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Organic Carbon Transport in the Columbia River

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Total organic carbon (TOC) levels in the Columbia River measured monthly from May 1973 to December 1974 ranged from a maximum of 270 μ mol l⁻¹ during late spring and early summer to a minimum of 150 μ mol l⁻¹ during late autumn. Sampling locations were directly behind the spillway at the Bonneville Dam, 230 km upstream, and at Kalama, Washington, 128 km upstream from the river mouth. The average annual TOC contribution from the Columbia River drainage to the north-eastern Pacific is 4.9×10^{10} mol with an average concentration of approximately 195 μ mol l⁻¹. Of this TOC annual export, 89% is dissolved organic carbon (DOC) and 11% is particulate organic carbon (POC). The TOC and DOC levels were most highly correlated with increased oxygen saturation and discharge, while POC correlated more closely to high instream primary productivity as indicated by higher pH and oxygen supersaturation.

Variability of DOC in the main channel of the Columbia River from Portland, Oregon, to the estuary during a June 1974 cruise was minimal. The DOC concentrations ranged from $221-260 \ \mu mol \ 1^{-1}$ with no significant upstream or downstream gradients. Diel variation also was slight, varying randomly during 24 h between $235-257 \ \mu mol \ 1^{-1}$. The relative annual constancy of the DOC is indicative of the refractory nature of a significant proportion of the dissolved organic load of the Columbia River.

Introduction

The Columbia River is the second largest river on the North American continent with approximately 2×10^{11} m³ of water entering the Pacific Ocean annually from a basin of 670 000 km² (Figure 1). The basin consists of about 85% of forest and open range, 12%

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Figure 1. The lower Columbia River with major tributaries. The Bonneville and Kalama sites are shown along with sampling locations, marked with solid circles, for the 1 June 1974 cruise.

agricultural and 3% urban land. The annual discharge for the Columbia River is about 58% that of the Mississippi and constitutes 1% of the total river input to the oceans worldwide.

Published data on the total organic carbon (TOC), dissolved organic carbon (DOC) and particulate organic carbon (POC) levels of large rivers on an annual basis are scanty. Malcolm & Durum (1976) reported the distribution of organic carbon for the Mississippi River, its tributaries, the Ohio and Missouri, and three smaller rivers over a 9–18-month period. Albright (1977) measured DOC and POC for 8 months in the Fraser River, British Columbia, one of the largest North American rivers. P. M. Williams (1968, 1969) reported DOC concentrations of 100–300 μ mol 1⁻¹ during the dry-season in downriver portions of the Amazon. Richey *et al.* (1980) published DOC concentrations for stations at least 1000 km upriver in the Amazon during rising-water and high-water which ranged from 275– 825 μ mol 1⁻¹. Richey *et al.* (1980) also noted that no published data for the transport of organic carbon existed for a major river which encompassed a hydrologic year. Measurements of organic loads in smaller drainages of the U.S. and Canada are summarized in Moeller *et al.* (1979).

The objectives of this study were fourfold: (1) to determine seasonal variations in concentration and partitioning between dissolved and particulate fractions of the organic load of the Columbia as a reference point for future studies on a basin being increasingly impacted by rapidly growing population, agriculture and industry; (2) to examine natural seasonal variability in the concentration and form of organic matter relative to physical parameters of discharge rate and temperature, chemical parameters associated with the carbonate system, and nutrient distributions to provide tools for estimating past and predicting future export of organic matter by the Columbia River; (3) to assess upstream-downstream variability of organic load on the lower 200 km of the river for detectable point source inputs or for an organic carbon decrease due to processing before the estuary; (4) to carefully measure the annual organic carbon export for a major river for use in global carbon flux studies and for estimation of riverine input to the estuary and north-eastern Pacific.

Methods

Samples were taken monthly directly behind the spillway at the Bonneville Dam, 230 km upriver, and at Kalama, Washington, 128 km upriver from the river mouth (Figure 1). The Bonneville site is upstream from the confluence of the Willamette River and the large metropolitan area of Portland, Oregon and the Kalama site is 38 km downstream. Both sites provided access to the main channel. In addition, on 1 June 1974 a cruise on the R/V Yaquina enabled sampling at 16 points along the Willamette and Columbia River to the estuary at Astoria, Oregon (Figure 1). Organic carbon was sampled dielly upriver from Astoria in river water with no measurable salt-water influence.

