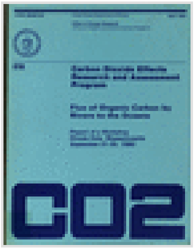

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Flux of Organic Carbon by Rivers to the Oceans

Report of a Workshop
Woods Hole, Massachusetts
September 21-25, 1980

Prepared by
Committee on Flux of Organic Carbon
to the Ocean
Division of Biological Sciences
National Research Council

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of Members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Committee on Flux of Organic Carbon to the Ocean

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INTRODUCTION

The relationship of climate to changes in atmospheric concentrations of carbon dioxide has provoked widespread interest and some concern. Combustion of fossil fuels appears to be the chief factor responsible for increasing the atmospheric carbon dioxide concentration over the last 100 years, but less than 50% of the carbon dioxide released from burning fuels can be accounted for in the atmosphere. Most of the remainder is taken up by the oceans. An undetermined amount may be sequestered by the terrestrial biomass and the soil, or indeed, over the same time scale, accelerated oxidation of terrestrial organic matter may be a net source of atmospheric carbon dioxide.

The transfer of organic carbon from land to the ocean represents a flux of potentially storable carbon, irreversible over many thousands, if not millions, of years. This transport of organic carbon to the oceans by rivers has received only superficial attention to date, but it is important if global carbon cycling is to be understood. The state of knowledge about the role of rivers in the transport, storage, and oxidation of carbon is the subject of this report, which summarizes a workshop held at Woods Hole, Massachusetts, in September 1980.

The main questions considered at the workshop were:

What is the best estimate that can be made now of the flux of organic carbon from land into rivers and from the rivers to the oceans? What is the fate of organic carbon in river water, sediments, flood plains, and coastal marine areas? How much is oxidized, stored, and exported? What are the chief limitations in making these estimates, e.g., hydrologic uncertainties, identification and measurement of the carbon species, and the influence of such episodic events as floods?

- How are these fluxes influenced by anthropogenic disturbances?

- Is the transport of organic carbon by rivers to the oceans a significant flux in the global carbon cycle? Is it important for a better evaluation of the global carbon cycle to improve the estimate of this flux? Has this flux or resultant storage changed with time?

- If an improvement of the estimate is desirable, then is it feasible to attempt such an improvement? What data are needed and how might they be obtained?

Papers prepared by some of the participants to aid these discussions make up Part II of this report. These data and the discussions of the participants form the basis of this report.

TERRESTRIAL SOURCES OF ORGANIC CARBON

The first step in determining the role of rivers in the global carbon cycle is to identify the terrestrial sources of carbon. There are three categories of carbon transported by rivers: (1) particulate organic carbon (POC), including leaf litter, woody debris and soil organics; (2) dissolved organic carbon (DOC), resulting from leaching and decomposition of organic carbon in plants and soils; and (3) dissolved inorganic carbon (DIC), such as bicarbonate and carbonate ions and dissolved carbon dioxide.

POC enters the river via direct litterfall, overland flow and bank erosion, and slumping. DOC, on the other hand, enters via the drainage waters. Sources of DOC include direct precipitation, leaching from living plants in throughfall and stemflow, and decomposition and leaching of organic matter in the soil profile. DIC is produced by reaction of dissolved CO_2 with silicate and carbonate rocks in the drainage basin; a small amount is derived from the oxidation of organic matter to form carbonic acid that then, as part of the ground water and river system, can release CO_2 to the atmosphere.

Identification of the types of terrestrial carbon transferred by rivers to the oceans is essential in determining the types of materials lost by metabolic processes in the oceans and to identify the terrestrially derived carbon stored in marine deposits. Both the chemical and isotopic properties of the organic compounds are used as indicators in making these identifications.

A variety of organic compounds (including vascular plant hydrocarbons and fatty acids, diterpenoid lipids, sterols, lignins and some carbohydrates) can be used to identify and characterize terrestrially derived organic materials in rivers, estuaries, and the oceans. Such modular tracers have the advantage that they provide a wealth of information about biological and geographic sources of carbon. Their chief disadvantage is that only a small amount of the total organic material is directly represented. So far, such indicators of sources have been used primarily on samples of particulate matter found in lake or marine
sediments. There are relatively few studies of the molecular

composition of organic materials, being transported from land to sea. Better methods for identifying and tracing dissolved organic materials at the molecular level are particularly needed at this time to define the sources and fates of this quantitatively important component of the total carbon flux into the oceans.

Stable and radioactive isotopes of carbon also have been used to indicate sources. Terrestrial carbon and marine carbon have different $\delta^{13}C$ values (-26 for terrestrial, -21 for marine, relative to the Peedee belemnite [PDB] isotope standard) and attempts have been made to use this criterion to distinguish between these two sources in riverine and nearshore deposits. These studies indicate that terrestrially derived particulate carbon probably is limited to nearshore marine sediments.

