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GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1817-F

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ORGANIC SUBSTANCES IN WATER

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ABBREVIATIONS

CAE .... Carbon alcohol extract.
CCE .... Carbon chloroform extract.
C:N .... Carbon to nitrogen ratio.

DOC	Dissolved organic carbon.
ETR	Equal transit rate.
ft^3/s	Cubic feet per second.
kg	Kilogram.
KN	Kjeldahl nitrogen.
lb/in^2	Pounds per square inch.
mg/l	Milligrams per litre.
ml	Millilitres.
μm	Micrometres.
SIC	Suspended inorganic carbon.
SOC	Suspended organic carbon.

ORGANIC CARBON AND NITROGEN CONCENTRATIONS AND ANNUAL ORGANIC CARBON LOAD OF SIX SELECTED RIVERS OF THE UNITED STATES

By Ronald L. Malcolm and Walton H. Durum

ABSTRACT

The organic carbon load during 1969–70 of each of the six rivers in this study is substantial. The 3.4-billion-kilogram (3.7-million-ton) and 47-million-kilogram (52-thousand-ton) annual organic carbon loads of the Mississippi River and the Brazos River (Tex.), respectively, were approximately equally distributed between dissolved and suspended phases, whereas the 725-million-kilogram (79.8-million-ton) organic load of the Missouri River was primarily in the suspended phase. The major portion of the 6.4-million-kilogram (7.3-thousand-ton) and the 19-million-kilogram (21-thousand-ton) organic carbon loads of the Sopchoppy River (Fla.) and the Neuse River (N.C.), respectively, was in the dissolved phase.

DOC (dissolved organic carbon) concentrations in most rivers were usually less than 8 milligrams per litre. SOC (suspended organic carbon) concentrations fluctuated markedly with discharge, ranging between 1 and 14 percent, by weight, in sediment of most rivers. DOC concentrations were found to be independent of discharge, whereas SOC and SIC (suspended inorganic carbon) concentrations were positively correlated with discharge. Seasonal fluctuations in DOC and SOC were exhibited by the Missouri, Neuse, Ohio, and Brazos Rivers, but both SOC and DOC concentrations were relatively constant throughout the year in the Mississippi and Sopchoppy Rivers.

The carbon-nitrogen ratio in the sediment phase of all river waters averaged less than 8:1 as compared with 12:1 or greater for most soils. This high nitrogen content shows a nitrogen enrichment of the stream sediment over that in adjacent soils, which suggests that different decomposition and humification processes are operating in streams than in the soils.

The abundance of organic material in the dissolved and suspended phase of all river waters in this study indicate a large capacity factor for various types of organic reactivity within all streams and the quantitative importance of organic constituents in relation to the water quality of rivers and streams.

INTRODUCTION

Organic substances in river waters and river sediments are very diverse in quality, quantity, and source. Hundreds of new organic compounds are synthesized each year, with many of them finding their way into the streams and other surface waters as a result of man's activities. Some of the major sources of these organic substances include plant and animal debris deposited in a stream from terrestrial sources, wastes from municipal treatment facilities, industrial wastes, and eutrophic activity within the stream itself.

This complex assemblage of carbonaceous organic material has been found to significantly influence water quality. Organic substances found in stream water can affect the distribution of ions between water and sediment phases carried in the stream (Baas-Becking and Moore, 1959; Jenne and Wahlberg, 1968; Jenne, 1968; Glenn, 1973; Jenne, 1976). Organic substances can solubilize clay minerals (Malcolm and others, 1969), can strongly complex certain trace metals (Malcolm and others, 1969; Malcolm, 1972; Schnitzer and Kahn, 1972), and can have a high cation-exchange capacity as compared with clay minerals (Kennedy, 1965; Malcolm and Kennedy 1970; Schnitzer and Kahn, 1972).

Organic materials are food sources for the diversity of heterotrophic microorganisms which thrive in streams. The nitrogen and phosphorous components of organic substances on sediment particles and dissolved in water are significant sources of nutrients for algae and other autotrophic organisms. DOC (dissolved organic carbon) has also been associated with nuisance algae blooms (Wright and Mills, 1967; King, 1970; Forester, 1972).

Because of the various roles and reactivity of organics within the stream, the amount of these substances must be determined in representative streams such that the magnitude of the preceding reactions can be established. The carbon content of surface water has not been studied in a systematic manner, largely because of the poor accuracy and the lack of precision of chemical methods. Recent advances in technology with various types of carbon analyzers has enabled the accurate determination of all organic carbon in the dissolved and sediment phases in water.

Brooks (1970) found that the DOC concentrations in the Brazos River ranged from 2.8 to 7.0 mg/l during the spring of 1970. POC (particulate organic carbon) varies between 1 and 16 mg/l, but was generally less than DOC concentrations. During a 1-year study, Weber and Moore (1967) reported that the DOC of the Little Miami River at Cincinnati, Ohio, averaged 6.4 mg/l and showed no seasonal cycle. Fredericks and Sackett (1970) determined the mean DOC and POC concentrations in the Gulf of Mexico to be less than 1 mg/l and 0.2 mg/l, respectively. POC (particulate organic carbon) and SOC (suspended organic carbon) are essentially synonomous terms, except for method dependency. POC has been associated with glass-fiber filtration, whereas SOC has been associated with plastic or metal filtration. POC values should be slightly lower than SOC values because most glass fiber filters have a larger average pore size (typically 2 μm (micrometres)) whereas plastic and metal membrane filters are typically 0.45 μm with a narrow range of pore sizes. Therefore, POC values are usually lower than SOC values because some of the particulate organic material between 0.45 μm and 2 μm passes through the glass filter and is included in the DOC phase.