Samples were drawn from a large volume wide-mouth Niskin sampler, filled at approximately 1-5 m below the surface. Subsamples were then transferred to 1-l glass bottles, which had been fired overnight at 465 °C. Samples from two different depths were taken at each station. No major gradients were detected between the two samples at each station and the average concentrations have been reported. Bedload sampling was not attempted and our equipment precluded accurate sampling of near-bottom gradients and bedload transport. The series of large dams on the mainstream of the Columbia was thought to reduce large particulate organic bedload transport to the estuary. but our calculation of POC export must be considered as a conservative estimate.

Oxygen samples were fixed at the sampling sites (Carpenter, 1965) and pH and water temperature measured. Sample bottles were completely filled, stoppered tightly, and stored on ice until analysed immediately upon return to the lab. Alkalinity was measured by titration with 0.1000 N HCl (Park *et al.*, 1969) and total carbon dioxide by a gas chromatography technique (Park *et al.*, 1964). Phosphate, nitrate plus nitrite, and silicate were analysed on a Technicon Autoanalyzer • (Atlas *et al.*, 1971). TOC, DOC and POC were measured by wet oxidation with potassium persulfate ($K_2S_2O_8$) to CO₂ (Menzel & Vaccaro, 1964) on six replicate samples. The DOC was measured following filtration through 0.45 µm prefired silver filters, and POC was determined both by difference and direct analysis of the filters. Average difference for six replicates determined directly and indirectly never exceeded 6 µmol 1⁻¹. The precision at a 95% confidence interval for the TOC, DOC and POC analyses averaged 4 µmol 1⁻¹.

Controversy has centered upon the completeness of oxidation of organic material by the potassium persulfate wet oxidation method (P. J. Williams, 1969; Gordon & Sutcliffe, 1973; Sharp, 1973). However, recent comparisons of automated photochemical methods, high-temperature combustion techniques, and wet oxidation with $K_2S_2O_8$ have shown the wet oxidation technique to be about 10-15% lower in seawater (Collins & Williams, 1977; Gershey *et al.*, 1979). Closer agreement between the persulfate method and other techniques was found in freshwater (Goulden & Brooksbank, 1975). Additional tests of the completeness of recovery of CO_2 with $K_2S_2O_8$ oxidation in freshwater are presented in Table 1. Average recovery for 23 compounds was 95% with volatilization and incomplete oxidation of higher molecular weight proteinaceous compounds the major causes of lower recoveries. Our results along with earlier studies suggest that recovery of DOC from the Columbia River samples was underestimated by no more than 5-10%.

Compound	Concentration (µmol 1 ⁻¹)	Recovery (%)	Standard deviation (%)		
Urea	42 & 83	102.0	1.4		
2-AEP	33 & 67	101.0	0.0		
Syringic acid	11 & 18	101.4	5.9		
L-tryptophan	33 & 67	101.0	4.9		
Phloroglucinal dehydrate	33 & 67	100.0	1.3		
ATP	33 & 67	100.8	5.2		
L-lysine HCl	33 & 67	100.0	0.0		
Sulfanilamide	33 & 67	100.0	0.1		
Humic acid	42 & 83	98.0	2.2		
1,10-phenanthroline	42 & 83	97.0	3.6		
Glutathione	33 & 67	96.1	1.0		
Benzoic acid	42 & 83	95.0	3.1		
Albumin	33 & 67	92.9	1.3		
Mannitol	33 & 67	92.1	0.5		
Vanillin	33 & 67	91.6	6.4		
Chitin (crustacean shell)	17, 33 & 67	91.3	3.6		
Hemin	42 & 83	90.0	4.1		
D-glycogen	33 & 67	89.3	6.4		
Acetic acid	42 & 83	88.0	3.3		
L-cysteine HCl	42 & 83	88-0	2.8		
Casein	42 & 83	87.0	2.1		
Adenine	12 & 15	83-8	2.6		

TABLE I. Per cent recovery and standard deviation by potassium persulfate oxidation for selected organic compounds in freshwater at concentrations between II and $83 \ \mu mol \ l^{-1}$

Results

The Columbia River's flow and temperature during the period of sampling exhibited strong seasonal variability (Figure 2). Temperatures ranged from 3 °C in January to 21 °C in August. River flow downriver of the Willamette River confluence was characterized by two distinct peaks of high discharge with minima occurring in late summer and early fall. The first peak was triggered by spring runoff from snowmelt in the higher elevations of the basin, culminating in a maximal discharge in June. The second peak was produced by heavy rain during winter in western Oregon, swelling the Willamette River tributary to 40% of the total Columbia River flow. Numerous dams on the Columbia dampen the extremes of discharge historically associated with the river but the bimodal discharge pattern remains apparent. Extremes of discharge during 1974 range from 0.25 km³ day⁻¹ to 1.5 km³ day⁻¹ with an annual output of 230 km³ year⁻¹.