The distinction between soil-derived carbon and carbon in modern land plants is made possible by considering a radioactive isotope of carbon, ^{14}C. Soil carbon has been shown by a number of workers to be ^{14}C-old (low ^{14}C content), whereas the ^{14}C content of land plants generally reflects the ambient atmospheric composition. Land plants grown since 1954 are enriched with ^{14}C resulting from nuclear weapons testing. Thus, the ^{14}C content of DOC and POC is a measure of the contribution of modern plant and soil carbon to the total riverine flux of carbon at any point along the course of the river. If restricted to continental shelf estuaries, the contribution from marine planktonic carbon may be identified by considering both ^{14}C and ^{13}C. The ^{14}C content of plankton closely reflects that of the local ocean surface.

STORAGE AND TRANSPORT OF CARBON BY RIVERS

Rivers are among the more fascinating and dynamic features of the earth. They range in size from rivulets and streams to large, deep rivers, and their temporal and geographic complexities are at the same time awesome and scientifically intriguing. Despite this interest, most rivers remain largely unknown from a quantitative standpoint. Large rivers transport impressive amounts of dissolved and particulate material from terrestrial drainage basins to the oceans, but the exact quantity remains elusive. Rivers also contain an extensive and diverse biota on their floodplains and in their waters.

A large river tends to integrate the biogeochemical activities within the drainage basin. For example, the total carbon observed in a river is a mixture of carbon that originated from different sources and entered the river via various pathways (Figure 1). Thus, the amount and composition of organic carbon at any one site in a river is dependent on both in situ activities and events in the watershed. Qualitative and quantitative changes in the load of organic matter are brought about by specialized biological communities and physical retention processes throughout the drainage basin.

Not all organic carbon that enters a river is processed immediately or exported. Some is stored in river sediments or on