DOC and SOC are quantitative organic water quality parameters, whereas CCE (carbon chloroform extract) and CAE (carbon alcohol extract) are only qualitative indices of organic water quality in the dissolved phase. Suspended sediment is not usually included in the CCE or CAE determination. The CCE and CAE methods are based upon the extraction of organic substances onto activated charcoal columns with subsequent elution from the charcoal with chloroform or alcohol. Such methods are only qualitative because the relative percentage of all the organic compounds in the water which are sorbed by the charcoal is not determined. The relative recovery of the sorbed organic compounds from the activated charcoal by solvent elution is also not determined.

ACKNOWLEDGMENTS

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APPROACH AND OBJECTIVES

The Missouri, Mississippi, Ohio, Brazos (Tex.), Neuse (N.C.), and Sopchoppy (Fla.) Rivers are representative streams found within different climatic regions within the United States. Inorganic water chemistry, discharge, sediment load, and other hydrologic parameters of these rivers are routinely monitored by the U.S. Geological Survey. Because Survey personnel must regularly visit these monitoring stations for equipment maintenance and water sampling, this situation enabled the periodic additional collection of suspended-sediment and water samples for organic analyses.

The overall objective of this study is to learn more about the quantity and quality of organic matter as organic carbon and nitrogen that is transported by major streams of the United States. During the 1-year reconnaissance study, it was intended that sufficient data be collected for a given stream to establish changes in organic concentrations and load with season of the year and discharge, to evaluate the relative importance of the dissolved organic load to the particulate organic load, and to estimate the annual dissolved and suspended organic load of the river.

EXPERIMENTAL METHODS

SAMPLE COLLECTION

The six participating U.S. Geological Survey District Offices were asked to collect a total of 15-20 composite ETR (equal transit rate) samples from each of the selected streams over a period of 1 year. Samples were to be taken whenever large changes in streamflow or chemistry occurred such that possible changes in organic load and distribution would be detected.

The sampling sites were as follows: Neuse River near Goldsboro, N.C. (ETR sample from bridge); Brazos River at Richmond, Tex. (ETR sample from bridge); Ohio River at Metropolis, Ill. (ETR sample from Paducah Dam); Mississippi River near Luling Ferry, La., St. Francisville, La., and Belle Chasse, La. (ETR sample obtained by pumping from boat); and Missouri River at Nebraska City, Nebr. (pumping point sample from 4 ft above the bed at the quality water monitor); and the Sopchoppy River near Sopchoppy, Fla. (ETR sample from bridge). An index map giving the locaion of the six rivers and respective sampling sites is shown in figure 1.

SAMPLE FILTRATION AND PRESERVATION

A 4- to 10-litre ETR sample was collected at each sampling. The exact volume of each sample, date and time of collection, river temperature and gage height, and name of collector were noted on the sample tag. The ETR sample was immediately pressure filtered at the site or taken to the laboratory with an elapsed transit time of less than 6 hours. The pressure filter used was as described by Skougstad and Scarbro (1958). The plexiglass barrel was fitted with a 4-inch 0.45 μm vinyl metracel filter. Maximum filtration pressure by tire pump or compressed nitrogen never exceeded 40 lb/in^2 (pounds per square inch). The pressure filter assembly was refilled with unfiltered sample as necessary and the first 75 percent of the sample filtrate was discarded. Then 65–75 ml of sample filtrate was collected in a 100-ml plastic bottle, labeled, and immediately frozen. The vinyl metrical membrane filter was leached with 2 or more litres of sample before the filtrate was collected to completely free the new filter of detergent film, which contaminated the first portion of the filtrate with organic carbon. Filtration continued until the entire sample was filtered. Sample containers were rinsed with a small amount of filtrate to assure complete transfer of the sediment to the filter membrane. The moist membrane filter with the suspended sediment was placed in a petri dish, labeled, sealed with tape, and immediately frozen.

After a number of samples were processed, the samples were packed in Dry Ice and sent to the Denver laboratory by air freight. The sediment pads were thawed and the sediment carefully removed from the filter pad into deionized water with gentle rubbing, using a rubber policeman.