The CO₂ system of the Columbia River was characterized by measuring pH, total carbon dioxide (Σ CO₂) and alkalinity (Figure 3). Maximum pH was observed during summer months and a generally lower pH occurred at Kalama due to the input of lower pH water from the Willamette River. A major snowmelt contribution to the total discharge in June 1974 caused the Σ CO₂ and alkalinity minima. Generally lower Σ CO₂ and alkalinity at Kalama was also attributable to the influence of the Willamette River drainage. Alkalinity in the Columbia River is predominantly carbonate alkalinity. Park *et al.* (1969) measured 94% carbonate alkalinity with the surplus alkalinity mainly resulting from organic acids. Calculations using the 1973 and 1974 data yielded 88% carbonate alkalinity and 12% surplus alkalinity.

Distinct seasonal fluctuations in nutrient chemistry of the Columbia River were found during the study and have been reported previously (Park *et al.*, 1970, 1972; and Figure 4).



Figure 2. (a) Temperature, (b) flow rate and (c) O_2 saturation at Bonneville (\bigcirc) and Kalama (\bigcirc) from May 1973 to December 1974.

Maximum nutrient concentrations occurred in late winter and minima in the summer. Nitrogen is generally considered the limiting macronutrient and was below the level of detection at either Bonneville or Kalama during 5 months of 1973 and in July of 1974. The molar ratio of nitrate plus nitrite to phosphate varied from approximately 2 : 1 in summer to 19 : 1 in late winter.

Oxygen saturation often exceeded 110% during late spring and summer months with winter levels usually below 100% (Figure 2). To what extent oversaturation was attributable to greater turbulence during increased river discharge or to primary production is unknown, although the general inverse relationship between the nutrient chemistry and O_2 saturation points to the potential importance of phytoplankton production as the O_2 source. It is probable that both factors are significant in producing supersaturation. Cooler temperatures,



Figure 3. (a) pH, (b) alkalinity and (c) total CO₂ at Bonneville (\bullet) and Kalama (\circ) from May 1973 to December 1974.

decreased light and increased turbidity suppress primary production in winter and biological and chemical oxygen demand decreased O_2 saturation below 100%.

The organic fraction of the Columbia River was dominated by DOC (Figure 5). Spring and early summer maxima were apparent, but seasonal variability was much lower than for inorganic nutrients. The DOC concentrations ranged from $139-197 \mu mol l^{-1}$ at Kalama and from $115-184 \mu mol l^{-1}$ at Bonneville. Minima in both 1973 and 1974 occurred during late fall.



Figure 4. (a) Phosphate, (b) nitrite plus nitrate and (c) silicate at the Bonneville (\bullet) and Kalama (\odot) sampling sites from May 1973 to December 1974.

The POC showed much greater variability with minima in late fall and winter (Figure 5). Periods of high flow in late spring and early summer coupled with times of longer photoperiod coincided with the highest levels of POC. Asterionella species were observed on filters at the time of high POC in the June 1973 sample at Kalama. Cushing (1967) documented peaks of both Asterionella and Fragilaria sp. on the Columbia in the spring of 1964. The POC concentration ranged over more than an order of magnitude annually in contrast to the more invariant but higher DOC levels.



Figure 5. Organic carbon concentrations for the Columbia River at Bonneville (\bullet) and Kalama (\circ) from May 1973 to December 1974 as (a) TOC, (b) DOC and (c) POC.

The concentration of all the organic fractions at Kalama was consistently higher than those found at Bonneville. A probable source, the Willamette River, was measured seasonally near its confluence. Since it was consistently lower in TOC, DOC and POC than the mainstem Columbia, increases between the two sites must result from discharge of organic material into the Columbia from the large metropolitan areas of Portland, Oregon, and Vancouver, Washington, and their associated industry.

A cruise was undertaken in June of 1974 on the lower 200 km of the Columbia River to measure the degree of variability for TOC, DOC and POC. A plot of TOC vs. distance



Figure 6. The TOC (\times), DOC (\odot) and POC (\Box) concentrations measured on 1 June 1974 on the lower 200 km of the Columbia River. Samples collected in the Willamette River are enclosed in squares.

from the river mouth demonstrates the absence of a downstream concentration gradient (Fig. 6). A range of only 39 μ mol 1⁻¹ or 16% of the average for all stations was encountered. Willamette River samples taken during the cruise again were lower in TOC and DOC, but with comparable POC concentrations to the Columbia.

