2	9.2	3.6
Mississippi River below Vicksburg, Miss.	94.0	4.1	1.9
Old River Outflow Channel near Knox Landing, La.	94.0	4.1	1.9
Mississippi River near St. Francisville, La.	95.9	2.9	1.2
Mississippi River below Belle Chasse, La.	81.6	16.6	1.7

[1] See table 29 for method of determining relative percentages.

The organic-carbon and nitrogen contents of the silt and clay and colloid fractions are given in table 14. The organic-carbon and nitrogen percentages are greater than most of the data for the centrifuged samples in table 8 for sampling cruise 2. Possibly autochthonous production was greater during this late spring cruise than during the previous late fall cruise; this production may be indicated by the greater carbon and nitrogen contents of the silt and clay and colloid fractions. The carbon and nitrogen contents of the mineral colloid fractions in table 14 appear to be especially sensitive to sites where autochthonous production should be significant—such as the Ohio River at Olmsted, Ill.

Table 14.–Organic-carbon and nitrogen contents of silt and clay, mineral-colloid, and organic-colloid fractions of suspended sediment from sampling cruise 3, May–June 1988

[ND, not determined]

Sampling site	Silt and clay fraction		Mineral-colloid fraction		Organic-colloid fraction	
	Carbon (percent)	Nitrogen (percent)	Carbon (percent)	Nitrogen (percent)	Carbon (percent)	Nitrogen (percent)
Mississippi River near Winfield, Mo.	13.43	2.22	23.22	ND	ND	ND
Illinois River below Meredosia, Ill.	8.67	1.31	20.07	2.60	45.51	3.77
Missouri River at Hermann, Mo.	3.52	.50	10.76	1.05	ND	ND
Mississippi River at St. Louis, Mo.	5.21	.64	15.04	1.59	ND	ND
Mississippi River at Thebes, Ill.	3.82	.57	14.47	1.87	ND	ND
Ohio River at Olmsted, Ill.	3.67	.54	19.01	2.36	ND	ND
Mississippi River below Hickman, Ky.	3.28	.47	14.52	1.77	40.64	3.66
Mississippi River at Fulton, Tenn.	3.25	.49	12.71	1.59	ND	ND
Mississippi River at Helena, Ark.	3.71	.54	12.20	1.47	34.09	4.11
White River at Mile 11.5, Ark.	3.13	.53	8.61	1.15	ND	ND
Mississippi River above Arkansas City, Ark.	3.45	.49	9.63	1.28	ND	ND
Yazoo River at Mile 10, Miss.	3.29	.53	12.48	1.16	ND	ND
Mississippi River below Vicksburg, Miss.	3.80	.53	11.02	1.49	25.16	1.87
Old River Outflow Channel near Knox Landing, La.	2.93	.40	10.49	.96	ND	ND
Mississippi River near St. Francisville, La.	1.97	.25	7.52	.89	ND	ND
Mississippi River below Belle Chasse, La.	4.48	.56	14.01	1.75	ND	ND

The low carbon to nitrogen ratios of the silt and clay fractions (7.2 to 9.5) was noted to be only slightly larger than the Redfield C:N ratio for phytoplankton, which may indicate a large percentage of autochthonous carbon in the silt and clay fraction (Leenheer, 1991). The amide II band at 1,550 cm^{-1} in infrared spectra of silt and clay, mineral-colloid, and organic-colloid fractions (Leenheer, 1991) is direct evidence that suspended sediments from sampling cruise 3 contain large amounts of proteinaceous matter.

The organic-carbon and nitrogen transport of the silt and clay and colloid fractions are given in table 15. The bulk of the organic-carbon and nitrogen transport occurs with the silt and clay because the bulk (about 95 percent) of the sediment is in the silt and clay fraction. The carbon transport in the colloid fractions generally differ by less than a factor of 2. A major portion of the silt and clay carbon and nitrogen transport is lost by sedimentation to the riverbed between St. Francisville and Belle Chasse, La. There also is a greater proportion of the carbon and nitrogen transport in the colloid fractions at the Belle Chasse site.

Table 15.--Organic-carbon and nitrogen transport on silt and clay and colloid fractions of suspended sediment from sampling cruise 3, May–June 1988

[Water-discharge and suspended-sediment-concentration data used to compute transport are reported by Moody and Meade (1992); ND, not determined]

Sampling site	Organic-carbon transport on silt and clay (metric tons per day)	Nitrogen transport on silt and clay (metric tons per day)	Organic-carbon transport on mineral colloids (metric tons per day)	Nitrogen transport on mineral colloids (metric tons per day)	Organic-carbon transport on organic colloids (metric tons per day)	Nitrogen transport on organic colloids (metric tons per day)
Mississippi River near Winfield, Mo.	613	101	ND	ND	ND	ND
Illinois River below Meredosia, Ill.	135	20	7.0	0.9	3.6	.3
Missouri River at Hermann, Mo.	339	55	36	3.5	[1]12	[1]1.2
Mississippi River at St. Louis, Mo.	891	109	95	10	[1]76	[1]7.6
Mississippi River at Thebes, Ill.	832	124	113	15	[1]175	[1]1.8
Ohio River at Olmsted, Ill.	286	42	73	9.1	[1]81	[1]8.1
Mississippi River below Hickman, Ky.	1,074	154	143	17	110	10
Mississippi River at Fulton, Tenn.	1,297	195	83	10	[1]180	[1]18
Mississippi River at Helena, Ark.	1,626	237	224	27	110	13
White River at Mile 11.5, Ark.	100	17	23	3.1	[1]15	[1]1.5
Mississippi River above Arkansas City, Ark.	1,936	275	241	32	[1]357	[1]36
Yazoo River at Mile 10, Miss.	13	2.0	5.1	.5	[1]6.3	[1].6
Mississippi River below Vicksburg, Miss.	1,893	264	239	33	253	19
Old River Outflow Channel near Knox Landing, La.	375	51	58	5.4	[1]103	[1]10
Mississippi River near St. Francisville, La.	1,965	249	227	27	[1]499	[1]50
Mississippi River below Belle Chasse, La.	310	39	197	25	[1]58	[1]5.8

[1] An estimate of 40 percent was made for the organic-carbon content and 4 percent for the nitrogen content.

Concentrations of colloidal organic carbon determined by two independent methods for sampling cruise 3 are given in table 16. The difference determination of the left column is erratic because the variance of the organic-carbon determination (+0.1 mg/L) is large relative to the magnitude of the data values. There is not a large degree of variability for colloid organic-carbon concentrations at various sampling sites.

Table 16.–Concentrations of colloidal organic carbon for sampling cruise 3, May–June 1988

[ND, not determined]

Sampling site	Colloidal organic carbon determined by total organic carbon of centrifuge effluent minus dissolved organic carbon of ultrafilter permeate (milligrams per liter)	Colloidal organic carbon determined from carbon analysis of isolated colloid fractions (milligrams per liter)
Mississippi River near Winfield, Mo.	1.0	ND
Illinois River below Meredosia, Ill.	1.0	0.4
Missouri River at Hermann, Mo.	.2	.4
Mississippi River St. Louis, Mo.	.4	.7
Mississippi River at Thebes, Ill.	.5	.9
Ohio River at Olmsted, Ill.	.5	.6
Mississippi River below Hickman, Ky.	ND	.4
Mississippi River at Fulton, Tenn.	.3	.4
Mississippi River at Helena, Ark.	.5	.5
White River at Mile 11.5, Ark.	.2	1.0
Mississippi River above Arkansas City, Ark.	.4	.9
Yazoo River at Mile 10, Miss.	.4	1.9
Mississippi River below Vicksburg, Miss.	0.0	.7
Old River Outflow Channel near Knox Landing, La.	0.0	.8
Mississippi River near St. Francisville, La.	0.0	1.5
Mississippi River below Belle Chasse, La.	.6	.5

SAMPLING CRUISE 4, MARCH–APRIL 1989

The sampling of cruise 4 began at Hardin, Illinois, on March 9, 1989, on the Illinois River and ended on the Mississippi River below Belle Chasse, Louisiana, on April 1, 1989. The two sampling site changes from cruise 3 is that the Illinois River was sampled at Hardin, Illinois, instead of below Meredosia, Illinois, and the Arkansas River was sampled at Pendleton, Arkansas.

Objectives and Approach

The major objective of the fourth sampling cruise was to intercept high-discharge conditions during the early spring runoff from the Ohio River and determine what effects high discharge had upon the nature and properties of natural organic substances in various phases. For the first time in four cruises, high-discharge conditions were observed in the Ohio River and sampling sites downstream.

A secondary objective was to investigate particle-size distributions and chemical fractionations that were occurring between the continuous-flow centrifugation and tangential-flow ultrafiltration steps. The approach was to process a separate set of water samples through the centrifuge and ultrafilter during the upriver part of the sampling cruise. Samples were collected from the Mississippi River at Memphis, Tenn., the Ohio River at Cairo, Ill., the Illinois River at Grafton, Ill., and the Missouri River at Hermann, Mo. Results of this study were published in a report by Rees and others (1991).

Dissolved Organic Matter

DOC concentrations and transport at the various sampling sites are presented in table 17. The high discharge (20,410 m^3/s) dominated the DOC transport, although the DOC concentration (of the Ohio River at Olmsted) was only one-half the DOC concentration of the Mississippi River just upstream from the confluence at Thebes, Ill. The low DOC concentration of the Ohio River is likely due to the fact that the river stage was falling during sampling. Peak of the DOC, which generally occurs during rising stage, had passed and DOC on the falling limb of the hydrograph was diluted by the large volume of water in the system. The organic-carbon transport downstream from the Ohio River confluence and downstream from the White and Arkansas River confluences are additive, which means at this particular sampling, DOC is a conservative constituent in the system. The cool waters of early spring (3–15°C) likely retarded the rate of instream biodegradation of DOC.

Table 17.–Dissolved organic-carbon concentrations and transport for sampling cruise 4, March–April 1989

[Transport was computed using water-discharge data reported by Moody and Meade (1993); ND, not detected]

Sampling site	Water discharge (cubic meters per second)	Dissolved organic-carbon concentration (milligrams per liter)	Load (metric tons per day)
Mississippi River near Winfield, Ill.	850	ND	ND
Illinois River at Hardin, Ill.	410	ND	ND
Missouri River at Hermann, Mo.	1,480	3.4	435
Mississippi River at St. Louis, Mo.	3,940	4.7	1,600
Mississippi River at Thebes, Ill.	4,890	4.2	1,774
Ohio River at Olmsted, Ill.	20,400	2.1	3,703
Mississippi River below Hickman, Ky.	24,700	2.8	5,970
Mississippi River below Fulton, Tenn.	24,800	2.8	6,002
Mississippi River at Helena, Ark.	25,900	2.7	6,042
White River at Mile 11.5, Ark.	1,500	2.6	337
Arkansas River at Pendleton, Ark.	1,900	3.5	574
Mississippi River above Arkansas City, Ark.	26,800	3.0	6,957
Yazoo River below Steele Bayou, Miss.	1,500	4.9	635
Mississippi River below Vicksburg, Miss.	26,600	2.9	6,652
Old River Outflow Channel near Knox Landing, Miss.	6,160	2.9	1,541
Mississippi River near St. Francisville, La.	23,100	2.9	5,793
Mississippi River below Belle Chasse, La.	22,500	3.0	5,827

The effect of allochthonous inputs upon the constitution of DOC in the Mississippi River is illustrated by the ^{1}H-NMR spectra of figure 11. The spectrum of the Mississippi River at Thebes, Ill. (spectrum A, fig. 11), is typical for humic-substance spectra from the Mississippi River at low flow (figs. 2, 7, and 8). However, dissolved humic substances isolated from the Ohio River (spectrum B, fig. 11) have greater spectral peak-height ratios of peaks 3 and 4 to peak 1 than were observed previously. These spectra ratio increases represent increases in the carbohydrate (peak 3) and phenol (peak 4) components of the dissolved humic-substance mixture. The source of these carbohydrate and phenol components arises from cellulose and lignin constituents of degraded plant materials washed into the river by surface runoff. The ^{1}H-NMR spectrum of dissolved humic substances isolated from the Mississippi River below Hickman, Ky. (spectrum C, fig. 11), is similar to spectrum B (the Ohio River sample), which indicates the humic-substance load is dominated by the Ohio River input as data from table 17 indicate.