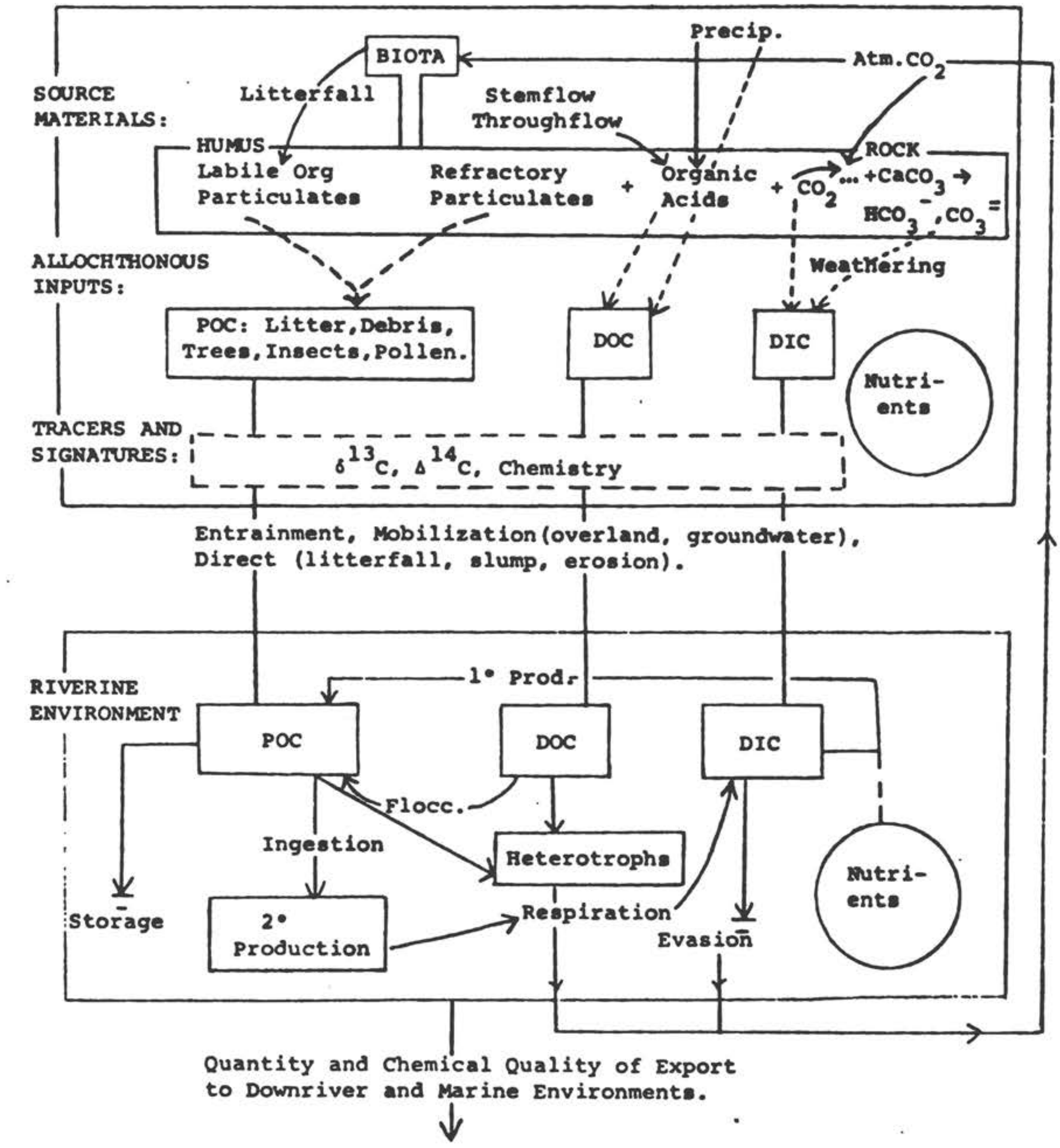

Figure 1. A general model of the biogeochemistry of carbon in rivers (modified from Richey, Part II). Terrestrial source materials originate as indicated. These materials, with their characteristic tracers, enter the river via several pathways, representing terra firma or floodplain inputs. Within the riverine environments, primary production (Macrophytes, Phytoplankton, and Terrestrial) sources also contribute carbon. The main carbon forms in the river are thus particulate organic C (POC: ranging in size from 0.45 μm to trees), dissolved organic C (DOC: < 0.45 μm), and dissolved inorganic C (DIC). The organic C in the river may be respired (in water, in the sediments), ingested, stored, exported, and flocculated. DIC may be lost through evasion.

the flood plain. These materials may be moved by extreme flooding events that occur on a time scale of tens of years or longer (which demonstrates the importance of discharge history). In turn, flood events, which regulate the flux and storage of large and small organic particles, are the elements of fluvial geomorphology that define the substrate for the establishment of biological communities.

A final aspect of river biogeochemistry is that the rivers carry chemicals, which may stimulate (nutrients) or retard (toxicants) photosynthesis and decomposition within the rivers and in nearshore waters. With increased amounts of industrial effluents, fertilizers, and sewage and other human wastes, the flux and storage of carbon by rivers may be changed accordingly.

Small Streams and Intermediate-sized Rivers

Organic matter budgets have been made for only a few small river basins in North America and such attempts have been even more limited elsewhere. These studies show that approximately 10-25% of the total dissolved and particulate matter output was organic, derived from small catchments (0.10-300 km^2) in North America and Europe (Arnet, 1978; Bormann _et_ _al_., 1974; Swanson _et_ _al_., in press). Although these values may not reflect streams draining arid lands or strongly eroding landscapes, they are markedly different from the low values of organic matter (a few %) previously reported for major rivers flowing into the ocean (Meybeck Part II).

Movement of organic carbon in a river basin can be viewed as a series of time steps down the valley as carbon is temporarily stored in tributaries, alluvial fans, and the floodplain. The residence times of carbon and sediments in these reservoirs increase downstream from decades to over 10,000 years. In small mountain streams and tributary channels, residence time of organic material may exceed decades and even centuries. Residence time for large POC in intermediate-gradient rivers and debris fans of tributaries may be on the order of hundreds to a few thousand years. On the extensive lowland flood plains and poorly drained wetlands, the period of storage of material may be on the order of thousands to tens of thousands of years.

Small tributary channels in North America can store, as particulate carbon, the equivalent of several hundred years of particulate carbon discharge and several decades of dissolved organic carbon discharge from a drainage basin (Fisher and Likens, 1970; Sedell et al, 1974; Triska et al., in press; G.W. Minshall and K.W. Cummins, personal communication). Relatively small annual changes in these accumulations could result in significant changes in the flux of organic carbon from the basin. These changes in yield would not be predicted by hydrologic equations for transport of organic matter.

Most small, high-gradient headwater streams are highly retentive of particulate organic material (Bilby and Likens, 1980; Fisher and Likens, 1973; Sedell et al., 1974). Fluvial systems (channel, alluvial fans, and floodplains) in forested zones of North America can accumulate from 4 to 8 moles* C/m^2 a year (Sedell et al., 1974; Triska et al., in press).

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* 12 g C = 1 mole C.