A diel series of samples also were taken in June at a station 19 km from the river mouth to evaluate temporal fluctuations as a source of error in the budget calculations. Manny & Wetzel (1973) and Klotz & Matson (1978) observed significant diel cycles for a small stream and river, respectively, which could produce serious error in budgetary calculations. However, diel variability of TOC on the Columbia was low, ranging from $235-257 \mu mol 1^{-1}$ with slightly higher but not significantly different concentrations at night. The DOC concentration ranged from $200-212 \mu mol 1^{-1}$ and the POC from $27-48 \mu mol 1^{-1}$. The diel measurements all fell within the range of TOC, DOC and POC values measured during the cruise the previous day. The time of day at which samples were taken does not appear to cause serious error in the calculated export of organic matter from the Columbia.

Using water year 1974, an annual chemical load was calculated from the average monthly flow and chemical measurements. The annual contribution from the Columbia River to the north-eastern Pacific Ocean is given in Table 2. The organic carbon was partitioned into 4.4×10^{10} mol DOC and 0.5×10^{10} mol POC. The TOC was 89% DOC and 11% POC in 1974. The single largest monthly input, accounting for 16% of the annual TOC, occurred in June, and over 50% of the TOC entered the estuary between April and July (Figure 7).

Nutrient output in 1974, except for the organic carbon data, can be compared to 1966 and 1967 export calculated by Park et al. (1972) (Table 3). Allowing for the slightly greater

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Annual export
Phosphate													
(10 ⁶ mol)	45.4	39.0	37.2	49.5	32.5	39.3	13.3	3.6	3.5	4.6	6∙o	8.2	282
Nitrate													
(10 ⁶ mol)	767	636	708	574	273	146	35	I	8	57	124	210	3540
Silicate													
(10 ⁸ mol)	58.2	49 · 0	60.0	71.7	66.8	62.0	30.0	13.1	10.2	13.6	16.4	23.8	475
Alkalinity								-	-	-		-	
(10 ⁹ equiv.)) 27.9	23.7	2 6·1	31.2	28.8	28.9	24.5	16.1	12.7	12.3	13.3	10.6	266
Total CO,	•••	•••		• •					•	Ū			
(10 ⁹ mol)	26.8	21.2	25.7	30.3	26.7	22.5	17.3	12.1	10.8	11.3	11.8	15.6	232
Oxvgen			-57	0-0	/	5	-, 0			- 5		- 0 -	-9-
(10 ⁹ mol)	11.7	0.2	0.0	11.0	11.3	12.0	7.4	3.8	3.0	3.3	3.7	5.3	02
TÒC	/	,,,	,-		5	/	/ 4	5-	5-	55	57	23	7 -
(TO ⁸ mol)	48.2	12.6	48.0	60.0	61.0	78.2	40·T	26.4	18.5	17.5	T 7·7	24.6	402
DOC		4- 0	400	000	01.0	10 3	47 *		10 3	-/ 5	-//		494
(10 ⁸ mol)	44.7	40.1	42.0	52.1	54.0	67.1	40.0	21.4	TE-8	16.0	17.5	24.4	428
POC	44 /	401	43 9	34 1	54 V	0/1	400	214	130	10 9	1/3	~4 4	430
(10 ⁸ mol)	3.2	2.2	4.1	7.9	7.0	11.5	0·1	5.0	2.7	0.6	0.5	0.5	54

TABLE 2. Monthly chemical input from the Columbia River into the north-eastern Pacific Ocean during 1974



Figure 7. The average monthly organic carbon input to the estuary from the Columbia River in mol month⁻¹ as measured at Kalama, Washington from June 1973 to December 1974.