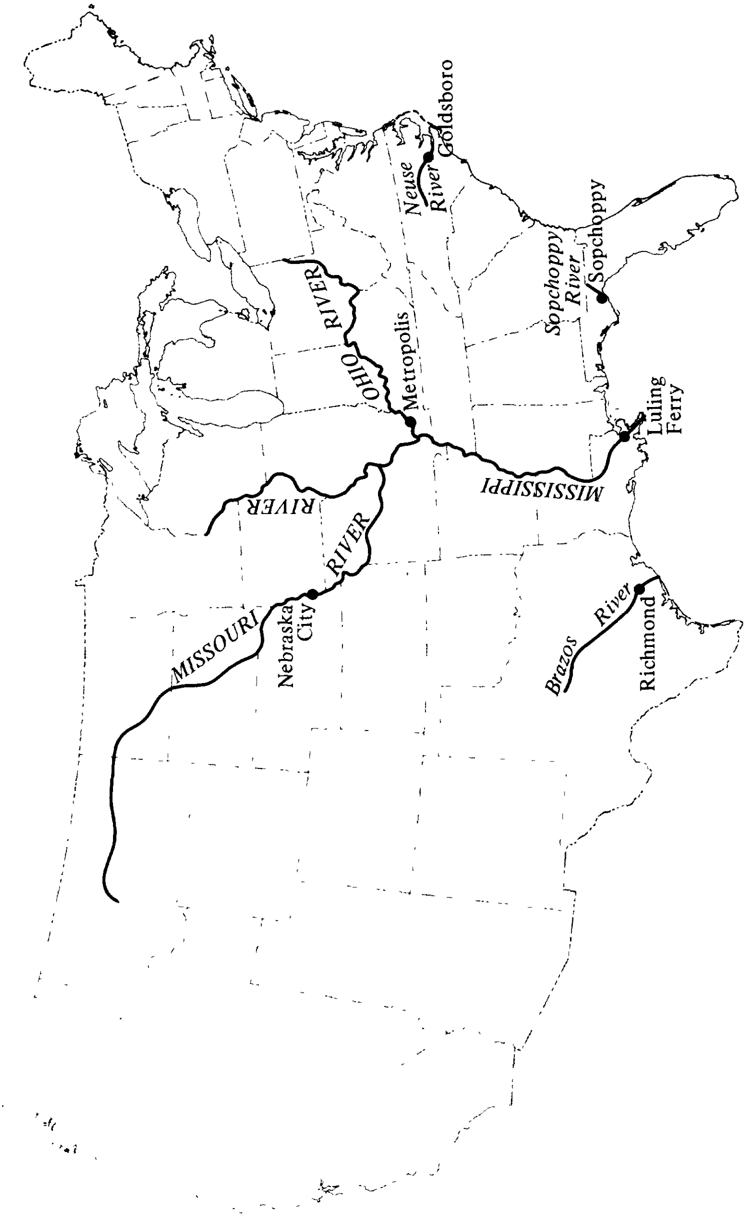

FIGURE 1.—Location of the six rivers and respective sampling sites of this report.

Greater than 99 percent of the sediment can be removed by this manner without filter contamination if the sediment cake is not allowed to dry on the filter. The suspended sediments were freeze-dried, weighed, and then stored in plastic vials.

The presently recommended method of organic carbon sampling (Malcolm and McKinley, 1972), using a stainless steel filter assembly, a silver-membrane filter, and a glass collection bottle was not employed because it was developed subsequent to this study. With the sampling and preservation techniques used, the only limitation of the data is that the DOC values should be considered to be minimal because some limited sorption of DOC on the plastic containers probably occurred.

SAMPLE ANALYSES FOR CARBON AND NITROGEN

DOC in the sample filtrates was determined by the Oceanography International Carbon Analyzer.[1] Duplicate 10-ml aliquots of each sample were acidified, purged free of inorganic CO_2 with nitrogen, then sealed in a glass ampule. Complete oxidation of organic carbon to CO_2 was achieved by a 24-hour digestion with persulfate at 170°C (Celsius). The glass ampule was broken in a closed system, and CO_2 was determined by infrared spectroscopy. The filtered water samples in the plastic bottles from which the aliquots were taken for DOC determinations were kept frozen until time of analysis. The samples were quickly thawed and shaken for 3 minutes before aliquots were taken. Contact time between the unfrozen water sample and the plastic container was minimized to limit the sorption of DOC on the container.

SOC of the suspended sediment samples was determined as a difference between total carbon on a Leco carbon analyzer[1] and inorganic carbon on a modified Van Slyke gasometric technique (Malcolm and others, 1973). KN (Kjeldahl nitrogen) contents of the suspended-sediment samples were determined by the semimicro Kjeldahl method of McKenzie and Wallace (1954). Kjeldahl nitrogen values are believed to closely approximate organic nitrogen values for the stream sediments studied, inasmuch as fixed or exchangeable NH_4^+ is believed to be small.

Suspended sediment samples were so small for the Sopchoppy River samples (14-200 mg) such that carbon and nitrogen contents could not be obtained by the Leco and semimicro Kjeldahl techniques. Carbon and nitrogen analyses for the samples were determined by microtechniques by Huffman Laboratories, Wheat Ridge, Colo.

CALCULATIONS

In order to sample the selected streams during a variety of flow conditions, the date of sampling within each month was variable. For the calculation of daily load parameters, the sample taken on a given date was

[1]Mention of specific products is for identification only and does not constitute endorsement by the U.S. Geological Survey.

assumed to be representative of half of the period between sampling intervals. The DOC load, in tons per day, for each stream was computed by multiplying the daily DOC concentration and daily mean discharge. The SOC and SIC (suspended inorganic carbon) loads, in tons per day, were calculated from the sediment concentration in the suspended-sediment water sample, the percent organic or inorganic carbon within the sediment phase, and the daily mean discharge. Monthly loads were the summation of daily loads over the month period. Annual loads for the Brazos, Missouri and Neuse Rivers were calculated from the first 12 months of data collection. Annual loads for the Mississippi, Ohio, and Sopchoppy Rivers were prorated for a 12-month period, based upon 9, 10, and 11 months of data, respectively. An annual DOC load for the Ohio River was not calculated because the DOC data for the first 5 months of the sampling period were lost during analysis.

RESULTS AND DISCUSSION

Carbon and nitrogen concentrations in water and suspended sediment for the six streams in this study are given in tables 1 and 2. Average DOC concentrations in the Brazos, Mississippi, Missouri, and Ohio Rivers are of similar magnitude (between 3 and 4 mg/l), but the Neuse River is somewhat higher at 7.1 mg/l. DOC concentrations in the Mississippi, Neuse, and Ohio Rivers are relatively constant throughout the year, whereas DOC concentrations for the Sopchoppy River are highly variable and show no definite trends within each season of the year.