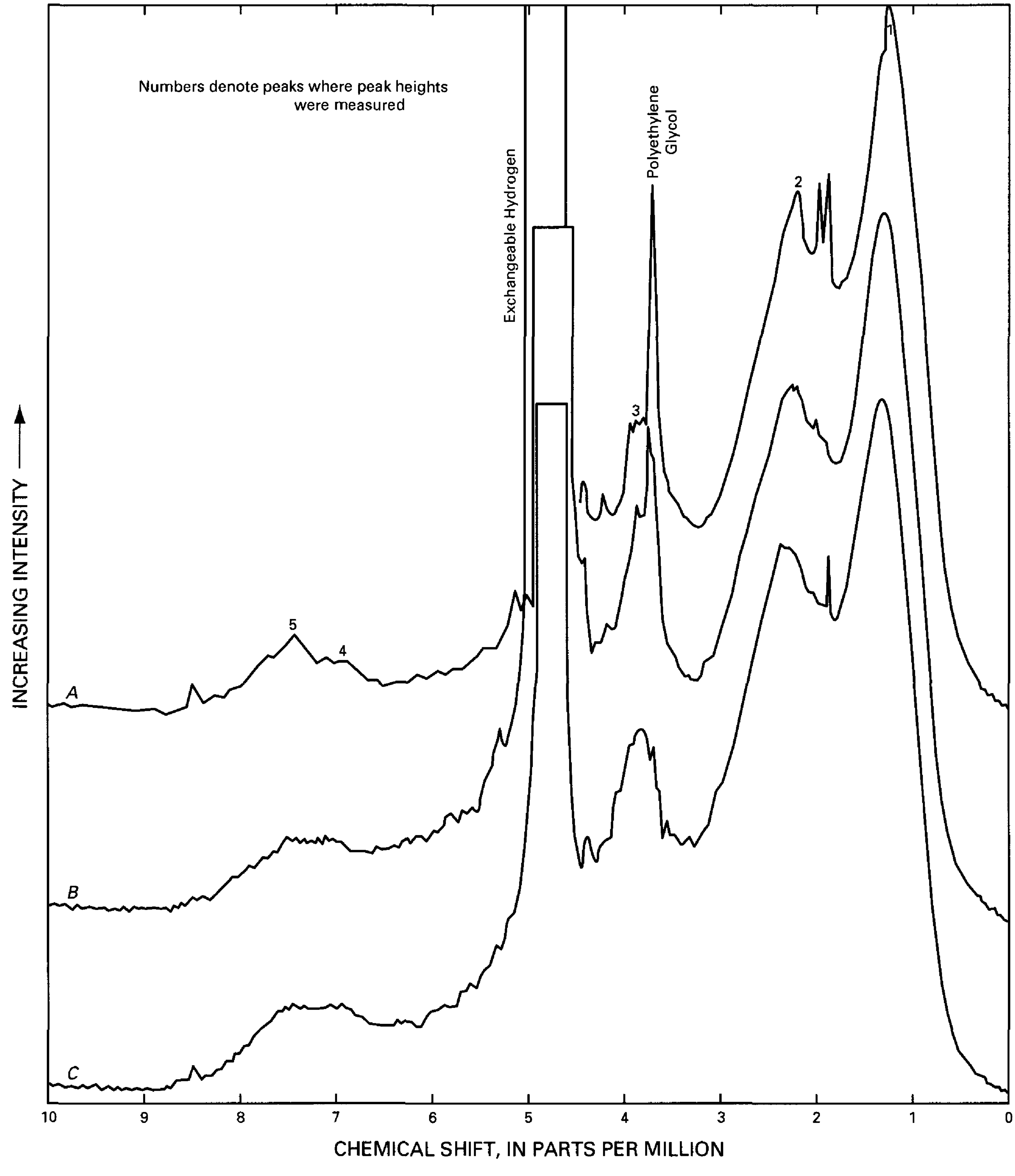

Figure 11.—^{1}H-nuclear magnetic resonance spectra of dissolved humic substances from the: (A) Mississippi River at Thebes, Ill., (B) Ohio River at Olmsted, Ill., and (C) Mississippi River below Hickman, Ky., sampled March 1989.

Additional allochthonous inputs of dissolved humic substances occurred downstream from the Ohio River confluence on this fourth sampling cruise. High discharges from the White, Arkansas, and Yazoo Rivers added additional humic substances derived from allochthonous sources. The ^{1}H-NMR spectra of dissolved humic substances isolated from the White River, the Yazoo River, and the Mississippi River below Belle Chasse, La., are shown in figure 12. The greatest spectral ratios of peaks 2, 3, 4, and 5 to peak 1 for dissolved humic substances characterized from the Mississippi River and its tributaries were observed for the White River and Yazoo River samples. The sample from the Mississippi River at Belle Chasse, La., (spectrum C, fig. 12) had greater spectral ratios of peaks 2, 3, 4, and 5 to peak 1 than the sample from the Mississippi River below Hickman, Ky. (spectrum C, fig. 11). These increases in spectral ratios clearly indicated increasing inputs of humic substances from allochthonous sources as sampling proceeded downstream in the Mississippi River.

Dissolved hydrophilic organic substances were also isolated and characterized during sampling cruise 4. No significant differences were observed for either the proportion (yield) or nature (^{1}H-NMR spectra) of these dissolved hydrophilic substances isolated during sampling cruise 4 from those isolated and characterized during sampling cruise 3.

Organic Matter in Suspended-Sediment Fractions

The relative percentages of silt and clay, mineral colloids, and organic colloids in the Mississippi River for the March–April 1989 sampling cruise are given in table 18. Because of the coarse silt and clay fraction lost from the centrifuge during the shutdown procedure, suspended-sediment weights for the silt and clay fraction from the pumped composite sample rather than the depth-integrated composite sample were used for the calculations in table 18. Because of the smaller volume processed, the depth-integrated composite sample had a larger loss of the coarse silt fraction than the pumped composite sample, and the silt and clay percentages were 1–2 percent lower for the depth-integrated composite fraction.

The relative size distribution of silt and clay and colloid fractions was similar to data from sampling cruise 3 (table 13), with two exceptions: (1) The organic-colloid percentage from the Mississippi River near Winfield, Ill., was exceptionally high compared to other sites. These data indicate a large bacteria population in the river at this point. (2) The mineral-colloid percentages were high for the White and Yazoo Rivers. High discharge and low specific conductance (White River, 150 µS/cm at 25°C; Yazoo River, 80 µS/cm at 25°C) may have disaggregated clay-mineral aggregates that normally isolate in the silt and clay fraction (Rees and others, 1991), so that they are recovered in the mineral-colloid fraction. Most silt and clay in Mississippi River samples was found to be aggregated colloidal material (Rees and others, 1991).

Organic-carbon, nitrogen, and fluorine contents of the silt and clay and mineral-colloid fractions from the March–April 1989 sampling cruise are shown in table 19. Fluorine determinations were run on the silt and clay fraction because infrared analyses of this fraction suggested the presence of Teflon in the silt and clay fraction; the Teflon contamination may have occurred because of wear of a Teflon bushing and nozzle in the continuous-flow centrifuge. Fluorine was detected, but levels were low enough so that effects on carbon contents were minor, as carbon is only 31 percent of the fluorine content in Teflon.

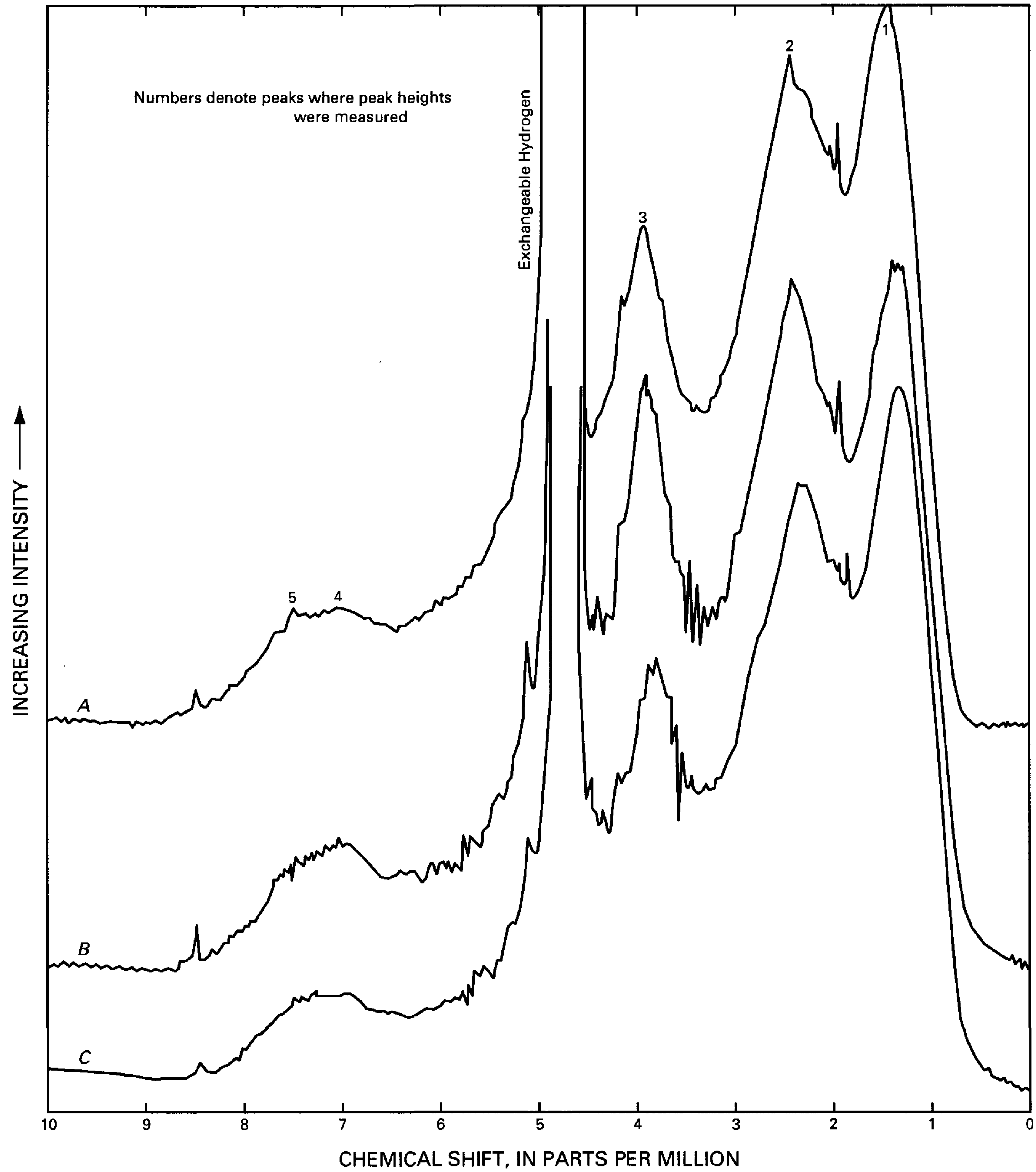

Figure 12.—^{1}H-nuclear magnetic resonance spectra of dissolved humic substances from the: (A) White River, Mile 11.5, Ark., (B) Yazoo River below Steele Bayou, Miss., and (C) Mississippi River below Belle Chasse, La., sampled March–April 1989.

Table 18.–Relative percentages[1] of silt and clay, mineral colloids, and organic colloids in the Mississippi River and some of its tributaries for the March–April 1988 sampling cruise

Sampling site	Percent silt and clay (centrifuged)	Percent mineral colloids (ultrafiltered and centrifuged)	Percent organic colloids (ultrafiltered and dialyzed)
Mississippi River near Winfield, Ill.	82.6	4.1	12.7
Illinois River at Hardin, Ill.	95.5	2.7	1.8
Missouri River at Hermann, Mo.	91.1	8.0	0.9
Mississippi River at St. Louis, Mo.	93.0	5.4	1.6
Mississippi River at Thebes, Ill.	89.1	9.5	1.4
Ohio River at Olmsted, Ill.	91.8	7.7	0.5
Mississippi River below Hickman, Ky.	91.1	9.5	0.4
Mississippi River below Fulton, Tenn.	90.2	9.0	0.8
Mississippi River at Helena, Ark.	89.4	10.1	0.5
White River at Mile 11.5, Ark.	51.1	45.4	3.5
Yazoo River below Steele Bayou, Miss.	68.1	27.0	4.9
Mississippi River below Vicksburg, Miss.	86.0	12.4	1.6
Old River Outflow Channel near Knox Landing, La.	88.2	11.2	0.6
Mississippi River near St. Francisville, La.	87.1	12.4	0.5
Mississippi River below Belle Chasse, La.	89.5	9.8	0.7

[1] See table 29 for method of determining relative percentages.

Table 19.—Organic-carbon content, nitrogen content, and atomic C:N ratio of silt and clay and mineral-colloid fractions of suspended sediment from sampling cruise 4, March–April 1989.

[Fluorine content of silt and clay fraction is also included; ND, not determined]

Sampling site	Silt and clay fraction				Mineral-colloid fraction		
	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio	Fluorine (percent)	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio
Mississippi River near Winfield, Mo.	15.93	2.59	7.2	0.36	28.96	4.74	7.1
Illinois River at Hardin, Ill.	3.32	.29	13.4	.15	8.83	1.05	9.8
Missouri River at Hermann, Mo.	2.50	.24	12.4	.87	7.15	.85	9.8
Mississippi River at St. Louis, Mo.	5.01	.74	7.8	.10	10.67	1.67	7.5
Mississippi River at Thebes, Ill.	4.09	.51	9.4	.08	7.35	1.10	7.8
Ohio River at Olmsted, Ill.	2.35	.19	14.7	.08	3.39	.48	8.2
Mississippi River below Hickman, Ky.	2.56	.26	11.6	.10	4.76	.55	10.1
Mississippi River below Fulton, Tenn.	2.44	.25	11.3	.10	4.27	.53	9.4
Mississippi River at Helena, Ark.	2.35	.23	12.1	.17	4.51	.60	8.8
White River at Mile 11.5, Ark.	1.95	.18	12.3	.28	3.03	.44	8.0
Arkansas River at Pendleton, Ark.	3.08	.31	11.8	.42	ND	ND	ND
Mississippi River above Arkansas City, Ark.	2.24	.23	11.6	.07	ND	ND	ND
Yazoo River below Steele Bayou, Miss.	1.42	.19	8.8	.13	2.32	.40	6.8
Mississippi River below Vicksburg, Miss.	2.23	.22	11.6	.06	4.14	.52	9.3
Old River Outflow Channel near Knox Landing, La.	1.76	.18	11.5	.30	3.22	.48	7.8
Mississippi River near St. Francisville, La.	2.18	.19	13.8	.12	3.84	.54	8.3
Mississippi River below Belle Chasse, La.	1.85	.18	11.8	.52	3.62	.51	8.28

The contrast between allochthonous inputs and autochthonous inputs to carbon and nitrogen in the silt and clay and colloid fractions is especially apparent among the different sampling sites. Sites where autochthonous inputs dominate (Mississippi River near Winfield, at St. Louis, and at Thebes) are characterized by high contents of carbon and nitrogen on the suspended-sediment fractions and by low C:N ratios (table 19). The tributaries and other sites have low carbon and nitrogen contents and high C:N ratios except for the low C:N ratio of the Yazoo River sample. The high discharges on the Ohio, White, Arkansas, and Yazoo Rivers resulted in the organic fraction of suspended sediment in the Lower Mississippi River being derived from allochthonous inputs. In contrast, autochthonous inputs from the Upper Mississippi River dominated the suspended-sediment characteristics downstream to the confluence with the Ohio River.