1966	1967	1974
2.0 × 1014	2·3×10 ¹⁴	2.5 × 1014
6·9×10 ¹⁰	7.4 × 1010	9.2 × 1010
2·1 × 10 ¹⁰	2·3 × 10 ¹¹	2·7 × 10 ¹¹
$2.1 imes 10^{11}$	2·3 × 10 ¹¹	2·3 × 10 ¹¹
1.2×10^{8}	0.8 × 108	2.8×108
2·5 × 10°	2·8×10°	3.2 × 108
$3.3 imes 10_{10}$	3.2 × 1010	4.8 × 1010
	1966 $2 \cdot 0 \times 10^{14}$ $6 \cdot 9 \times 10^{10}$ $2 \cdot 1 \times 10^{10}$ $2 \cdot 1 \times 10^{11}$ $1 \cdot 2 \times 10^{8}$ $2 \cdot 5 \times 10^{9}$ $3 \cdot 3 \times 10^{10}$	19661967 $2 \cdot 0 \times 10^{14}$ $2 \cdot 3 \times 10^{14}$ $6 \cdot 9 \times 10^{10}$ $7 \cdot 4 \times 10^{10}$ $2 \cdot 1 \times 10^{10}$ $2 \cdot 3 \times 10^{11}$ $2 \cdot 3 \times 10^{11}$ $2 \cdot 3 \times 10^{11}$ $1 \cdot 2 \times 10^8$ $0 \cdot 8 \times 10^8$ $2 \cdot 5 \times 10^9$ $2 \cdot 8 \times 10^9$ $3 \cdot 3 \times 10^{10}$ $3 \cdot 5 \times 10^{10}$

TABLE 3. Annual chemical budgets for the Columbia River in 1966, 1967 and 1974

runoff in 1974, little difference in the inorganic carbon output occurred in the basin. The nutrient elements in 1974 did show increased export, particularly for phosphate, which was approximately double the 1966 output and triple that of 1967. The effect of this increase in available nutrients on TOC, DOC and POC is unknown.

Linear regression analysis was used to test for correlation between the organic carbon fractions and the measured physical and chemical parameters. For TOC, DOC and POC at Bonneville and for TOC and DOC at Kalama, per cent O_2 saturation predicted the greatest amount of variation of the measured variables, and for POC at Kalama, per cent O_2 saturation closely followed pH with a correlation coefficient, R^2 , of 0.48. The correlation between the organic fractions and per cent O_2 saturation was positive; increased O_2 saturation occurred during periods of higher organic carbon. Explanation for the significant correlations displayed by per cent O_2 saturation with TOC, DOC and POC was probably due to the combined effects of physical and biological processes. Physical processes were associated with greater turbulence and flow velocity during high runoff which enhanced O_3 supersaturation and organic carbon load, particularly with passage over the numerous dams impounding the lower Columbia. Biological factors which influence O_2 saturation values and organic carbon concentrations were algal primary production (positively) and heterotrophic decomposition (negatively).

In an attempt to distinguish physically dominated processes from the biochemically linked processes influencing the correlation of per cent O_2 saturation with TOC, DOC and POC, a simple linear regression was performed on the dependent variables, TOC, DOC and POC, for both Kalama and Bonneville with per cent O_2 saturation excluded as a potential independent variable. A physical variable, flow rate, replaced O^2 saturation as the best predictor variable for TOC and DOC. Hydrogen ion activity, which is sensitive to biological activities such as photosynthesis and respiration, physical phenomena such as turbulence, and chemical weathering reactions, was then most highly correlated with POC.

Discussion

The annual discharge of organic material from the Columbia River differed markedly from that of the Mississippi. Although the Columbia delivers three-fifths as much freshwater to the ocean as does the Mississippi, its organic load of 4.9×10^{10} mol was less than one-fifth of the 2.8×10^{11} mol carried by the Mississippi (Malcolm & Durum, 1976). The average annual concentration of TOC, DOC and POC in the Mississippi River was 600, 283 and 317μ mol 1⁻¹, respectively, and 195, 174 and 21 µmol 1⁻¹ in the Columbia River. Thus the major difference between the Columbia and Mississippi was found in the load of suspended particulate organic matter. The absolute annual export to the ocean by the Mississippi was 1.3×10^{11} mol or 1.75 million tons of DOC and 1.5×10^{11} mol or 1.95 million tons of POC. The Columbia, by comparison, delivered 4.4×10^{10} moles or 0.58 million tons of DOC and 0.5×10^{10} moles or 0.07 million tons of POC.

The variability in the carbon fractions in both the Columbia and Mississippi was greatest for particulate organics. Monthly DOC concentrations ranged from 139–197 μ mol 1⁻¹ at Kalama on the Columbia and from 183–375 μ mol 1⁻¹ at three sites on the lower Mississippi (Malcolm & Durum, 1976). POC displayed a more variable distribution ranging from 2–72 μ mol 1⁻¹ at Kalama to 92–508 μ mol 1⁻¹ on the lower Mississippi. Seasonal trends showed slightly higher DOC concentrations from March–July for the Columbia, while POC varied widely with higher spring and summer levels. The Mississippi data do not allow a critical evaluation of the seasonal trends in DOC and POC as a maximum of seven data points yearly at one station were reported.