DOC concentrations show a definite trend to increase during the winter months in the Brazos and Missouri Rivers. As shown in table 1, DOC concentrations in the Brazos River increase gradually each month from 1.7 mg/l during October to more than 7 mg/l during February and then decrease gradually to near 2 mg/l from April to June. The low DOC concentrations during the late spring, summer, and early fall may be due to bacterial and algal assimilation of DOC during more eutrophic stream conditions. The postulation is supported by the facts that (1) algal tissue was evident in the suspended sediment samples during the summer and fall, and (2) SOC and KN parameters increased significantly in the suspended sediment phase during the same period. A similar trend was observed for the Missouri River with DOC concentrations increasing gradually from between 2 and 3 mg/l in late fall to a maximum of about 9 mg/l during March of both 1969 and 1970, and then decreasing to about 3 mg/l during the summers. The DOC minima were not related to maxima in SOC or KN concentrations in the Missouri River, nor with observation of bacterial or algal growth. High DOC concentrations during the spring are probably related to the large number of feedlots in the local area where the river was sampled. Feedlot wastes accumulate in the frozen state during the winter, but thaw rapidly during the warmer spring rainy season. A large flush of dissolved organic constituents from these wastes

TABLE 1.—*Carbon and nitrogen concentrations in water and suspended sediment for selected streams*

Date	Time	Discharge (ft^3/s)	Sediment concentration (mg/l)	Percent by weight			DOC[1] (mg/l)	SOC (mg/l)
				SOC in sediment	KN in sediment	SIC in sediment		
08114000 Brazos River at Richmond, Texas (Lat 29° 34' 56" Long 95° 45' 27")								
7-24-69	1200	1,760	58	4.11	0.45	1.70	(a) 2.7	2.4
							(b) 3.2	
8-19-69	1240	1,520	23	13.8	2.19	2.19	(a) 2.9	3.2
							(b) 2.9	
9-16-60	1220	1,070	44	11.4	.95	1.70	(a) 2.5	5.0
							(b) 2.3	
10-08-69	1530	1,070	22	11.2	1.52	1.48	(a) .5	2.5
							(b) 1.7	
10-20-69	1100	1,360	36	7.13	.95	1.88	(a) 1.7	2.6
							(b) 1.8	
11-03-69	1200	5,230	315	1.54	.25	1.26	(a) 3.2	4.9
							(b) 3.1	
12-18-69	0800	4,900	258	1.33	.26	.57	(a) 4.5	3.4
							(b) 5.3	
1-15-70	0840	6,200	183	.79	.31	1.00	(a) 4.5	1.4
							(b) 4.8	
2-19-70	1230	4,600	111	2.04	.33	0.12	(a) 5.2	2.3
							(b) 7.7	
3-16-70	1330	20,800	909	.46	.20	1.39	(a) 4.7	4.2
							(b) 4.7	
4-21-70	1230	15,300	402	1.54	.19	.57	(a) ---	6.2
							(b) 2.6	
6-01-70	1200	15,700	779	.70	.20	1.69	(a) 2.1	5.5
							(b) 2.4	

73734200 Mississippi River near St. Francisville, Louisiana (Lat 30° 45' 30" Long 91° 23' 45")								
1-28-69	1100	480,000	251	1.76	----	0.10	3.9	4.4
2-20-69	1100	997,000	147	2.53	0.25	.20	2.7	3.7
3-25-69	0930	428,000	386	1.33	.15	.20	4.1	5.1
4-07-69	1030	645,000	220	1.78	.22	.10	3.1	3.9
6-05-69	1400	518,000	272	2.09	.22	.15	3.6	5.7
9-09-69	1030	196,000	136	1.79	.39	.15	2.8	2.4
6-17-70	1030	-------	326	1.76	.42	.15	4.1	5.7
73744000 Mississippi River at Luling Ferry, Louisiana (Lat 29° 56' 19" Long 90° 21' 49")								
1-30-69	1300	551,000	---	----	----	----	3.1	-----
3-27-69	0955	420,000	111	2.32	0.27	0.20	2.2	2.6
4-14-69	0900	644,000	282	2.16	.19	.10	2.9	6.1
6-05-69	1100	518,000	82	2.47	.26	.15	3.8	2.0
9-11-69	0930	197,000	31	3.55	.45	.15	2.8	1.1
6-25-70	1030	-------	181	1.61	.42	.15	3.7	2.9
7374525 Mississippi River near Belle Chasse, Louisiana (Lat 29° 51' 25" Long 89° 58' 40")								
1-30-69	1100	551,000	218	1.96	0.20	0.10	4.5	4.3
2-27-69	1100	894,000	358	1.64	.16	.20	4.2	5.9
3-27-69	1305	420,000	109	2.86	.21	.20	3.6	3.1
4-14-69	1125	644,000	245	1.91	.19	.10	2.7	4.7
6-05-69	0900	518,000	94	2.45	.18	.15	3.4	2.3
9-11-69	1115	197,000	35	4.57	.58	.15	2.7	1.6
06807000 Missouri River at Nebraska City, Nebraska (Lat 40° 40' 55" Long 95° 50' 48")								
1-20-69	1100	23,000	8.3	8.20	1.20	.33	4.5	0.7
2-12-69	1015	24,000	4.1	10.89	1.05	.34	7.4	0.5
3-19-69	1035	70,200	3,068	6.25	.15	.16	9.0	190
4-11-69	1430	99,000	1,076	2.53	.24	.31	3.5	27
5-19-69	1300	53,800	60	4.31	.24	.38	3.6	2.6
6-20-69	1300	42,100	215	2.36	.31	.32	3.2	5.1
7-31-69	1120	48,600	1,152	1.84	.14	.32	1.9	21

See footnote at end of table.