Organic-carbon and nitrogen transport of the various suspended-sediment fractions for sampling cruise 4 are presented in table 20. The transport is dominated by sediment inputs from the Ohio River. The organic fraction that appears to be the most conservative with discharge is the mineral-colloid fraction. Even inputs of tributaries whose discharge is small compared to the discharge of the Mississippi River, such as the White and Yazoo Rivers, can be detected by increases in the mineral-colloid fraction. The Upper Mississippi River has the greatest relative amount of transport in the organic-colloid fraction, whereas the Lower Mississippi and Ohio Rivers have most of the transport in the silt and clay and mineral-colloid fractions.

The colloid transport is converted into organic-carbon concentrations in table 21. Colloidal organic-carbon concentrations were slightly greater for the early spring period of sampling cruise 4 than for the late spring period of sampling cruise 3 (table 16). The greater total suspended-sediment concentration during the fourth cruise also likely increased the colloidal organic-carbon concentrations. The difference method (left column, table 21) appears to underdetermine the colloidal organic-carbon concentration compared to concentrations determined from carbon analysis of the isolated colloids (right column, table 21), although there is a high degree of analytical variance in the difference method. Colloidal organics may not be efficiently determined by the persulfate oxidation method in freshwater systems, as was found previously for marine systems (Sugimura and Suzuki, 1988).

Table 20.—Organic-carbon and nitrogen transport of silt and clay and colloid fractions of suspended sediment from sampling cruise 4, March–April 1989

[Water-discharge and suspended-sediment concentration data used to compute transport are reported by Moody and Meade (1993)]

Sampling site	Silt and clay transport		Mineral-colloid transport		Organic-colloid transport[1]	
	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)
Mississippi River near Winfield, Mo.	222	36	20	3.3	86	8.6
Illinois River at Hardin, Ill.	111	9.7	8.4	1.0	25	2.5
Missouri River at Hermann, Mo.	213	20	53	6.3	34	3.4
Mississippi River at St. Louis, Mo.	1,079	110	133	21	148	15
Mississippi River at Thebes, Ill.	1,617	202	310	46	248	25
Ohio River at Olmsted, Ill.	5,782	468	700	99	536	54
Mississippi River below Hickman, Ky.	6,614	672	1,282	148	453	45
Mississippi River below Fulton, Tenn.	6,463	609	1,129	140	940	94
Mississippi River at Helena, Ark.	6,253	612	1,356	180	595	60
White River at Mile 11.5, Ark.	56	5.1	77	11	78	7.8
Yazoo River below Steele Bayou, Miss.	187	25	121	21	378	38
Mississippi River below Vicksburg, Miss.	5,367	529	1,437	180	1,791	180
Old River Outflow Channel near Knox Landing, La.	1,322	135	307	51	204	20
Mississippi River near St. Francisville, La.	4,400	383	1,103	155	463	46
Mississippi River below Belle Chasse, La.	4,695	457	1,006	141	794	79

[1] Organic-carbon and nitrogen transport calculations for the organic-colloid fraction were made by estimating 40 percent organic carbon and 4 percent for organic nitrogen.

Table 21.–Concentrations of colloidal organic carbon for sampling cruise 4, March–April 1989

[ND, not determined]

Sampling site	Colloidal organic carbon determined by total organic carbon of centrifuge effluent minus dissolved organic carbon of ultrafilter permeate (milligrams per liter)	Colloidal organic carbon determined from carbon analyses of isolated colloid fractions (milligrams per liter)
Mississippi River near Winfield, Mo.	ND	3.0
Illinois River at Hardin, Ill.	ND	.9
Missouri River at Hermann, Mo.	0.2	.7
Mississippi River at St. Louis, Mo.	.2	.7
Mississippi River at Thebes, Ill.	.6	1.3
Ohio River at Olmsted, Ill.	.5	.7
Mississippi River below Hickman, Ky.	.2	.8
Mississippi River below Fulton, Tenn.	.2	.9
Mississippi River at Helena, Ark.	.4	.9
White River at Mile 11.5, Ark.	.6	1.2
Arkansas River at Pendleton, Ark.	.4	ND
Mississippi River above Arkansas City, Ark.	.3	ND
Yazoo River below Steele Bayou, Miss.	1.5	3.8
Mississippi River below Vicksburg, Miss.	.4	1.4
Old River Outflow Channel near Knox Landing, La.	.3	1.0
Mississippi River near St. Francisville, La.	.4	.8
Mississippi River below Belle Chasse, La.	.2	.9

SAMPLING CRUISE 5, JUNE 1989

The sampling of cruise 5 began on the Illinois River at Hardin, Illinois, on June 4, 1989, and ended on the Mississippi River below Belle Chasse, Louisiana, on June 28, 1989. No significant changes in sampling sites were made from cruise 4.

Objectives and Approach

An objective in the scheduling of this cruise was to determine herbicide transport in the lower Mississippi River after the spring application of herbicides. In this objective, only partial success was achieved because only the lower part of the river system was affected by rising stage resulting from runoff from agricultural lands.

Another objective was to finish the characterization work on dissolved organic substances. Sufficient data on dissolved organic substances were collected throughout the five cruises to predict its properties based upon the season and flow regimes of the rivers at various sampling sites. A continuing objective during each cruise was to quantify the carbon and nitrogen transport in the various phases at the various sites. This work was repeated during sampling cruise 5.

Initial work was begun on development of methodology for spectrometric characterization of organic substances in suspended sediments and bottom sediments. Bottom sediments were collected with a pipe dredge in relatively quiescent sections of the river where fine material accumulated. These bottom samples were subjected to a series of chemical and physical separation procedures to separate the organic material for spectrometric characterization. Suspended-silt and -clay samples also were collected from the Illinois River at Hardin, Ill., the Missouri River at Hermann, Mo., and the Mississippi River at Helena, Ark., for the initial evaluations of organic extraction methodologies for sediment characterization.

Dissolved Organic Matter

DOC concentrations and transport at the various sampling points for the June 1989 sampling cruise are presented in table 22. The DOC concentrations and transport inputs to the Lower Mississippi River system are unique in that a greater proportion of the DOC transport, as measured at Vicksburg, comes from both the Upper Mississippi River, as measured near Winfield, Mo., and from the Arkansas River. Each of these rivers contributes about 18 percent of the DOC transport, whereas the transport contributions were significantly less on the previous sampling cruises. The DOC concentration measured in the Upper Mississippi River near Winfield, Mo., was the highest measured for any sample collected up to this point. These significant DOC concentrations may be related to the fact that samples were collected as the river stage was rising. Although the stage rise was fairly small, elevated DOC concentration is related to initial increases in stream discharge (McDowell and Likens, 1988). The DOC transport is about additive at the Upper Mississippi River-Illinois River-Missouri River confluence, at the Upper Mississippi River-Ohio River confluence, and at the Arkansas River-Lower Mississippi River confluence.

Table 22.–Dissolved organic-carbon concentrations and transport for sampling cruise 5, June 1989

[Transport was computed using water-discharge data reported by Moody and Meade (1993)]

Sampling site	Water discharge (cubic meters per second)	Dissolved organic-carbon concentration (milligrams per liter)	Transport (metric tons per day)
Mississippi River near Winfield, Mo.	2,320	6.4	1,263
Illinois River at Hardin, Ill.	780	4.5	303
Missouri River at Hermann, Mo.	1,760	3.7	562
Mississippi River at St. Louis, Mo.	4,760	5.0	2,056
Mississippi River at Thebes, Ill.	5,230	5.1	2,300
Ohio River at Olmsted, Ill.	8,760	3.2	2,422
Mississippi River below Hickman, Ky.	14,100	3.7	4,504
Mississippi River at Fulton, Tenn.	15,300	3.8	5,023
Mississippi River at Helena, Ark.	16,900	3.8	5,562
Arkansas River at Pendleton, Ark.	3,600	4.3	1,334
Mississippi River above Arkansas City, Ark.	23,300	3.5	7,058
Yazoo River below Steele Bayou, Miss.	1,070	4.7	435
Mississippi River below Vicksburg, Miss.	24,800	3.3	7,077
Old River Outflow Channel near Knox Landing, La.	4,890	3.3	1,278
Mississippi River near St. Francisville, La.	19,000	3.2	5,264
Mississippi River below Belle Chasse, La.	20,100	3.4	5,893

The nature of humic substances in the Mississippi River and its tributaries is similar to what was observed on previous cruises. At the beginning of the cruise where river stages were low to average, dissolved humic substances were typified by the ^{1}H-NMR spectrum of figure 13, spectrum A. In this spectrum, the ratio of peak 5 to peak 1 indicated a predominantly allochthonous source, but the small ratio of peak 4 to peak 5 indicated that phenolic substances had been removed through degradation or sorption onto sediments. As the cruise proceeded downriver, inputs of fresh allochthonous humic substances from tributaries at high river stage, such as the Arkansas River (fig. 13, spectrum B), increased the proportion of fresh humic substances until the Mississippi River near Belle Chasse, La., contained predominantly humic substances of minimal alteration (fig. 13, spectrum C).

The process of how dissolved humic substances are altered in the Mississippi River system was indicated by examining the hydrophilic-substance fraction of these samples presented in figure 13. The results are shown in figure 14. Spectrum A, the Illinois River at Hardin, Ill., is significantly different from the hydrophilic fractions of the Arkansas River (spectrum B) and the Mississippi River below Belle Chasse, La., (spectrum C). The acid metabolites of degraded humic substances were captured in the hydrophilic fraction of the Illinois River sample. Degradation of carbohydrates to carbohydrate acids is shown by the additional peak in figure 14 spectrum A at 4.2 ppm, and degradation of aromatic rings is shown by shift of aromatic protons from 7.4 ppm (spectrum A, fig. 13) to 7.7–8.0 ppm (spectrum A, fig. 14). This aromatic proton shift results from the buildup of carboxyl groups on aromatic rings during oxidation.

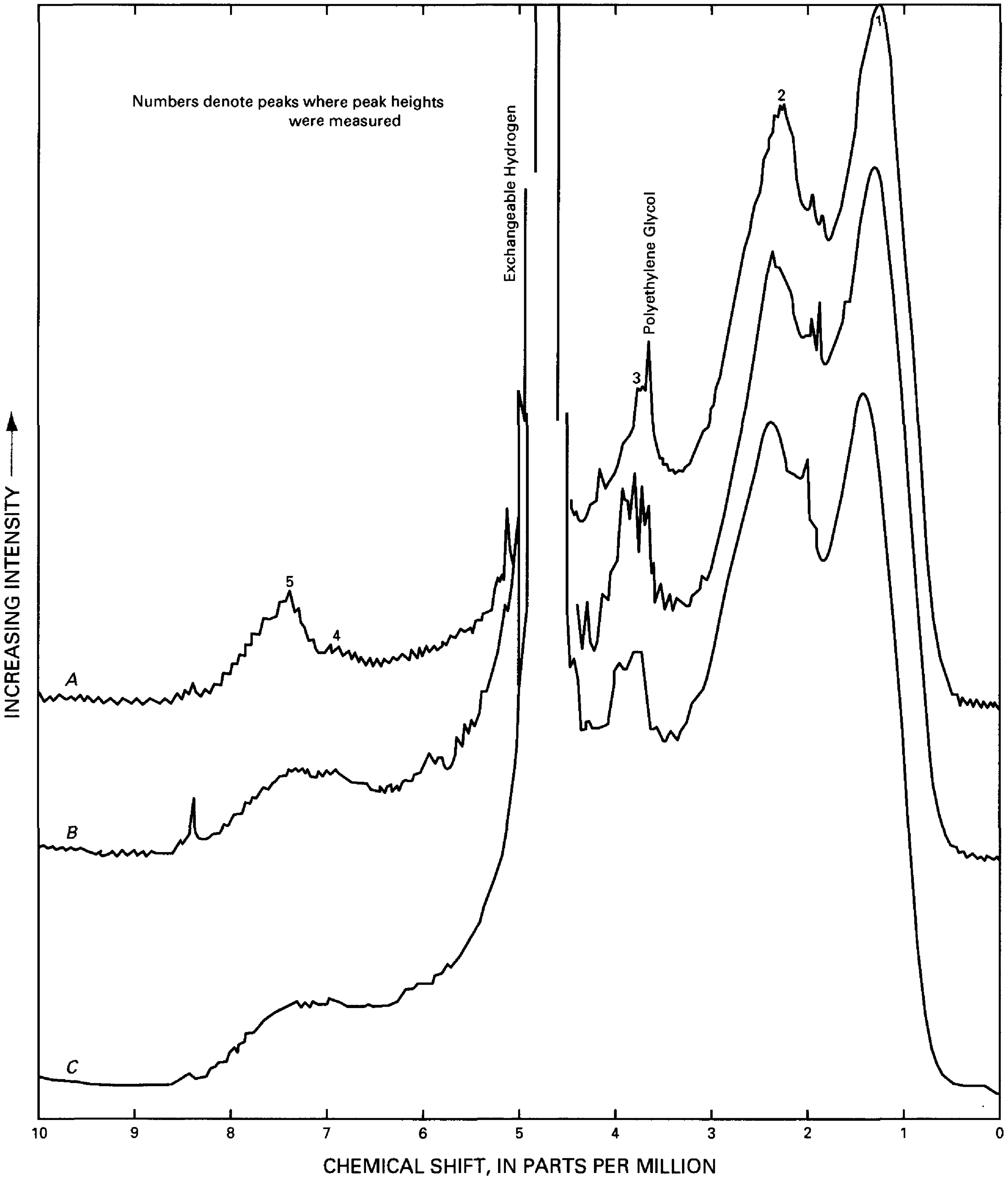

Figure 13.—^{1}H-nuclear magnetic resonance spectra of dissolved humic substances from the: (A) Illinois River at Hardin, Ill., (B) Arkansas River at Pendleton, Ark., and (C) Mississippi River below Belle Chasse, La., sampled June 1989.