The TOC and DOC concentrations in the Columbia River appear to be linked to physical parameters. Reuter & Perdue (1977) argued that the majority of TOC in natural waters is from geopolymers eluted by meteoric waters from soil organic matter. If the primary source for the TOC and DOC were autochthonous compounds from primary production, a dilution effect would be predicted during times of increased runoff. Instead, both the TOC and DOC concentrations in the Columbia are positively correlated with discharge. In addition, the constancy of the TOC concentration along the lower 200 km of the river and throughout a diel study in June is indicative of the refractory nature of a significant proportion of the dissolved organic load. This is not to imply that a biologically significant and rapidly overturning dissolved organic fraction is not present, but that the recalcitrant forms mask this subfraction (Dahm, 1981).

For POC, primary production in the Columbia River is a potentially important source. Several observed chemical responses paralleled patterns which would be caused by primary production. Per cent O_2 saturation was closely correlated to pH; O_2 saturation was highest during summer months at the same time pH was at its maximum. If primary production was responsible for O_2 supersaturation during summer, pH would also be expected to be at a maximum as a result of fixation of CO_2 . Diatoms were abundant on filters from these samples and were a significant proportion of the POC. Highest levels of POC were observed during late spring and early summer, the period during which primary production has been noted to be greatest (Cushing, 1967). The Columbia River carries low concentrations of suspended organic carbon; monthly samples of plankton biomass near Hanford, Washington, indicated that POC occasionally could be accounted for by primary producer biomass alone (Cushing, 1967). The series of impoundments on the Columbia River probably maximize the role of primary producers in this river. Impoundments tend to settle out POC, increase retention time, promote nutrient remineralization and, therefore, enhance total algal production.

The fate of the riverine DOC and POC in the estuary and Columbia River plume was not followed in this study. However, Hedges & Mann (1979) used δ^{13} C and lignin oxidation products off the coast of southern Washington to investigate the sources, transport and chemical stability of terrigenous POC from the Columbia River. The POC from the Columbia River was dominated by gymnosperm woods and non-woody angiosperm tissues with an average δ^{13} C of $-25 \cdot 5\%$. Marine organic matter is essentially absent in lignin compounds and heavier isotopically ($\sim -21 \cdot 5\%$). These differences were used to differentiate marine and terrigenous POC in coastal sediments. Similar techniques have not yet been applied to DOC in the estuary and Columbia River plume, but appear as potentially powerful tools in unraveling the fate of DOC undergoing riverine transport to the ocean. Adequate annual organic carbon export budgets have been reported for only two of the 20 largest rivers, the Columbia and the Mississippi. No annual estimates for TOC, DOC and POC have yet been published for the Amazon, which contributes 20% of all river water input to the oceans, although P. M. Williams (1968, 1969) has published DOC concentrations for sites near the river mouth which ranged between 100–250 μ mol 1⁻¹. If 250 μ mol 1⁻¹ is assumed as an average DOC concentration, then the dissolved carbon exported yearly from the Amazon would be 1.4×10^{12} mol or about 18 million tons. Concentrations of TOC, DOC and POC from the next four largest rivers after the Amazon (Congo, Orinoco, Yangtze and Bramaputra) are not known.

In estimating the flux of organic carbon to the ocean from riverine input, the data from the Columbia and Mississippi point out the need for careful sampling of the suspended load. Published DOC values for the Amazon, Mississippi and Columbia and the summary of DOC concentrations in smaller freshwater systems compiled by Moeller *et al.* (1979) suggest that, except for grossly polluted systems, DOC concentrations rarely range more than one order of magnitude annually. The assumption of an average world river DOC concentration between approximately 200-500 μ mol 1⁻¹ based on the limited available data may therefore prove a good estimate. Conversely, Holland (1978) lists suspended sediment loads for the 20 largest rivers which range from 8 mg kg⁻¹ for the St. Lawrence to 3400 mg kg⁻¹ for the Ganges, a range of nearly three orders of magnitude. If the suspended sediment loads are indicative of the range of POC concentrations encountered in the largest rivers worldwide, careful sampling on an annual basis of the rivers with high suspended sediment loads and discharge must be undertaken before an accurate global riverine carbon flux to the ocean can be estimated.

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