TABLE 1.—*Carbon and nitrogen concentrations in water and suspended sediment for selected streams*

Date	Time	Discharge (ft^3/s)	Sediment concentration (mg/l)	Percent by weight			DOC (mg/l)	SOC (mg/l)
				SOC in sediment	KN in sediment	SIC in sediment		
9-30-69	1110	53,400	844	1.28	.09	.31	2.7	11
10-21-69	1000	49,600	904	1.45	.11	.35	2.4	13
11-28-69	1030	39,100	3,986	.55	.09	.27	4.9	22
12-30-69	1300	20,000	66	4.30	.42	.23	1.9	2.8
1-26-70	1100	19,000	73	3.51	.48	.34	6.0	2.6
2-24-70	1100	36,800	913	1.53	.31	.34	6.3	14
3-12-70	1300	33,600	718	1.02	.27	.34	8.4	7.3
4-08-70	1400	43,600	980	.71	.16	.32	4.1	7.0
5-22-70	1105	38,500	370	1.07	.35	.50	3.6	4.0
6-09-70	1130	41,200	484	1.27	.32	.50	4.8	6.1
02089000 Neuse River near Goldsboro, North Carolina (Lat 35° 20' 15" Long 77° 59' 50")								
6-12-69	0930	1,170	62	5.61	0.63	0	5.6	3.5
7-31-69	1145	855	49	7.23	----	0	8.0	3.5
8-11-69	1110	8,420	28	9.89	0.83	0	9.2	2.8
9-25-69	1030	3,500	41	7.71	----	0	10	3.2
10-29-69	1200	535	14	10.72	.84	0	8.8	1.5
11-26-69	1000	836	8.3	13.28	.95	0	5.3	1.1
12-29-69	1100	4,150	89	3.71	.71	0	7.3	3.3
1-29-70	1430	1,400	23	10.43	.88	0	4.1	2.4
2-26-70	1130	7,670	2.5	6.66	.63	0	8.8	0.2
3-30-70	1030	4,520	28	6.99	1.31	0	7.2	2.0
4-29-70	1045	2,630	61	8.03	1.15	0	8.9	4.9
5-21-70	0930	665	43	9.76	2.51	0	4.9	4.2
6-10-70	1130	328	28	13.92	3.92	0	4.8	3.9

03611500 Ohio River at Metropolis, Illinois (Lat 37° 8' 51" Long 88° 44' 27")								
2-04-69	1250	738,000	123	3.58	0.32	0.16	----	4.4
2-18-69	1100	532,000	107	3.45	.39	.16	----	3.7
3-05-69	1320	137,000	34	4.05	.41	.16	----	1.4
4-02-69	1025	244,000	44	4.81	.62	.16	----	2.1
5-05-69	1145	209,000	42	3.39	.41	.15	----	1.4
6-03-69	1225	113,000	50	3.75	.53	.15	----	1.9
6-17-69	1015	111,000	37	3.58	.42	.15	----	1.3
7-03-69	1215	185,000	48	2.65	.32	.15	2.7	1.3
7-16-69	1100	171,000	23	3.51	.44	.20	4.0	0.8
8-04-69	1215	84,500	49	3.37	----	.20	2.3	1.6
9-03-69	1245	66,800	14	6.09	.93	.20	1.2	0.9
10-02-69	1245	64,400	22	4.62	.66	.30	3.4	1.0
11-04-69	1340	80,700	43	3.50	.49	.30	3.4	1.5
11-21-69	1000	152,000	42	4.74	.49	.30	2.5	2.0
12-03-69	1320	239,000	61	3.26	.39	.30	5.2	2.0
02327100 Sopchoppy River near Sopchoppy, Florida (Lat 30° 07' 45" Long 84° 29' 40")								
5-28-69	1800	27	2.9	40.0	1.60	0	17	1.2
7-09-69	1000	1.8	2.8	28.4	3.87	0	6.2	0.8
7-23-69	1720	804	5.1	36.6	2.04	0	20	1.9
9-09-69	1200	24	3.5	37.6	4.68	0	36	1.3
10-13-69	1020	48	0.5	35.3	----	0	19	0.2
11-13-69	1310	4.0	0.5	35.3	----	0	10	0
12-17-69	----	33	6.7	38.4	7.16	0	40	2
1-15-70	----	358	3.8	32.5	4.49	0	52	1
2-18-70	----	261	14.2	33.3	4.44	0	41	4

[1] DOC values for the Brazos River as given for filtration at 10 lb/in^2 (a) and 40 lb/in^2 (b).

TABLE 2.—*Average carbon and nitrogen concentrations in water and suspended sediment for selected streams*

Stream	DOC (mg/l)	SOC (mg/l)	Percentage SOC in sediment	Percentage KN in sediment	SOC/KN ratio or C/N ratio	Percentage SIC in sediment
Brazos	3.3	3.6	4.67	0.65	7.2	1.30
Mississippi	3.4	3.8	2.28	.28	8.1	.15
Missouri	4.6	20	3.12	.35	8.9	.34
Neuse	7.1	2.8	9.00	1.30	6.9	0
Ohio	3.1	1.8	3.93	.49	8.0	.20
Sopchoppy	27	1.6	35.3	4.04	8.7	0

should be expected immediately after the spring thaw. Other explanations for the high spring DOC concentrations may be due to the accumulation of organic airborne pollutants in winter snowfall or the decomposition of organic constituents in soils of the area which would flush during the spring season.

There is an indication that the Mississippi River is more eutrophic in the late summer than other seasons. SOC and KN concentrations in the sediment were substantially higher during September of 1969 and 1970 than for other periods. DOC concentrations were also slightly lower than average during this period. Unfortunately, Mississippi River sampling was not continued during the fall of 1969 or 1970; therefore, the postulated higher eutrophic activity could not be further substantiated.

All samples for DOC from the Brazos River were pressure filtered at both 10 lb/in^2 and 40 lb/in^2 to determine if microbial cell rupture occurred at higher filtration pressures, which would result in a concurrent increase in DOC concentrations. Statistical evaluation of the data indicate no significant differences between DOC concentrations at 10 lb-in^2 versus 40 lb/in^2 filtration pressures. From personal discussions with microbiologists and algalogists, it is generally accepted that most bacterial and algal cells will not rupture at such low pressures as 10–40 psi when the organisns are in a well-cushioned aqueous environment. There is considerable danger of cell rupture by shear forces when the organisms are forced onto the filter membrane at high pressures. This condition would exist during the very terminal period of sample filtration. Because none of the DOC samples were taken at the very end of the filtration, there should be no problem of DOC concentration being pressure dependent.