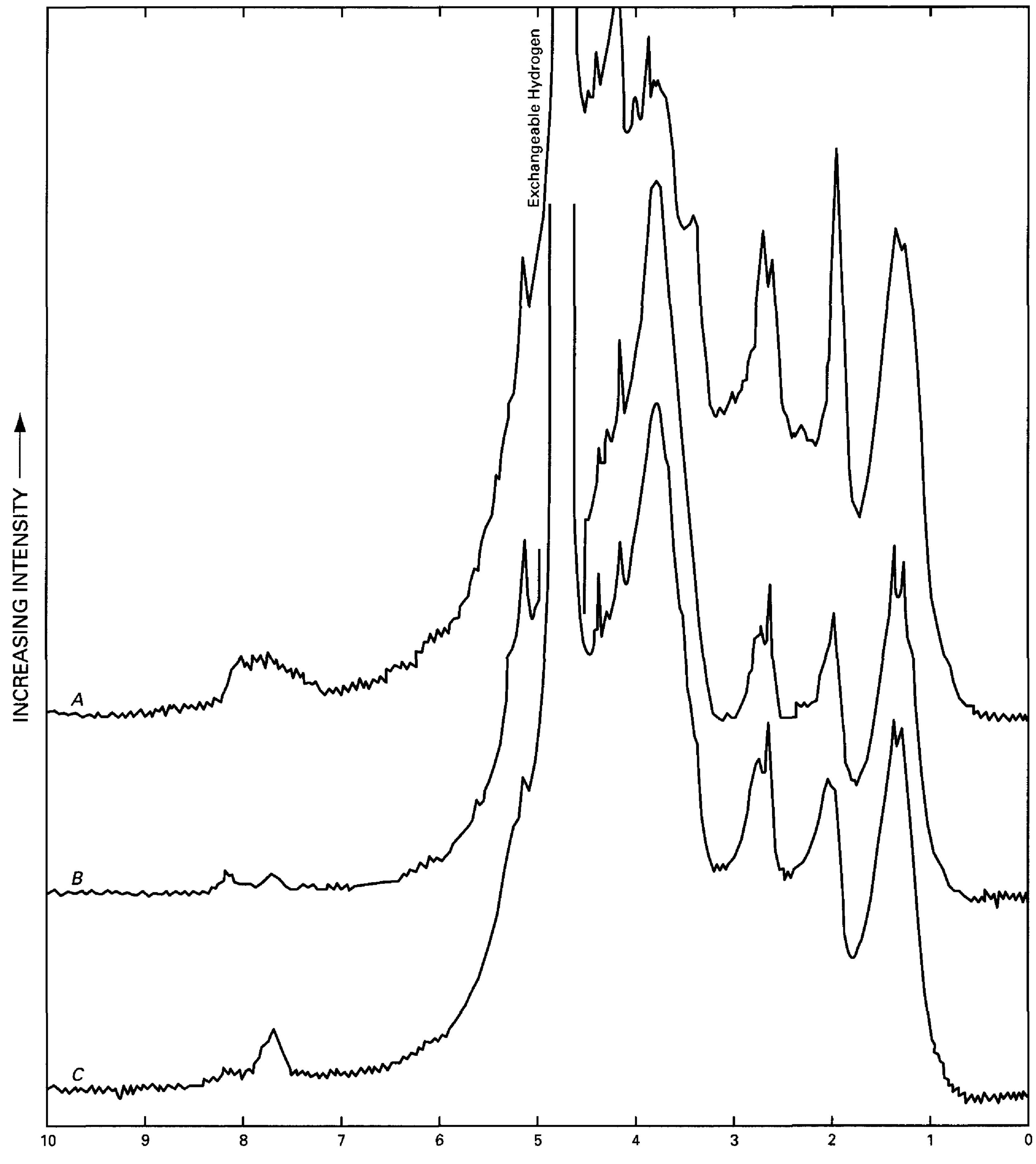

Figure 14.—^{1}H-nuclear magnetic resonance spectra of dissolved hydrophilic substances from the: (A) Illinois River at Hardin, Ill., (B) Arkansas River at Pendleton, Ark., and (C) Mississippi River below Belle Chasse, La., sampled June 1989.

These results do not rule out selective sorption processes in altering the nature of dissolved humic substances but definitely confirm the importance of oxidative degradation processes (possibly both biotic and abiotic) in changing the character of dissolved humic substances. The low DOC values and their decrease downriver during sampling cruise 1 (table 1) also indicate instream degradation of dissolved humic substances as a significant process when river stage is low and water temperatures are warm.

Organic Matter in Suspended-Sediment Fractions

The relative percentages of silt and clay, mineral colloids, and organic colloids in the Mississippi River and some of its tributaries for sampling cruise 5 are given in table 23. A typical distribution of relative percentages for the various sampling sites was found. The Upper Mississippi River sampled near Winfield, Mo., had the highest percentage of organic colloids, and the Arkansas, White, and Yazoo Rivers had the highest percentages of mineral colloids. Inputs of mineral colloids from the Arkansas, White, and Yazoo Rivers in the lower part of the Mississippi River are indicated by small increases in the mineral-colloid percentages at the below Vicksburg and Old River Outflow Channel sites.

Table 23.--Relative percentages[1] of silt and clay, mineral colloids, and organic colloids in the Mississippi River and some of its tributaries for the June 1989 sampling cruise

[ND, not determined]

Sampling site	Percent silt and clay (centrifuged)	Percent mineral colloids (ultrafiltered and centrifuged)	Percent organic colloids (ultrafiltered and dialyzed)
Mississippi River near Winfield, Mo.	89.5	7.9	2.6
Illinois River at Hardin, Ill.	98.7	1.0	.3
Missouri River at Hermann, Mo.	96.1	3.5	.4
Mississippi River at St. Louis, Mo.	93.2	5.9	.9
Mississippi River at Thebes, Ill.	92.7	6.7	.6
Ohio River at Olmsted, Ill.	94.1	5.9	ND
Mississippi River at Hickman, Ky.	94.2	5.2	.6
Mississippi River at Fulton, Tenn.	93.5	6.1	.4
Mississippi River at Helena, Ark.	93.7	6.1	.2
White River at Mile 11.5, Ark.	84.6	14.9	.5
Arkansas River at Pendleton, Ark.	83.0	15.6	1.4
Mississippi River above Arkansas City, Ark.	92.2	7.2	.6
Yazoo River below Steele Bayou, Miss.	81.7	17.3	1.0
Mississippi River below Vicksburg, Miss.	88.9	10.3	.7
Old River Outflow Channel near Knox Landing, La.	88.8	10.9	.3
Mississippi River near St. Francisville, La.	92.1	7.6	.3
Mississippi River below Belle Chasse, La.	93.2	6.4	.4

[1] See table 29 for method of determining relative percentages.

The elemental composition of the various suspended-sediment fractions is given in table 24. Fluorine percentages in the silt and clay fraction were lower than for the previous sampling cruise because a Teflon drag bushing in the continuous-flow centrifuge, which probably was the source of much of the fluorine content, was replaced by a treated wood bushing.

Typical increases in organic-carbon content of suspended sediment fractions were observed in proceeding from the silt and clay fraction (about 2–4 percent) to the mineral-colloid fraction (about 4–11 percent) to the organic-colloid fraction (about 25–40 percent). The atomic C:N ratio was somewhat elevated for most sites sampled on sampling cruise 5 compared to previous cruises; this elevated ratio indicates sediment contained a significant proportion of allochthonous material, which is consistent with the moderate to high stages of the river during cruise 5.

The organic-carbon and nitrogen transport for the various sediment-size fractions are presented in table 25. The transport of organic carbon in the mineral-colloid fraction are remarkably additive compared to the silt and clay transport when proceeding downriver. Especially remarkable is the additivity of the mineral-colloid transport at St. Louis for inputs from the Illinois River, the Upper Mississippi River, and the Missouri River. The organic carbon in the silt and clay fraction at these sampling points is not at all additive. Furthermore, the total masses of the mineral colloids are not additive; only the organic-carbon component is additive.

To gain further insight into the independent variations in the organic-carbon component of the silt and mineral-colloid fractions, the transport was converted into organic-carbon concentrations in table 26. The maximum variation between colloidal organic carbon concentrations was a factor of 3.2, whereas there was more than an order of magnitude variation between silt and clay organic carbon concentrations. The variations in colloidal organic-carbon concentrations in table 26 tend to parallel the variations in dissolved organic-carbon concentrations in table 22; the colloidal organic-carbon concentrations were 16–40 percent of the dissolved organic-carbon concentrations. The independent variations in the silt and clay and colloidal organic-carbon concentrations were among the most significant findings of this study, and the various mechanisms responsible for colloidal organic carbon acting as a conservative, dissolved constituent in water merits additional research.

Results of the work involving infrared spectral characterization of organic substances extracted from suspended silt and clay collected from the Mississippi River at Helena, Ark., are shown in figure 15. The initial extraction of sediment was by methylisobutyl ketone (MIBK) under both acid and alkaline conditions (Rice and MacCarthy, 1989). The MIBK extract after drying is shown in spectrum A. This extract appears to consist of aliphatic hydrocarbons, aliphatic alcohols, and aliphatic ester lipids. The next extraction in the sequence was by acid pyrophosphate designed to extract adsorbed fulvic acid from soils and sediments (Gregor and Powell, 1986). The spectrum of this extract (spectrum B, fig. 15) has a peak pattern typical for fulvic acid. The next extract was by a mixture (95 percent dimethyl sulfoxide, 4 percent water, and 1 percent HCl) recommended by Hayes (1985) for extraction of soil humic substances. This extract, after removal of the dimethylsulfoxide by dialysis and the silica by hydrofluoric acid (HF), gave the spectrum shown in spectrum C (fig. 15). This spectrum indicated a protein-rich substance that also contained lipids and humic substances.

Table 24.—Organic-carbon content, nitrogen content, and atomic C:N ratio of silt and clay, mineral-colloid, and organic-colloid fractions of suspended sediment from sampling cruise 5, June 1989.

[Fluorine content of silt fraction also is included]

Sampling site	Silt and clay fraction				Mineral-colloid fraction			Organic-colloid fraction[1]	
	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio	Fluorine (percent)	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio	Organic carbon (percent)	Nitrogen (percent)
Mississippi River near Winfield, Mo.	4.38	0.57	9.0	0.11	11.29	0.63	20.9	40	4.0
Illinois River at Hardin, Ill.	2.60	.24	10.8	.05	6.34	1.67	4.5	30	3.0
Missouri River at Hermann, Mo.	2.87	.26	13.1	.06	2.51	.38	7.7	20	2.0
Mississippi River at St. Louis, Mo.	3.50	.36	11.3	.08	7.76	1.00	9.1	35	3.5
Mississippi River at Thebes, Ill.	3.58	.39	10.6	.08	6.61	.83	9.1	40	4.0
Ohio River at Olmsted, Ill.	2.63	.26	11.8	.06	7.20	.99	8.5	40	4.0
Mississippi River below Hickman, Ky.	2.78	.31	10.6	.07	5.12	.46	13.2	35	3.5
Mississippi River at Fulton, Tenn.	2.30	.26	10.4	.08	4.36	.48	10.6	35	3.5
Mississippi River at Helena, Ark.	2.17	.23	10.9	.06	4.42	.44	11.7	35	3.5
White River at Mile 11.5, Ark.	1.86	.26	8.3	.06	4.36	.44	11.6	30	3.0
Arkansas River at Pendleton, Ark.	2.68	.35	8.9	.09	5.42	.37	17.1	30	3.0
Mississippi River above Arkansas City, Ark.	2.33	.24	11.3	.06	4.54	.54	9.8	25	2.5
Yazoo River below Steele Bayou, Miss.	1.20	.14	10.6	.06	2.85	.54	6.2	20	2.0
Mississippi River below Vicksburg, Miss.	2.16	.20	12.5	.08	4.57	.39	13.7	30	3.0
Old River Outflow Channel near Knox Landing, La.	2.32	.23	11.7	.08	4.27	.47	10.6	30	3.0
Mississippi River near St. Francisville, La.	1.97	.21	8.2	.07	4.07	.44	10.8	30	3.0
Mississippi River below Belle Chasse, La.	1.90	.20	11.6	.06	4.58	.72	7.4	30	3.0

[1] Carbon and nitrogen percentages on organic colloids were estimated using infrared spectral data.

Table 25.--Organic-carbon and nitrogen transport on silt and clay and colloid fractions of suspended sediment from sampling cruise 5, June 1989

[Water-discharge and suspended-sediment-concentration data used to compute transport are reported by Moody and Meade (1993); ND, not determined]

Sampling site	Silt and clay transport		Mineral-colloid transport		Organic-colloid transport	
	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)
Mississippi River near Winfield, Mo.	572	70	123	69	144	14.4
Illinois River at Hardin, Ill.	1,224	113	30	7.9	43	4.3
Missouri River at Hermann, Mo.	1,975	176	63	9.5	57	5.7
Mississippi River at St. Louis, Mo.	1,636	169	230	30	158	16
Mississippi River at Thebes, Ill.	1,751	192	234	29	126	13
Ohio River at Olmsted, Ill.	2,154	213	370	51	ND	ND
Mississippi River below Hickman, Ky.	4,112	454	418	38	293	29
Mississippi River at Fulton, Tenn.	5,145	579	636	70	334	33
Mississippi River at Helena, Ark.	6,280	674	844	84	219	22
White River at Mile 11.5, Ark.	106	15	44	4.4	10	1.0
Arkansas River at Pendleton, Ark.	469	61	178	12	89	8.9
Mississippi River above Arkansas City, Ark.	7,321	755	1,114	132	511	51
Yazoo River below Steele Bayou, Miss.	245	27	124	23	50	5.0
Mississippi River below Vicksburg, Miss.	6,300	590	1,554	138	689	69
Old River Outflow Channel near Knox Landing, La.	1,390	139	314	35	61	6.1
Mississippi River near St. Francisville, La.	4,596	481	783	85	228	23
Mississippi River below Belle Chasse, La.	5,218	536	863	136	314	31

Table 26.--Concentrations of silt and clay and colloidal organic carbon for sampling cruise 5, June 1989

[ND, not determined]

Sampling site	Silt and clay organic carbon determined from carbon analysis of isolated silt and clay fractions (milligrams per liter)	Colloidal organic carbon determined from carbon analysis of isolated colloid fractions (milligrams per liter)
Mississippi River near Winfield, Mo.	2.9	1.4
Illinois River at Hardin, Ill.	18.2	1.1
Missouri River at Hermann, Mo.	13.0	.8
Mississippi River at St. Louis, Mo.	4.0	.8
Mississippi River at Thebes, Ill.	3.9	.8
Ohio River at Olmsted, Ill.	2.8	ND
Mississippi River below Hickman, Ky.	3.4	.6
Mississippi River at Fulton, Tenn.	3.9	.7
Mississippi River at Helena, Ark.	4.3	.7
White River at Mile 11.5, Ark.	1.4	.7
Arkansas River at Pendleton, Ark.	1.5	.9
Mississippi River above Arkansas City, Ark.	3.6	.8
Yazoo River below Steele Bayou, Miss.	2.7	1.9
Mississippi River below Vicksburg, Miss.	2.9	1.0
Old River Outflow Channel near Knox Landing, La.	3.6	1.0
Mississippi River near St. Francisville, La.	2.3	.6
Mississippi River below Belle Chasse, La.	3.0	.7

The last treatment was to destroy the inorganic constituents of the silt and clay with HCl-HF (Leenheer and Moe, 1969), leaving the remaining inorganic materials as an insoluble residue. This residue (spectrum D, fig. 15) consisted of proteins and Teflon powder (peaks at 1,220 and 1,169 cm^{-1}). The Teflon came from wear of Teflon components in the centrifuge and possibly the Teflon bellows pump. From weighing the extracts and residues of this sequential extraction procedure coupled with carbon and infrared spectral analyses, only about 50 percent of the total organic carbon was extracted by this series of selective extractions. The high protein content was believed to cause most of the difficulty in achieving greater extraction efficiencies.

As a result of these extraction experiments, a conceptual model of an organic coating on Mississippi River silt and clay was derived (Leenheer, 1991). The mechanistic means (including hydrogen-bonding, electrostatic, ligand exchange, and nonpolar partitioning interactions) by which a series of organic and inorganic contaminants associate with organic coatings on sediments are illustrated in this model. Lipid structures, into which nonionic organic contaminants such as polychlorinated biphenyls can partition, and appear to be important for nonpolar partitioning interactions. Proteins appear to be strongly bound to mineral surfaces through multiple interactions, and the proteins also appear to serve as a substrate for binding of humic substances and various contaminants.

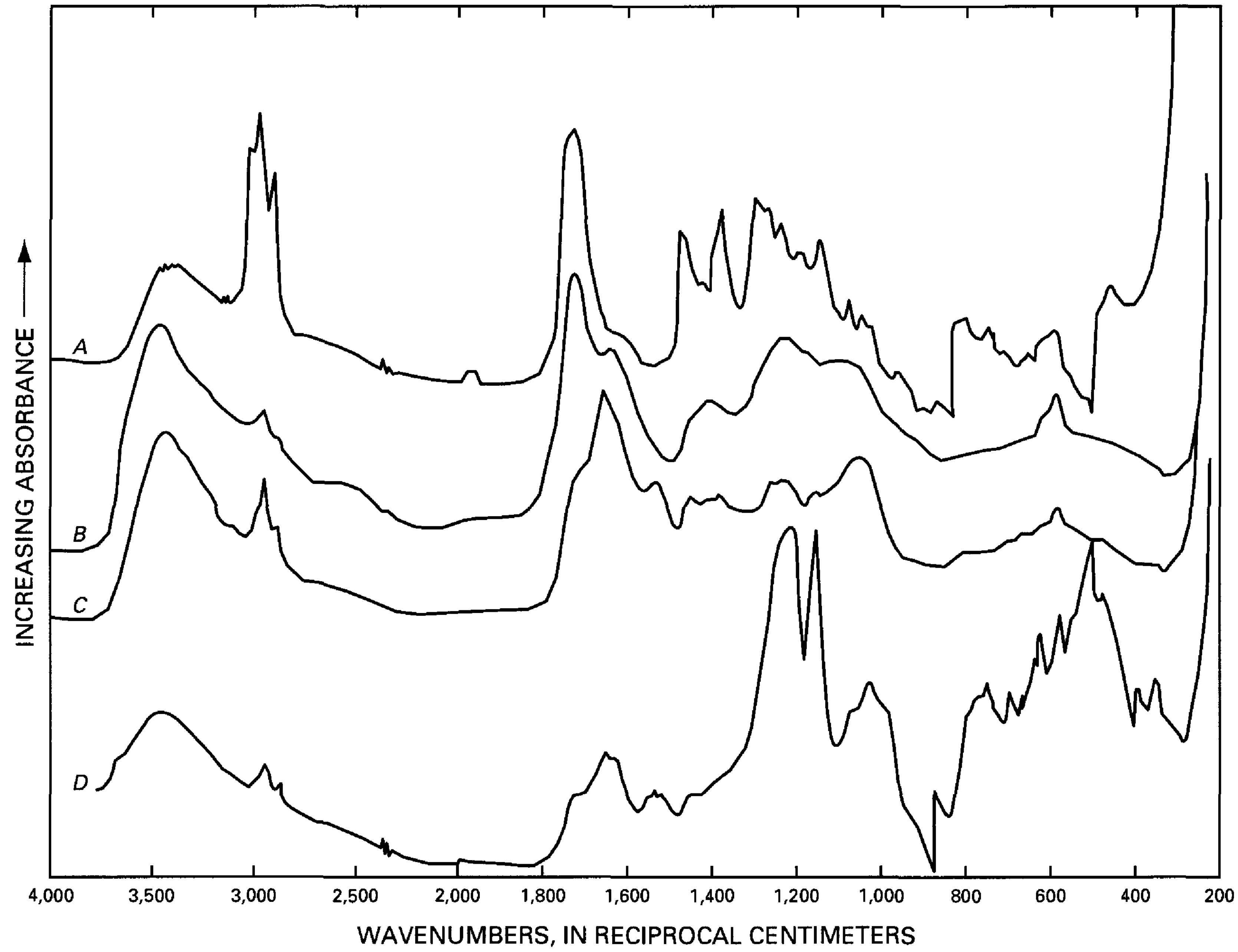

Figure 15.--Infared spectra of organic substances extracted from suspended silt and clay from the Mississippi River at Helena, Ark. Spectrum A is from methylisobutyl ketone extraction; spectrum B is from acid pyrophosphate extraction; spectrum C is from acid dimethylsulfoxide extraction; spectrum D is the organic residue after destroying the inorganic substances with a mixture of hydrochloric and hydrofluoric acids.

SAMPLING CRUISE 6, FEBRUARY–MARCH 1990

The sampling of cruise 6 began on the Cumberland River near Smithland, Kentucky, on February 23, 1990, and ended on the Mississippi River below Belle Chasse, Louisiana, on March 14, 1990. The Cumberland, Tennessee, and Wabash Rivers were sampled for the first time during this cruise. Other new sampling sites added during cruise 6 were the Mississippi River near Cache, Illinois, and the Ohio River at Uniontown, Kentucky. Sites sampled on cruise 5 that were not sampled on cruise 6 were the Mississippi River at Thebes, Illinois, and sites on the Illinois, Missouri, White, Arkansas, Yazoo, and Old Rivers.

Objectives and Approach

An objective of sampling cruise 6 was to examine the Ohio River system in greater detail during early spring runoff. Large discharge occurred (about 16,000 m^3/s) in the Ohio River as compared to an average discharge of 7,700 m^3/s (Moody and Meade, 1993).

With respect to specific project objectives, specific studies of the dissolved organic-carbon fractions in water were discontinued with the exception of measuring and interpreting dissolved organic-carbon concentrations. Data obtained on the nature of dissolved organic constituents were regarded as sufficient so that time and fiscal resources could be diverted to more specific studies of sedimentary organic substances.

All silt and clay fractions from this cruise were extracted with MIBK, and this extract was characterized by ^{1}H-NMR spectrometry to determine if there were significant variations in the nature of lipids that act as carriers of organic contaminants on the sediment. The silt and clay fractions were not dried before their extraction, using the procedure of Rice and MacCarthy (1989).

Dissolved Organic Carbon

DOC concentrations and transport at the various sampling sites are presented in table 27. DOC transport in the Mississippi River downstream from the confluence of the Arkansas and White Rivers were about double the transport during the March–April 1989 sampling cruise (table 17), during which DOC transport was the highest of the previous cruises. The Arkansas and White Rivers, which were not sampled during sampling cruise 6, added significant amounts of carbon. Assuming conservative mixing of DOC transport, the DOC concentration inputs from the Arkansas and White Rivers were calculated to average 5.4 mg/L. Conservation of DOC transport was observed at the Olmsted, Ill., sampling site on the Ohio River for inputs from the Ohio, Wabash, Cumberland, and Tennessee Rivers. This conservation of transport is somewhat surprising as it took 5 days to obtain samples at all these sites, and the same body of water was not being sampled because of the time interval. Conservation of DOC transport also was noted at the below Hickman, Ky., site for inputs from the Upper Mississippi and Ohio Rivers.

Table 27.--Dissolved organic-carbon concentrations and transport for sampling cruise 6, February–March 1990

[Transport was computed using water-discharge data reported by Moody and Meade (1991b)]

Sampling site	Water discharge (cubic meters per second)	Dissolved organic-carbon concentration (milligrams per liter)	Transport (metric tons per day)
Ohio River at Uniontown, Ky.	6,620	3.3	1,887
Wabash River near New Haven, Ill.	2,340	5.0	1,011
Cumberland River near Smithland, Ky.	2,170	2.9	544
Tennessee River near Calvert City, Ky.	6,570	2.5	1,419
Ohio River at Olmsted, Ill.	16,100	3.4	4,730
Mississippi River near Cache, Ill.	4,240	5.3	2,079
Mississippi River below Hickman, Ky.	21,000	3.6	6,529
Mississippi River below Fulton, Tenn.	22,800	3.7	7,292
Mississippi River at Helena, Ark.	23,300	3.7	7,462
Mississippi River above Arkansas City, Ark.	33,200	4.2	12,048
Mississippi River below Vicksburg, Miss.	34,100	4.2	12,381
Mississippi River near St. Francisville, La.	26,300	4.1	9,324
Mississippi River below Belle Chasse, La.	26,700	3.8	8,776

Organic Matter in Suspended-Sediment Fractions

A recovery study was performed during sampling cruise 6 to determine where the significant losses were in the field and laboratory processing of suspended-sediment fractions. A coarse silt fraction, which was lost into the centrifuge sump during the backflow through the centrifuge bowl and bowl-bottom sealing unit during the shutdown procedure, was quantitated by flushing the sump with water, measuring the volume, and determining the suspended-sediment concentration by filtration, drying, and weighing. Losses of sediment during laboratory processing procedures (sample transfers, centrifugations, freeze-drying, and weighing) were estimated by taking a representative aliquot of the suspended silt and clay recovered from the centrifuge before laboratory processing and determining sediment concentrations (and mass) by filtration, drying, and weighing the filtrate. Comparison with silt and clay weights after laboratory processing gave an estimate of laboratory processing loss. The results for samples from nine sites where complete sets of data were obtained are presented in table 28.