The average SOC concentrations in suspended sediment are similar in magnitude (between 2 and 4 percent) for the Brazos, Mississippi, Missouri and Ohio Rivers, but the Neuse River is somewhat higher (9.0 percent), and the Sopchoppy River is significantly higher (35.3 percent). KN percentages follow the same trend as SOC in the respective rivers. SOC and KN percentages are relatively constant during the year for the Ohio, Mississippi, and Sopchoppy Rivers but are highly variable in the Brazos, Neuse and Missouri Rivers where greater than tenfold concentration changes occur.

Although SOC and KN percentages vary greatly the average C:N or SOC:KN ratios in all river sediments are relatively constant between 7-9 with an average of 8.0 for all river samples. Contrastingly, C:N ratios for soils in a continental drainage basin such as the Mississippi River would be much higher, in the range of 9:1 to 25:1. The finding of a low C:N ratio in stream sediments is consistent with many previous unpublished analyses performed in our laboratory. This finding further substantiates our working hypothesis that the major portion of the organic constituents in stream sediments are either of stream origin or have been considerably reworked or reconstituted by the stream microflora such that the natural organics are substantially different in chemical composition from soil organic material. The greater concentrations and availability of nitrogen within the stream enable a rapid incorporation of nitrogen into microbial cells and detrital organic material. This phenomenon is especially profound in the Sopchoppy River sediment where the average C:N ratio is 8.7, but is commonly 30–40:1 in the soils of the area.

SIC percentages for the Neuse and Sopchoppy Rivers are zero as expected for these acid river waters. The small SIC values for the Brazos and Missouri Rivers are a reflection of the calcareous soils and parent materials within each watershed. Trace SIC values in the Mississippi River are the result of neutralization of part of the calcareous sediment from some of its tributaries and spillage of limestone and dolomite during river-barge transport. Trace SIC values for the Ohio River are believed to be almost entirely due to spillage from barges transporting limestone and dolomite.

Monthly and annual discharges of water, organic carbon, and inorganic carbon for selected streams are given in tables 3 and 4, respectively. DOC loads for the Sopchoppy and Neuse Rivers are consistently higher than the SOC load during every month of the year. The DOC load accounts for 96 percent and 70 percent of the total organic load in the respective rivers. This finding was as expected for the tea-colored Sopchoppy River but was not postulated for the Neuse River.

DOC, SOC, and water discharges for the Neuse River are relatively constant throughout the period 1969–70, with generally no greater than fourfold variation in any one of the parameters. The relatively constant monthly discharge of the Neuse River is due to the relatively uniform distribution of rainfall throughout the year and because it is not a controlled-flow lock-and-dam stream, such as the Ohio, Missouri, or Mississippi Rivers. The combination of large reserves of available soil moisture and high mean annual temperature for the watershed support a luxuriant native vegetative cover for the gently sloping landscape during most of the year. Therefore, soil erosion as a source of SOC would be reduced to a minimum. The source of DOC load is believed to be a combination of natural factors and municipal discharges from the upstream cities of Durham and Raleigh, N.C.

TABLE 3.—*Monthly discharge of water, inorganic carbon, and organic carbon for selected streams*

[Leaders (...) indicate no data available]

Period	Discharge (millions of tons)	DOC (tons)	SOC (tons)	SIC (tons)
08114000 Brazos River at Richmond, Tex. (lat 29°34'56", long 95°45'27")				
1969				
July	234	703	553	229
August	132	218	408	83
September	159	435	730	107
October	102	226	286	98
November	199	679	930	726
December	376	1,840	1,290	553
1970				
January	455	2,140	660	833
February	395	2,550	892	75
March	1,860	8,880	7,550	22,600
April	1,090	3,040	6.510	3,540
May	836	2,010	4,770	7,960
June	575	1,320	3,130	7,590
7374525 Mississippi River near Belle Chasse, La. (lat 29°51'25", long 89°58'40")				
1969				
January	38,100	145,000	166,000	8,960
February	69,400	250,000	322,000	28,400
March	44,500	151,000	184,000	19,900
April	56,200	156,000	270,000	14,700
May	58,200	197,000	236,000	13,500
June	31,900	115,000	118,000	7,160
July	42,400	143,000	133,000	8,050
August	25,900	72,500	44,300	2,620
September	17,400	48,700	29,700	1,760
06807000 Missouri River at Nebraska City, Nebr. (lat 40°40'55", long 95°50'48")				
1969				
February	1,780	13,200	790	050
March	3,640	31,900	180,000	17,200
April	6,290	22,900	171,000	21,000
May	4,290	15,400	11,100	880
June	3,990	12,900	19,300	2,720
July	4,400	10,300	69,100	11,800
August	4,650	8,970	96,900	17,000
September	4,590	12,400	49,600	13,200
October	4,410	10,900	55,100	13,600
November	3,760	15,800	73,200	32,500
December	2,300	7,960	34,600	48,000
1970				
January	1,540	6,930	4,110	4,490
February	2,210	13,700	23,600	5,030
March	3,070	22,500	23,800	8,220
April	3,460	14,100	23,800	11,400
May	3,340	12,200	13,500	6,250

TABLE 3.—*Monthly discharge of water, inorganic carbon, and organic carbon for selected streams*—Continued