The major source of suspended-sediment loss was to the centrifuge sump during the shutdown procedure; losses varied between about 8 and 21 percent, and the average loss was 11 percent. The average loss due to laboratory processing of samples was 5.2 percent, but the variability of the data indicated that variance of the loss determinations was near the variance of the losses. The average total recovery for all nine sites was 98.1 percent; the completeness of recoveries, with the exception of the below Hickman, Ky., site for some unknown reason, indicates that the two major sources of sediment loss were identified. These results rule out significant losses, on a weight-percentage basis of total silt and colloid concentrations, of colloids recovered from the ultrafiltration process.

Table 28.—Recovery study of suspended-sediment fractions[1] from the Ohio, Mississippi, and Tennessee Rivers during sampling cruise 6, February–March 1990

[ND, not determined]

Sampling site	Percent of suspended sediment[1] determined by filtration, drying, and weighing a representative aliquot of silt and clay suspension recovered from centrifuge	Percent of suspended sediment[1] determined by freeze-drying and weighing a representative split	Percent laboratory drying, sample transfer, and weighing losses determined by subtracting data in second column from data in first column	Percent of suspended sediment[1] lost to waste sump in centrifuge during shutdown procedure	Mineral-colloid fraction recovered from ultrafilter (percent of suspended sediment[1])	Organic-colloid fraction (percent of suspended sediment[1])	Total accounted recovery of suspended sediment[1], in percent
Ohio River at Uniontown, Ky.	81.0	76.3	4.7	13.8	6.8	0.3	101.9
Tennessee River near Calvert City, Ky.	73.1	70.1	3.0	7.5	20.6	1.5	102.7
Ohio River at Olmsted, Ill.	80.6	66.5	14.1	11.3	9.3	.6	101.8
Mississippi River below Hickman, Ky.	66.6	66.1	.5	9.2	9.2	.5	85.5
Mississippi River below Fulton, Tenn.	60.8	67.0	-6.2	20.7	10.1	ND	97.8
Mississippi River at Helena, Ark.	67.7	65.8	1.9	14.8	7.4	.6	90.5
Mississippi River above Arkansas City, Ark.	76.7	69.5	7.2	8.3	11.5	ND	96.5
Mississippi River below Vicksburg, Miss.	84.9	72.3	12.6	8.2	11.9	.5	105.5
Mississippi River near St. Francisville, La.	77.0	68.3	8.7	12.4	11.6	ND	101.0
Average recoveries	74.3	69.1	5.2	11.8	10.9	.7	98.1

[1] The sand fraction was not included in suspended-sediment concentrations.

The findings of this loss study were applied to the calculation of carbon and nitrogen transport data from the previous cruises where sources of losses were not yet identified. Calculation of silt and clay and colloid distributions by taking silt and clay masses from pumped composite sample data and multiplying colloid masses obtained from the depth-integrated composite sample by a volume factor difference between the pumped and depth-integrated samples potentially can minimize these errors apparent in depth-integrated composite sample data because of the greater mass (about 5 times) of silt and clay in the pumped composite sample. This greater mass should minimize both the losses due to laboratory processing and the percent of silt and clay lost from the centrifuge during shutdown because of greater suspended-sediment loading of the centrifuge bowl. Comparison of recovery percentages on the composite sample (with losses figured into the appropriate fractions to give valid distributions) with relative percentages calculated from combining the pumped composite sample and depth-integrated composite data, as described above, are presented in table 29. Within the variance of the data set, the averages show there is no detectable bias when the data are calculated by combining pumped composite sample data for silt and clay percentages and depth-integrated composite sample data for colloid percentages. Therefore, data in tables 13, 18, and 23 were calculated by combining pumped composite sample data for silt and clay percentages with depth-integrated composite sample data for colloid percentages.

A more significant error than calculation of sediment distribution percentages might be the analysis of carbon and nitrogen in the silt and clay fraction in which the coarse silt, which potentially has a lower organic matter percentage, has been lost. Organic carbon and nitrogen percentages on silt and clay from the pumped composite sample were consistently lower than these percentages from the depth-integrated composite sample because the pumped composite sample should contain a greater percentage of the coarse silt fraction. Therefore, organic-carbon data on the silt and clay from the pumped composite sample also were used for carbon transport calculations. As a result of these recovery studies, a new drain housing assembly was purchased for the continuous-flow centrifuge so that this coarse silt fraction could be recovered at the end of a centrifuge run without contaminating the sample by recovering it from the sump.

Organic-carbon and nitrogen data for the silt and clay fraction recovered from the February–March 1990 sampling are presented in table 30. A significant finding is the abrupt decrease in C:N ratios in the Ohio River between Uniontown and Olmsted because of inputs of sedimentary organic materials derived from autochthonous sources by the Cumberland and Tennessee Rivers. Even though the Cumberland and Tennessee Rivers were at high discharge (2,170 m^3/s, for the Cumberland River and 6,570 m^3/s for the Tennessee River; Moody and Meade, 1993), it appears the reservoirs of the Tennessee Valley Authority (TVA) system were acting as a trap for allochthonous organic-sediment inputs and were exchanging these silts and clays for silts and clays with organic material from autochthonous sources, which had been accumulating in the reservoir during low-water periods. The Wabash and upper Ohio Rivers do not have significant reservoir systems like TVA where this process can occur, and C:N ratios from these rivers were much greater. As determined in previous cruises, the Upper Mississippi River also contributes sedimentary organic matter of low C:N ratios into the system. This situation appeared to be the case during this sampling of the Mississippi River near Cache, Ill. The percent of carbon on the silt and clay fraction appeared to decrease downriver; this decrease might have been the result of instream mineralization processes of carbon. Resuspension of silt and clay from bottom sediments on which carbon mineralization had already occurred may also likely occur during high-water periods.

Table 29.--Recovery percentages of silt and clay, mineral colloids, and organic colloids in the Cumberland, Ohio, Mississippi, Tennessee, and Wabash Rivers during sampling cruise 6, February–March 1990

[Data in parentheses are relative percentages computed by determining the relative proportions of silt and clay from the pumped composite sample (plus mineral colloid plus organic colloids from depth-integrated composite sample) times (volume of pumped composite sample) divided by volume of depth-integrated composite sample; ND, not determined]

Sampling site	Percent silt and clay (centrifuged)	Percent mineral colloids (ultrafiltered and centrifuged)	Percent organic colloids (ultrafiltered and dialyzed)
Ohio River at Uniontown, Ky.	94.9	6.8	0.3
	(92.0)	(6.8)	(.3)
Wabash River near New Haven, Ill.	89.7	16.7	.7
	(83.8)	(16.8)	(.7)
Cumberland River near Smithland, Ky.	(83.4)	(14.4)	(2.2)
Tennessee River near Calvert City, Ky.	80.5	20.6	1.5
	(78.3)	(20.3)	(1.4)
Ohio River at Olmsted, Ill.	91.9	9.4	.6
	(88.0)	(11.3)	(.7)
Mississippi River near Cache, Ill.	(82.2)	(16.4)	(1.3)
Mississippi River below Hickman, Ky.	75.8	9.2	.5
	(88.2)	(11.2)	(.6)
Mississippi River below Fulton, Tenn.	81.5	10.2	ND
	(88.7)	(11.2)	ND
Mississippi River at Helena, Ark.	82.6	7.4	.6
	(90.7)	(8.7)	.6
Mississippi River above Arkansas City, Ark.	85.1		
	(88.1)	(11.9)	ND
Mississippi River below Vicksburg, Miss.	93.1	11.9	.5
	(87.2)	(12.3)	.5
Mississippi River near St. Francisville, La.	89.4	11.6	ND
	(86.8)	(13.2)	ND
Mississippi River below Belle Chasse, La.	80.3	9.6	ND
Recovery percentage average	87.2	12.4	.7
Relative percentage average	(86.5)	(11.5)	(.7)

Table 30.--Organic-carbon and nitrogen percentages of the suspended-silt and -clay fraction from sampling cruise 6, February–March 1990

Sampling site	Percent organic carbon of silt and clay fraction	Percent nitrogen of silt and clay fraction	Atomic C:N ratio
Ohio River at Uniontown, Ky.	2.65	0.28	11.04
Wabash River near New Haven, Ill.	2.62	.30	10.2
Cumberland River near Smithland, Ky.	2.35	.43	6.4
Tennessee River near Calvert City, Ky.	1.99	.30	7.7
Ohio River at Olmsted, Ill.	2.41	.29	9.7
Mississippi River near Cache, Ill.	2.76	.47	6.9
Mississippi River below Hickman, Ky.	2.19	.27	9.5
Mississippi River below Fulton, Tenn.	2.12	.26	8.2
Mississippi River at Helena, Ark.	2.43	.30	8.1
Mississippi River above Arkansas City, Ark.	2.11	.27	9.1
Mississippi River below Vicksburg, Miss.	1.95	.25	9.1
Mississippi River near St. Francisville, La.	2.02	.27	8.7
Mississippi River below Belle Chasse, La.	1.72	.23	8.7

Determinations of carbon and nitrogen transport on the silt and clay fraction and of the silt and clay organic-carbon concentrations are presented in table 31. Transport at the Ohio River sites are high, as would be expected during a high discharge period, but the relatively low transport and concentrations from the Cumberland and Tennessee Rivers compared to the fact that over half of the discharge of the Ohio River at Olmsted, Ill., comes from the Cumberland and Tennessee Rivers show how efficient the reservoirs of the TVA system are as traps for sedimentary organic matter. The sum of the organic-carbon and nitrogen transport for the upper Ohio, Wabash, Cumberland, and Ohio Rivers agree moderately well with measured values for the transport in the Ohio River at Olmsted, Ill. Inputs of silt and clay organic carbon and nitrogen from the White and Arkansas Rivers are not as apparent in the Lower Mississippi River as these inputs were for the dissolved organic-carbon data in table 27. This is additional evidence that organic carbon and nitrogen on the silt and clay fraction is not as conservative as dissolved organic carbon.

Research performed on sampling cruise 5 identified the importance of hydrocarbons, lipid esters, and fatty acids extracted by MIBK as carriers of organic contaminants on the suspended-silt and clay fraction. Numerical relations between MIBK extract yields and organic carbon and nitrogen on suspended silt and clay are presented in table 32.

There appears to be an inverse relation trend between extract yield normalized to carbon content and the atomic C:N ratio for the first seven sampling sites in table 32. At sites farther downstream, this relation breaks down; instream mineralization of organic matter and resuspension of low-organic-carbon silts and clays may obscure the trends in this data set for the samples in the lower portion of the Mississippi River. The relation of extract yield with atomic C:N ratios indicates extractable hydrocarbons and lipids are related to the nature of the source of organic matter. To obtain additional characterization of these MIBK extracts, H-NMR spectra of the extracts were determined.

Table 31.—Transport of silt and clay organic carbon and nitrogen and silt and clay organic-carbon concentrations from sampling cruise 6, February–March, 1990

[Water discharge and suspended-sediment-concentration data used to compute transport are reported by Moody and Meade (1991b)]

Sampling site	Organic-carbon transport on suspended silt and clay (metric tons per day)	Nitrogen transport on suspended silt and clay (metric tons per day)	Organic-carbon concentration on suspended silt and clay (milligrams per liter)
Ohio River at Uniontown, Ky.	2,851	301	5.0
Wabash River near New Haven, Ill.	660	76	3.3
Cumberland River near Smithland, Ky.	118	22	.6
Tennessee River near Calvert City, Ky.	430	65	.8
Ohio River at Olmsted, Ill.	4,248	511	3.1
Mississippi River near Cache, Ill.	961	163	2.4
Mississippi River below Hickman, Ky.	5,535	682	3.0
Mississippi River below Fulton, Tenn.	5,225	641	2.7
Mississippi River at Helena, Ark.	6,511	804	3.2
Mississippi River above Arkansas City, Ark.	6,719	860	2.3
Mississippi River below Vicksburg, Miss.	6,290	806	2.1
Mississippi River near St. Francisville, La.	3,901	521	1.7
Mississippi River below Belle Chasse, La.	4,450	595	1.9

Table 32.—Relations between methylisobutyl ketone (MIBK) extract yields and organic carbon and nitrogen on suspended silt and clay from sampling cruise 6, February–March 1990

Sampling site	Percent MIBK extract yield of silt organic carbon	Atomic C:N ratio
Ohio River at Uniontown, Ky.	2.5	11.04
Wabash River near New Haven, Ill.	1.6	10.2
Cumberland River near Smithland, Ky.	5.1	6.4
Tennessee River near Calvert City, Ky.	3.2	7.7
Ohio River at Olmsted, Ill.	2.2	9.7
Mississippi River near Cache, Ill.	8.8	6.9
Mississippi River below Hickman, Ky.	3.8	9.5
Mississippi River below Fulton, Tenn.	2.5	8.2
Mississippi River at Helena, Ark.	1.4	8.1
Mississippi River above Arkansas City, Ark.	3.4	9.1
Mississippi River below Vicksburg, Miss.	3.8	9.1
Mississippi River near St. Francisville, La.	2.0	8.7
Mississippi River below Belle Chasse, La.	1.2	8.7

Two general types of ^{1}H-NMR spectral patterns are shown in figure 16. Extracts from silts and clays with low C:N ratios (autochthonous source term) gave spectra similar to spectrum A, figure 16, whereas extracts from silts and clays with high C:N ratios (allochthonous source term) gave spectra similar to spectrum B, figure 16. The composition of the extract of spectrum A appears to be straight chain acids, lipids, and hydrocarbons (peaks 1 and 2), with some olefinic hydrocarbons (peak 4) in the mixture. The extract of spectrum B differs from spectrum A in that the peak height ratio of peak 1 to peak 2 is greater, meaning there are more branched hydrocarbon components. Peak 3 is also much greater in spectrum B. Peak 3 may be indicative of methyl groups attached to a doubly-bonded carbon, as is found in plant pigments such as the carotene hydrocarbons. No specific organic contaminants or classes of organic contaminants were detected in the ^{1}H-NMR survey of MIBK extracts of suspended silts and clays.

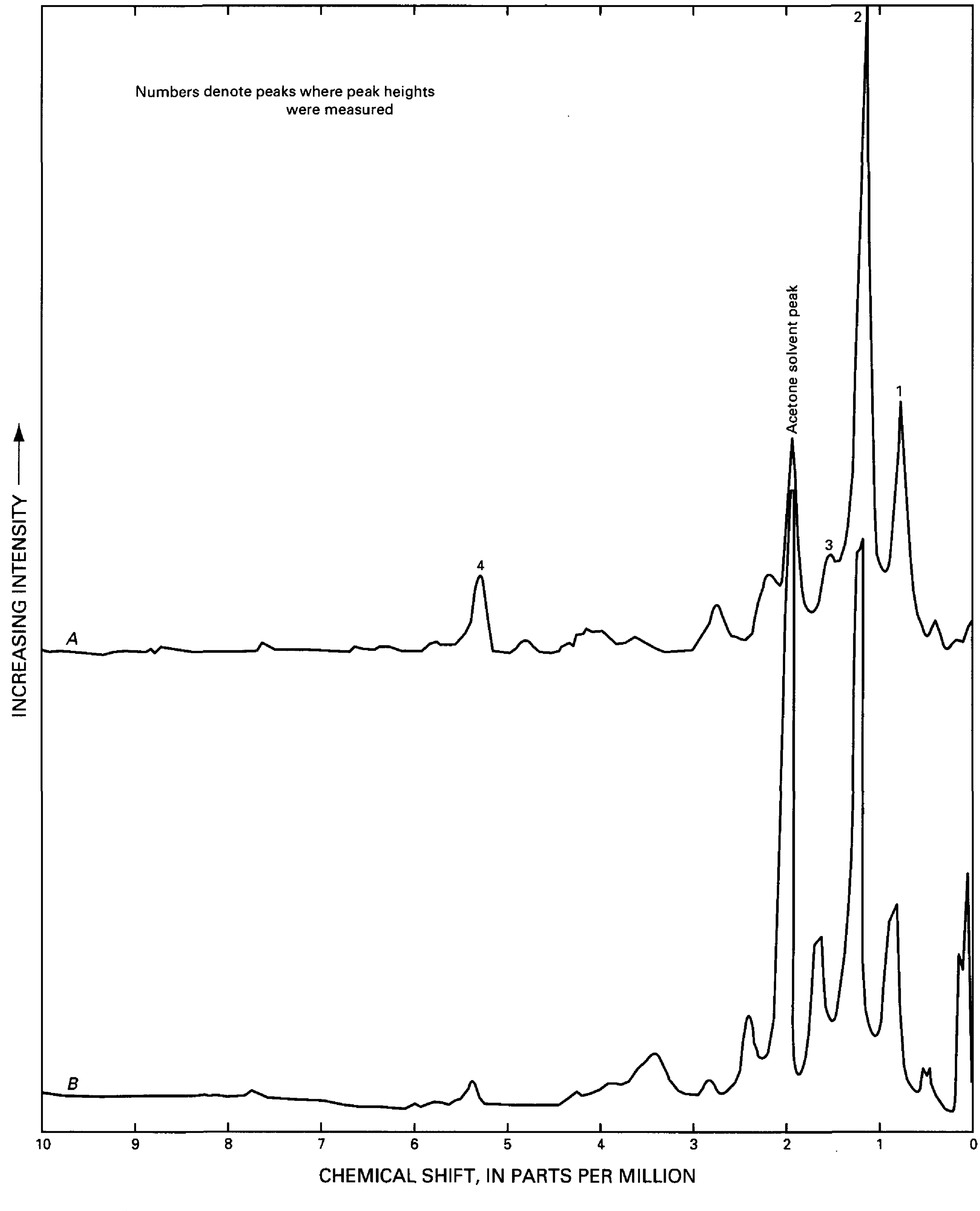

Figure 16.—^{1}H-nuclear magnetic resonance spectra of methylisobutyl ketone extracts of suspended silt sampled from the: (A) Mississippi River near Cache, Ill., and (B) Wabash River near New Haven, Ill., sampled February–March 1990.

SAMPLING CRUISE 7, MAY–JUNE 1990

The downstream sampling leg of cruise 7 began on the Illinois River at Valley City, Illinois, on June 7, 1990, and ended on the Mississippi River below Belle Chasse, Louisiana, on June 27, 1990. The Mississippi River sites sampled during the downstream leg of cruise 7 were below Grafton, Illinois; a special sample at St. Louis, Mo.; at Thebes, Illinois; below Memphis, Tennessee; below Vicksburg, Mississippi; near St. Francisville, Louisiana; and below Belle Chasse, Louisiana. Tributary sampling sites were the Illinois River at Valley City, Illinois; the Ohio River at Olmsted, Illinois; and the Yazoo River below Steele Bayou, Miss.

Approach and Objectives

The primary purpose of the seventh sampling cruise was to conduct a study of dissolved trace-metal concentrations in the lower Mississippi River supported by the National Stream Quality Accounting Network. However, the general long-term studies of organic-carbon and nitrogen transport in the dissolved and particulate phases were also continued during this cruise.

The major specific objective of sampling cruise 7 was to develop improved methodology for the characterization of organic substances in bed and suspended sediments. Therefore, a number of bed-and suspended-sediment samples were obtained during this cruise for the development of methods for organic-substance characterization that can be related to contaminant fate and transport. Data on extraction of organic substances from suspended sediment obtained on sampling cruise 5 indicated that it was impossible to extract and characterize more than 50 percent of the carbon on the sediment fractions. Therefore, an alternative strategy begun on sampling cruise 7 was to find a way of enriching the carbon on sediment fractions by dissolving the inorganic substances without altering the organic substances. The objective of this approach was to obtain high-quality solid-state ^{13}C-NMR spectra on the carbon in the various sediment fractions. These spectra could then be related to organic structure composition and variation in a manner analogous to the use of ^{1}H-NMR to characterize the dissolved organic-substance fractions in water.

Dissolved Organic Carbon

DOC concentrations and transport for the Mississippi River and some of its tributaries sampled in May–June 1990 are presented in table 33. This was the first sampling performed while the Upper Mississippi River and Missouri River were at high discharges. Organic-carbon transport at the Grafton, Ill., and Thebes, Ill., sites were the greatest for these locations on any sampling cruise. DOC inputs from the Missouri River doubled the transport on the Mississippi River between Grafton and Thebes. Based on this transport doubling and the increase in discharge, the DOC concentration of the Missouri River was computed to be 4.5 mg/L.

Not only were the transport values elevated for these high-discharge conditions, but the DOC concentrations were increased 1–3 mg/L over concentrations observed during the low-discharge conditions of the first three cruises. During sampling cruises 6 and 7, inputs of water high in DOC concentrations upstream from the Mississippi-Ohio Rivers confluence raised the DOC concentrations and transport in the Mississippi River downstream from this confluence. Instream degradation of DOC, observed during the first and third cruises, does not seem to be a significant process during high-discharge conditions.

Table 33.—Dissolved organic-carbon concentrations and transport for sampling cruise 7, May-June 1990

[Water-discharge data used to compute transport were reported by Moody and Meade (1993)]

Sampling site	Water discharge (cubic meters per second)	Dissolved organic-carbon concentration (milligrams per liter)	Dissolved organic-carbon transport (metric tons per day)
Illinois River at Valley City, Ill.	1,230	4.6	489
Mississippi River below Grafton, Ill.	5,040	5.8	2,526
Mississippi River at Thebes, Ill.	12,600	5.0	5,443
Ohio River at Olmsted, Ill.	9,550	3.3	2,723
Mississippi River below Memphis, Tenn.	20,800	3.9	7,009
Mississippi River below Arkansas City, Ark.	25,500	4.1	9,019
Yazoo River below Steele Bayou, Miss.	1,250	5.0	540
Mississippi River below Vicksburg, Miss.	27,300	3.9	9,196
Mississippi River near St. Francisville, La.	23,200	3.8	7,617
Mississippi River below Belle Chasse, La.	23,300	4.2	8,455

Organic Matter in Suspended and Bed Sediments

A somewhat limited set of data on suspended-sediment composition, concentrations, and transport was available when this report was written. Available data are presented in table 34. Because of the high discharges encountered from the Upper Mississippi and Missouri Rivers, record-high transport and concentrations of carbon and nitrogen were measured at the Thebes, Ill., sampling site on the Mississippi River. Most of this transport was input by the Missouri River between the Grafton, Ill., and Thebes, Ill., sites. The relatively high C:N ratio of 10.2 for organic matter on the suspended silt and clay at Thebes indicates an allochthonous origin. The decrease in transport in the downriver direction probably is not significant because this sampling cruise was not designed to sample the same body of water as it flows downstream (Lagrangian sampling).

The suspended- and bed-sediment samples collected during sampling cruise 7 were prepared for solid-state ^{13}C-NMR spectral analysis by dissolving interfering inorganic constituents (especially iron) without losing or altering sedimentary organic matter. A flow chart of selective mineral dissolution procedures is presented in figure 17.

The acid pyrophosphate procedure (Gregor and Powell, 1986) was placed first in the sequence to remove calcium and magnesium minerals that would form insoluble oxalates in the following extraction if they were not removed. Acid pyrophosphate solution also removes some of the iron. The next step, use of 0.15 molar oxalic acid at pH 3, was previously determined (Parfitt, 1989) to be the most efficient extractant for removing amorphous aluminum, iron, and silicon from soils.

Table 34.–Composition, concentrations, and transport of carbon and nitrogen in the suspended-silt fractions for sampling cruise 7, May–June 1990

[Water-discharge and suspended-sediment-concentration data used to compute transport were reported by Moody and Meade (1993); ND, not determined]

Sampling site	Percent organic carbon	Percent nitrogen	Atomic C:N ratio	Silt organic-carbon concentration (milligrams per liter)	Carbon transport (metric tons per day)	Nitrogen transport (metric tons per day)
Illinois River at Valley City, Ill.	2.98	0.41	8.5	2.6	280	39
Mississippi River below Grafton, Ill.	2.24	.28	9.7	9.7	4,233	528
Mississippi River at Thebes, Ill.	1.83	.21	10.2	19.2	20,918	2,400
Ohio River at Olmsted, Ill.	1.83	.24	8.9	2.9	2,395	314
Mississippi River below Memphis, Tenn.	2.06	.24	10.0	ND	ND	ND
Mississippi River below Arkansas City, Ark.	1.92	.24	9.3	ND	ND	ND
Mississippi River below Vicksburg, Miss.	2.00	.27	8.6	5.1	12,024	1,398
Mississippi River near St. Francisville, La.	1.83	.24	8.9	2.9	5,905	774
Mississippi River below Belle Chasse, La.	2.03	.26	9.1	3.2	6,375	816

The pyrophosphate and oxalate extractants also release adsorbed fulvic acid, which is recovered by adsorption chromatography on XAD-8 resin. The two hydrofluoric acid treatments were performed under dilute acid conditions at room temperature because a previous study (Preston and others, 1989) found that high concentrations (2.88 molar) and long reaction periods needed to completely remove silicates destroyed the carbohydrate portion of organic matter through acid hydrolysis. Dilute hydrofluoric acid destroys only hydrous silicates (clay minerals), but it does not attack silicon oxides (quartz).

Gentle mixing of the samples inside the dialysis tubing was achieved by placing the tubing inside a 1-L wide-mouth polyethylene bottle with the extracting solutions and rotating the bottle attached to the rim of a bicycle wheel at six revolutions per minute. This rotation resulted in a gentle inversion of the sediment inside the dialysis tubing so that the sediment mixed without physically abrading the tubing. The cellulose acetate dialysis tubing was chemically stable to all the extracting solutions, and it greatly facilitated the separation of colloidal sediments from the extracting solutions without filtration or centrifugation steps being necessary.