Period	Discharge (millions of tons)	DOC (tons)	SOC (tons)	SIC (tons)
02089000 Neuse River near Goldsboro, N.C. (lat 35°20′15″, Long 77°59′50″)				
1969				
June	129	721	450	0
July	123	932	429	0
August	258	2,350	736	0
September	101	1,050	323	0
October	107	1,050	277	0
November	116	827	152	0
December	138	954	387	0
1970				
January	148	843	414	0
February	330	2,130	422	0
March	247	1,920	333	0
April	284	2,240	907	0
May	90.2	633	412	0
03611500 Ohio River at Metropolis, Ill. (lat 37°8′51″, long 88°44′27″)				
1969				
February	44,200	......	175,000	7,800
March	15,500	......	26,100	950
April	32,000	......	54,600	1,000
May	19,500	......	31,600	670
June	11,400	......	16,400	740
July	14,000	46,300	15,600	900
August	10,500	19,300	13,900	720
September	6,190	12,800	5,810	270
October	7,360	25,000	9,390	720
November	11,400	35,100	21,300	1,530
December	16,000	82,900	31,900	2,920
02327100 Sopchoppy River near Sopchoppy, Fla. (lat 30°07′45″, long 84°29′40″)				
1969				
May	1.38	23.5	1.60	0
June	.34	5.24	.38	0
July	30.8	610	57.2	0
August	48.5	1,270	80.4	0
September	42.9	1,430	48.7	0
October	7.84	147	1.39	0
November	.40	4.4	.10	0
December	6.88	275	17.7	0
1969				
January	26.3	1,360	33.3	0
February	18.1	763	9.96	0

TABLE 4.—*Annual organic carbon load, inorganic carbon load, and discharge for the Sopchoppy, Neuse, Brazos, Missouri, Ohio, and Mississippi Rivers*

River	Discharge (millions of tons)	DOC (tons)	SOC (tons)	SIC (tons)
Sopchoppy	220	7,070	300	0
Neuse	2,070	15,500	5,240	0
Brazos	6,410	24,000	27,700	44,500
Missouri	43,400	171,000	637,000	160,000
Ohio	213,000	(1)	438,000	19,900
Mississippi	451,000	1,720,000	2,000,000	140,000

[1]Complete data not available.

For the 6 months of comparative data during low flow conditions, July to December 1969, the DOC load exceeds the SOC load in the Ohio River. The monthly SOC load is extremely variable throughout the year but is very closely related to discharge, as the highest and lowest SOC concentrations correspond to the highest and and lowest monthly water discharges.

The SOC load of the Missouri River exceeds the DOC load during every month of the sampling period except during February and May of 1969, and January of 1970, when the river was frozen. The SOC load exceeds the DOC load even during March of each year when DOC concentrations approach 9 mg/l. The annual SOC load accounts for almost 80 percent of the total organic load. The monthly DOC load is similar to the water discharge in that it is much less variable than the monthly SOC load. Likewise, during the 4 spring months when the data are repeated for 1969 and 1970, the DOC load for the same period each year is very similar in magnitude and shows the same monthly trends. The SOC load for this same period is not duplicated for the 2 years but is extremely variable as it is throughout the entire year.

Annual DOC and SOC loads are of almost equal magnitude in the Mississippi and Brazos Rivers, but the monthly fluctuations are very different. Water, SOC, and DOC loads are relatively invariant throughout the year in the Mississippi River with the SOC load being slightly greater than the DOC load, except for the lower flow period in late summer. Water, SOC, and DOC loads are extremely variable in the Brazos River, but there is a definite trend for the DOC load to exceed the SOC load during the winter and for the reverse to occur during other seasons of the year. One possible reason for these trends is the eutrophic level of the stream which was discussed previously in the paper.

The SIC load is a large portion of the total carbon load throughout the year in the Brazos River, is a large portion of the total load during some months in the Missouri River, and is a significant portion of the total carbon load of the Ohio and Mississippi Rivers. The inorganic carbon load exceeded the organic carbon load during 4 months of the year in the Brazos River and during 2 months of the year in the Missouri River.

Tables 1–4 indicate that total carbon measurement alone on stream sediments is not an index of organic carbon. Therefore, in all organic sediment studies, the total carbon load must be fractionated in organic and inorganic contributions by direct determination.

The Sopchoppy and Neuse Rivers are the opposite of the Missouri River in that 96 and 70 percent of the 35- and 15-million-pound carbon load, respectively, is in the dissolved phase. The DOC load for these rivers are consistently higher than the SOC during every month of the year. The average SOC and DOC concentrations are similar in magnitude for the Brazos, Missouri, Mississippi, and Brazos Rivers, but both are somewhat higher for the Neuse and are significantly higher for the Sopchoppy.

Correlation coefficients for the various discharge parameters are given in table 5. No correlation was found between discharge at time of sampling and DOC concentration. The high correlation between monthly water discharge and SOC load, monthly water discharge and SIC load, and SOC load and SIC load is understandable because the amount of sediment in suspension in a given stream is directly related to stream discharge and velocity. Almost all sediment particles are also coated with organic matter. The high correlation between DOC load and SOC load is reasonable because the sediment phase is known to be both a source and a sink for organic substances within the stream. With microbial, algae, and chemical changes within the stream the dynamic equilibria shift to favor replenishment of depleted species. Many organic materials have a low solubility in water; therefore, oversaturation can result in high DOC values with accumulation also in the sediment phase. The positive correlation between DOC load and SIC load for two of the three rivers containing SIC may be coincidental and not valid until a number of rivers containing SIC have been evaluated. However, in lakes and sluggish streams, SIC may serve as a significant source of CO_2 nutrient. The resulting increased biomass production could increase the DOC concentration by cell leakage and decomposition of dead cells.