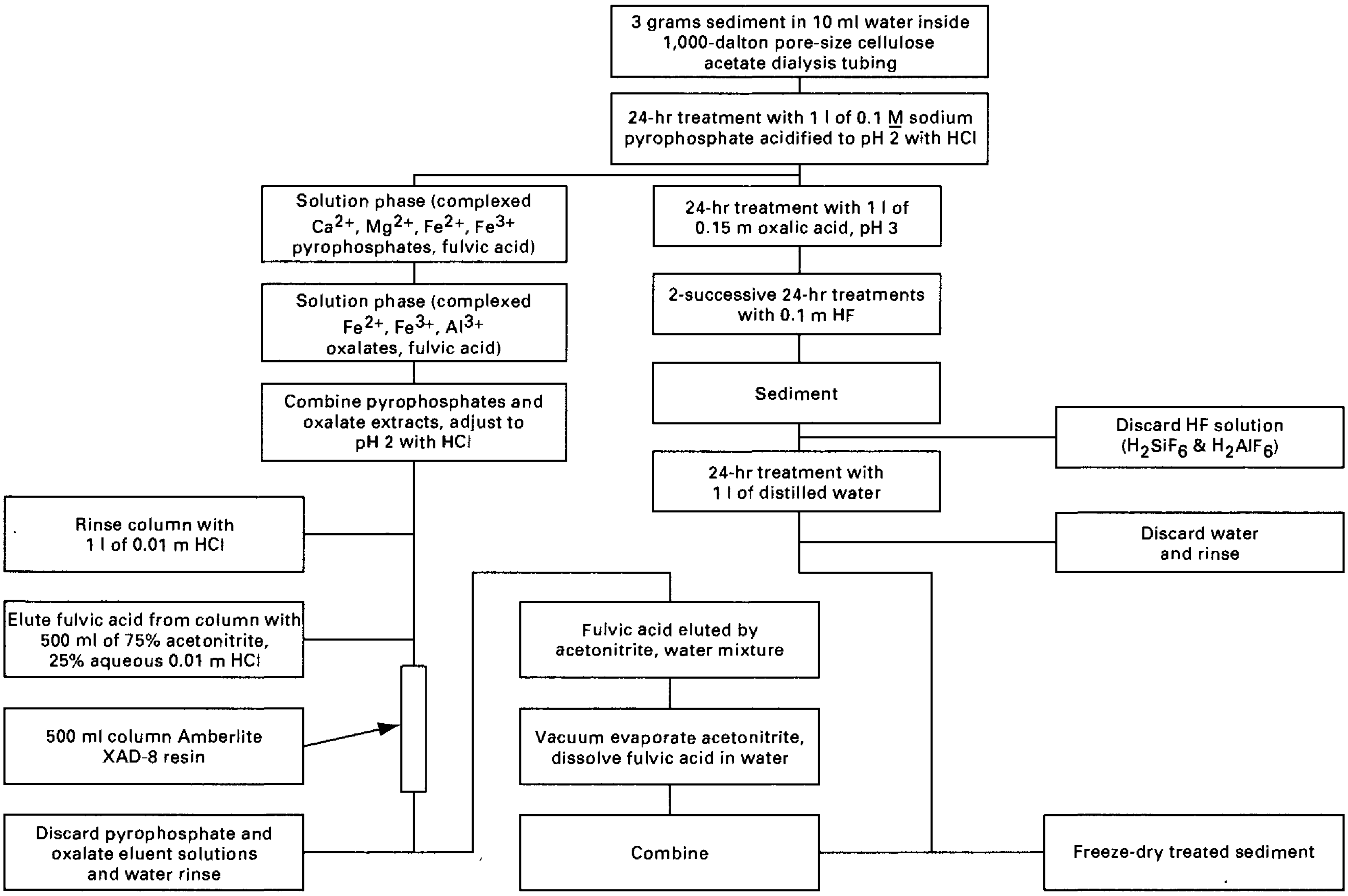

Figure 17.—Flow chart of procedures used to prepare sediment samples for solid-state ^{13}C-nuclear magnetic resonance spectral analysis.

The effect of selective mineral-dissolution treatments on suspended silts and clays and bottom muds on organic-matter recovery and composition is presented in table 35. The treatments removed an average of 59 percent of the weight of the suspended-silt and -clay samples and an average of 48 percent of the weight of the bottom mud samples. An average of 12 percent of the organic carbon was lost by these treatments, and increases in the C:N ratios indicated selective loss of organic-nitrogen compounds. The loss may be caused by low-molecular-weight amines and amino acids, which are released during the dilute acid treatments and these nitrogen compounds are too small to be retained by the dialysis membrane. The organic-carbon content was approximately doubled by the treatments; this doubling of organic-matter content is advantageous for ^{13}C-NMR spectral analysis. Infrared studies of these sediments after treatment indicated remaining mineral matter was largely quartz and mineral fluorides, such as magnesium-rich clays converted to insoluble magnesium fluorides.

Table 35.--Effect of selective mineral dissolution treatments on suspended-silts and -clays and bottom muds on organic matter recoveries and composition

Sampling site and sample	Percent carbon before treatment	Percent carbon after treatment	Percent nitrogen before treatment	Percent nitrogen after treatment	Percent weight loss	Percent organic carbon loss	Atomic C:N before treatment	Atomic C:N after treatment
Illinois River at Valley City, Ill.								
Suspended silt and clay	3.23	7.27	0.44	0.85	60.75	11.7	8.6	10.0
Mississippi River below Grafton, Ill.								
Suspended silt and clay	2.14	4.98	.25	.56	63.47	15.0	10.0	10.4
Bottom mud	1.26	2.67	.14	.26	45.94	-12.8	10.5	12.0
Mississippi River at St. Louis, Mo.								
Suspended silt and clay	1.78	3.42	.20	.32	52.11	8.0	10.4	12.5
Mississippi River at Thebes, Ill.								
Suspended silt and clay	1.82	3.64	.21	.36	57.60	15.2	10.1	11.8
Bottom mud	1.17	1.88	.16	.18	48.82	17.8	8.5	12.2
Ohio River at Olmsted, Ill.								
Suspended silt and clay	2.08	4.52	.24	.46	60.2	13.5	10.1	11.5
Bottom mud	1.44	3.02	.16	.27	48.5	10.5	13.0	13.1

A recent advance in ^{13}C-NMR spectrometry is the development of large-sample, magic-angle spinners that provide enhanced signal-to-noise ratios in the spectra (Zhang and Maciel, 1990). This new technology was applied to both treated and untreated suspended silts sampled at St. Louis, Mo. The results are shown in figure 18. Results on the untreated sample (spectrum A) are superior to previous results obtained with the small-volume, magic-angle spinner used for the colloids from sampling cruise 1 (fig. 5); and results on the treated sample (spectrum B) gave much better resolution of peaks than the untreated sample (spectrum A). The spectral band-broadening problem caused by iron in the untreated sample was solved by the treatment procedure, and the peak resolution and interpretation of the spectra were facilitated in spectrum B.

The organic matter of this silt and clay fraction appears to be a mixture of aliphatic hydrocarbons (peak at 30 ppm), carbohydrates (peak at 80 ppm), aromatic hydrocarbons (peak at 130 ppm), and carboxyl and amide functional groups (peak at 175 ppm) (fig. 18, spectrum B). Organic amines that occur near 45 ppm may have been lost from the sample by the treatment process. There was no detectable destruction of carbohydrates by acid hydrolysis during the treatment procedure in comparing the ratio of carbohydrate peaks to other peaks in the treated and untreated samples.

This knowledge of organic-matter structure can now be applied to studies of contaminant association with sediment. For example, nonionic, nonpolar organic contaminants such as PCB's are known to partition into aliphatic and aromatic hydrocarbon components of organic matter, and trace-metal contaminants are known to bind with carboxyl and amide functional groups.

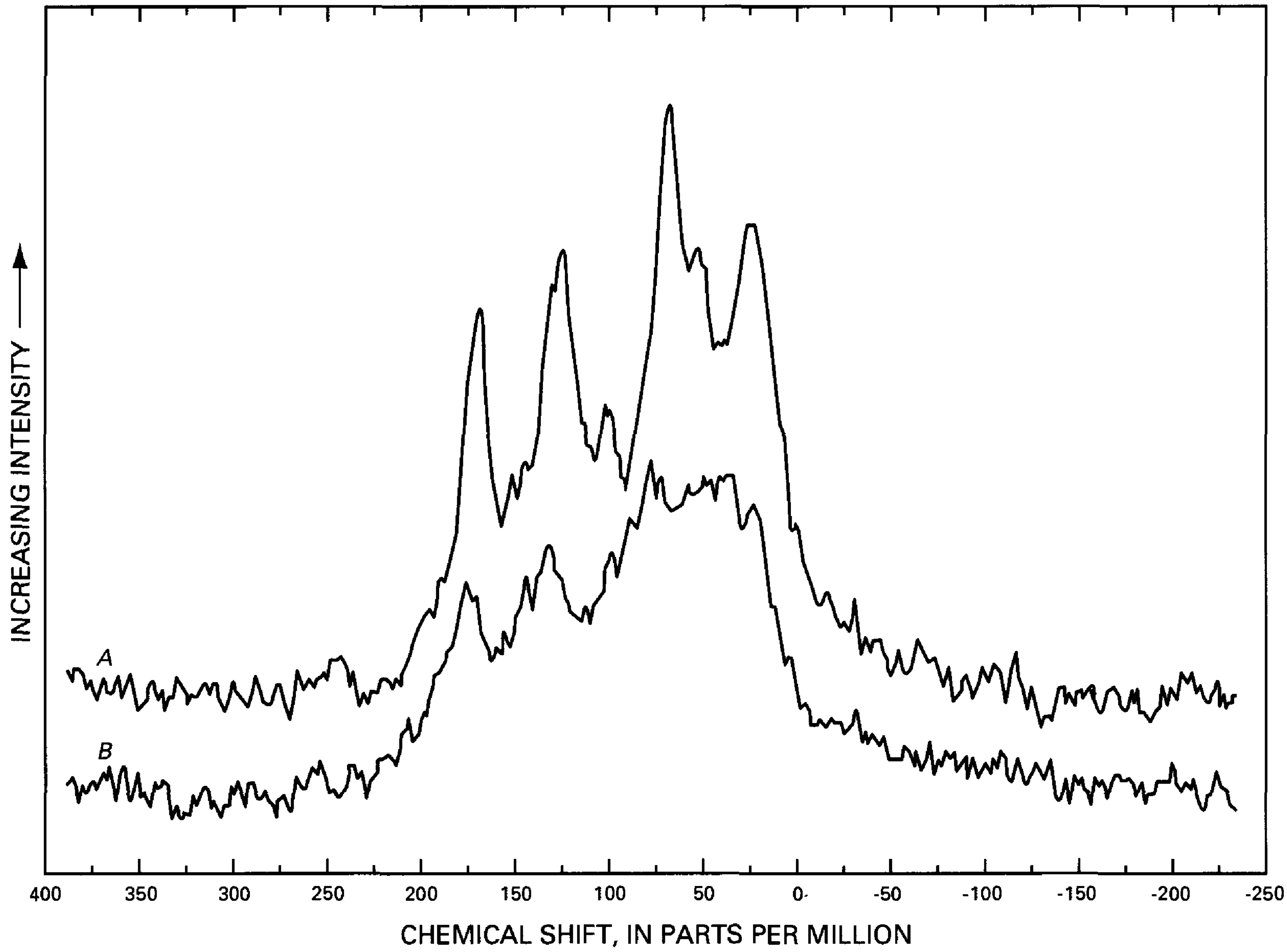

Figure 18.—Solid-state ^{13}C-nuclear magnetic resonance spectra of (A) untreated and (B) treated for iron removal of suspended silt and clay sampled from the Mississippi River at St. Louis, Mo., in June 1990.

CONCLUSIONS

Following are seven significant conclusions from this study that are arranged in order of decreasing importance:

1. The organic-carbon component in both the mineral-colloid fraction and organic-colloid fraction appears to be transported conservatively in river reaches and at river confluences where there are significant gains or losses in carbon in the silt fractions. It appears that organic-matter content is the major component that prevents colloid aggregation in Mississippi River suspended particulates of colloidal dimensions.
2. The discovery of polyethylene-glycol residue as the major anthropogenic organic contaminant in the Mississippi River (Leenheer and others, 1991).
3. Characterization of the entire dissolved organic-matter component under varying hydrologic and seasonal conditions revealed it originated from a variety of allochthonous and autochtonous sources. The isolation and characterization of the hydrophilic component of dissolved organic matter indicated oxidized carbohydrates as the major component of hydrophilic acids. Dissolved organic matter is usually transported in a conservative manner except during low-water periods of the summer when biodegradation processes were significant.
4. Development of a method to obtain solid-state, ^{13}C-NMR spectra of organic matter in sediments revealed that sedimentary organic matter consists of a mixture of lipids, carbohydrates, proteins, and humic substances. Progress in organic geochemical studies of sediments is partially dependent on advances in NMR spectrometry.
5. Characterization of sedimentary organic matter revealed that proteins, that are important in trace-metal binding, and lipids, that are important in nonpolar contaminant partitioning interactions, are major constituents of sedimentary organic matter. Proteins, in particular, are not generally recognized as being important as humic substances in aquatic sediments.
6. The data in the report provide extensive evidence that (A) Pools and reservoirs are traps for sedimentary organic matter of allochtonous origin, and (B) Navigation pools and reservoirs export organic material of autochthonous origin that is rich in nitrogen. These findings are not new and unique, but there is good quantitative transport data of organic carbon and nitrogen under varying hydrologic conditions that may help resource managers better understand the management of the Mississippi River system.
7. The quantitation of the bacterial organic colloid component of organic matter transported in the river. The magnitude of the mass of bacteria and bacterial organic carbon being transported is a significant finding. The bacterial carbon transport appears to be more conservative than the organic carbon associated with the silt fraction.

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