SUMMARY AND CONCLUSIONS

The organic carbon load of each of the rivers in this study is substantial. The 3.7×10^6-ton (3.4×10^9-kg) annual organic load of the Mississippi River was equally distributed between dissolved and suspended phases throughout the year with only small seasonal fluctuations in the magnitude of each. The DOC concentrations ranged between 2.2 and 4.5 mg/l with an average of 3.4 mg/l. SOC concentrations expressed as percent by weight of sediment ranged between 1.33 and 4.57 percent with an average of 2.28 percent. SOC concentrations expressed as mg/l of total sample ranged between 1.1 and 6.1 mg/l with and average of 3.8 mg/l. Almost one-third of the SOC load of the Mississippi River is contributed by the Missouri River, which accounts for less than 10 percent of the water

TABLE 5.—*Correlation coefficients of discharge parameters*

[Leaders (...) indicate complete data not available]

River	Degrees of freedom (d.f.)	Water discharge versus DOC concentration	Monthly water discharge versus monthly SOC load	Monthly water discharge versus monthly SIC load	Monthly DOC load versus monthly SOC load	Monthly DOC load versus monthly SIC load	Monthly SOC load versus monthly SIC load
Brazos	11	0.04	**0.95	**0.91	*0.78	**0.77	**0.84
Mississippi near Belle Chasse	8	.48	**.98	**.88	**.93	**.89	**.90
Missouri	15	-.10	**.62	.12	**.65	-.01	**.39
Neuse	11	.39	*.58	......	**.74	......	......
Ohio	10	......	**.92	**.79	......	......	**.94
Sopchoppy	9	.21	**.94	......	**.76	......	......

*Correlation coefficients at 5-percent level of significance with 8 d.f. = 0.632; 9 d.f. = 0.602; 10 d.f. = 0.576; 11 d.f. = 0.553; and 15 d.f. = 0.480.
**Correlation coefficients at 1-percent level of significance with 8 d.f. = 0.765; 9 d.f. = 0.735; 10 d.f. = 0.708; 11 d.f. = 0.684; and 15 d.f. = 0.606.

inflow to the Mississippi for the period of study. Approximately 54 percent of the SOC load of the Mississippi River near its junction with the Gulf of Mexico can be accounted for in the combined contributions of the Missouri and Ohio Rivers.

The 52×10^3-ton (47×10^6-kg) annual organic load of the Brazos River was also equally distributed between dissolved and suspended phases, but the DOC load exceeds the SOC load during the winter with the reverse trend for the other seasons. This trend was largely due to increasing DOC concentrations from 1.8 mg/l during October to above 7 mg/l during February. SOC concentrations were extremely variable ranging between 0.46 and 13.8 percent by weight of sediment or between 1.4 and 6.2 mg/l when expressed on a whole-sample basis. Marked eutrophic activity during low-flow conditions in the summer and fall is manifested by the 10 percent average SOC content from July to November. The SOC values for the Brazos as reported by Brooks (1970) are lower than those of this report. Differences are probably due to the coarseness of the glass-fiber filter which permits some silt and clay particles to pass thru the filter.

Over 80 percent of the 8.1×10^5-ton (7.4×10^8-kg) annual organic load of the Missouri River was in the suspended phase even though the average DOC concentration (4.6 mg/l) was slightly higher than the average for the Mississippi (3.4 mg/l). The high sediment load of the "Big Muddy" (the Missouri) has been documented for decades. The monthly SOC load was generally greater than the DOC load for all seasons except for a short period during the winter when the river was frozen. The DOC concentrations exhibit some fluctuations between 2 and 9 mg/l throughout the year with the highest concentration occurring in March of both sampling years.

The 2×10^3-ton (1.8×10^6-kg) and 7.4×10^3-ton (6.7×10^6-kg) annual organic load of the Neuse and Sopchoppy Rivers, respectively, is predominantely in the dissolved phase throughout all the year. The average DOC concentration of 7.1 mg/l for the Neuse is approximately twice the average for the Ohio, Missouri, Brazos, and Mississippi Rivers. Variations in DOC concentrations between about 6 and 50 mg/l in the Sopchoppy River were the greatest of all the rivers studied. SOC concentrations in the Sopchoppy were always low, less than 5 mg/l, and the average DOC concentration for the year exceeded 27 mg/l.

SIC can be a significant portion of the total carbon load in streams, especially in arid regions. SIC was present in four of the six rivers studied (Brazos, Missouri, Ohio, and Mississippi), with the annual SIC load exceeding the annual SOC load in the Brazos River. DOC concentrations in most U.S. rivers would be expected to be less than 10 mg/l except those highly polluted reaches or those draining swampy areas. SOC concentrations are highly variable between 1 and 10 mg/l and between 1 and 10 percent, by weight, depending upon the streamflow variables and the amount of suspended sediment in the water.

DOC concentrations were found to be independent of stream discharge. This finding further indicates that DOC concentration at any given time is a result of several dynamic processes within a given stream. Sorption, desorption, scouring of the bed material, growth of organisms, decomposition of organic litter, seasonal sources of organic substances, point sources of organic contamination, and other factors are important considerations in evaluating DOC and SOC concentrations. As shown by the data in this study, the concentration of DOC within a given stream varies with season and sources of contamination in a repeating pattern which is somewhat characteristic of the stream. By means of periodic sampling, the pattern can be established and generally understood. Significant deviation in DOC or SOC concentrations from the established pattern should be an indication for the need of more intensive sampling for specific organic substances or parameters.

The low C:N ratio within the sediment phase of all streams studied indicates that streams are significant accumulators of N. C:N ratios of most soils and residues are 12:1 or greater. The average C:N ratio of the streams studied was 8:1 with a narrow range from 6.9:1 to 8.9:1. This finding suggests that the slowly biodegradable end products of decomposition and humification within the stream may be different from those in soil systems.

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