Tentative global estimates derived from three different assumptions yield values from 4 to 78 x 10^{12} moles C/yr (Table 1) stored in upstream channel and floodplain areas. These values represent a significant, though poorly studied, part of river carbon flux and must be accounted for if one is to examine changes in carbon fluxes to oceans following deforestation and increased productivity in rivers due to nutrient additions over time scales of centuries. The large estimate for denudation of 900 x 10^{12} moles C/yr is included in Table 1 to emphasize that the bulk of the material eroded from uplands is deposited as colluvium and alluvium in the channels and floodplains of small and medium-sized streams. Whether this material should be treated as terrestrial carbon or as temporarily stored fluvial carbon is not clear. Potentially, land denudation does represent a large storage of carbon in small channels and floodplains. Because it is not possible to distinguish between these fluvial and terrestrial reservoirs, this value is not included in the range of carbon stored in floodplains and channels. For balance purposes in Figure 3, we adopt a value of 17 x 10^{12} moles C/yr for flux from rivers to continental sediments and assume that about 40% of this carbon accumulates in continental sediments.

For longer time scales (10^3 - 10^4 years), steady-state assumptions about storage and residence times of sediment may apply, but on shorter time scales, the steady-state assumption is not applicable since the quantities of sediment in storage may change dramatically because of changes in climate, tectonic events, or disturbance of terrestrial vegetation.

Organic Carbon Export via Rivers to the Oceans

The organic carbon that enters a river from terrestrial sources or is produced within a river by photosynthesis has three possible fates. As a result of such variables as chemical quality, particle size and density, geomorphology of the drainage basin affecting transit time, and water velocity, carbon is stored, oxidized, or exported to the marine environment. An attempt is made in this section to estimate the total organic carbon (TOC) exported by rivers to the marine environment.

Unfortunately, no systematic data, such as those based on rigorous sampling of representative rivers and hydrologic regimes, are available. Data on water discharge and total suspended sediments for large rivers of the earth are generally available, but data on concentrations of DOC and POC are few. Most of the available data are for temperate rivers, which are not necessarily characteristic of other areas. Thus, several methods of extrapolation have been used to arrive at an estimate.

Most of the estimates published prior to 1980 were based on some assumed average value of TOC concentration in rivers, usually from about 2 to 10 mg C/liter, times an average discharge. Most estimates considered TOC as DOC plus POC ($<$1 mm), although several were DOC only (Duce and Duursma, 1977; Garrels et al., 1975, Handa, 1977, Kempe, 1979; Meybeck, Part II; Reiners, 1973; Richey et al, 1980; Schlesinger and Melack, in press; Skopintsev, 1971; Stewart et al., 1978; Williams, 1971). Likens and Miller (1978) pointed out that coarse organic carbon (CPOC $>$ 1 mm) had been ignored and could increase the estimate of transport by order an of magnitude. Documented estimates of TOC ranged from 3 to 27 x 10^{12} moles C/yr. Reiners (1973) estimated this range to be 17 to 83 x 10^{12} moles C/yr, but provides no support for this estimate. This large range of estimated fluxes show the need for better estimates based on area-specific weightings.

Schlesinger and Melack (in press) used two methods of extrapolation from data on selected rivers to a global flux of TOC. In their first method they selected data for 12 rivers, mostly temperate, and plotted the (logarithmic) total annual organic carbon load as a function of (logarithmic) mean annual discharge, and extrapolated from this regression to a TOC export value of 33 x 10^{12} moles C/yr. Their second method was based on the denudation rate of TOC from terrestrial watersheds, and yielded an estimate of 34 x 10^{12} moles C/yr. To determine the organic carbon flux for the Asian rivers, they assumed a ratio for fine particulate organic carbon (FPOC) to total suspended solids (TSS) equal to that in average shale (FPOC/TSS = 0.9% carbon).

Meybeck (Part II) has provided the most thorough analysis of this genre. On the basis of data from about 100 rivers, he found inverse relationships between the DOC/TOC ratio and TSS, and between POC and TSS. Total carbon exports were then calculated from various relationships: DOC variation with climate, POC variation with TSS, and TOC export variation with runoff. The resulting total river export of TOC was estimated at 33 x 10^{12} moles C/yr, of which about 55% is in the dissolved form. Meybeck (Part II) cautioned that this estimate represents a <u>minimum</u> value and could easily increase if different assumptions for TOC export were used. The tropical zone accounted for more than 60% of the estimated flux and organic carbon represents about 45% of the total carbon carried by rivers. The estimate is of necessity biased toward colder regions and is based on measurements from rivers representing only 27% of total river discharge, worldwide.

The highest supported estimate, 83 x 10^{12} moles C/yr, was that of Richey et al. (1980). This estimate, however, includes that portion of the organic carbon oxidized within the river and includes a factor to account for the nonhomogenous distribution of TSS observed in the Amazon River; thus it was called a "total effective efflux" from the land, rather than direct input to the ocean.

Estimates to date generally are based on the larger rivers, as judged by discharge of water. These rivers do not necessarily have the greatest discharge of TSS. For example, Nordin (Part II) states that the Cho-Shui, in Taiwan, has a small discharge of water, yet carries a sediment load equivalent to that of the Mississippi River.

The various recent estimates converge on 33 x 10^{12} moles C/yr. This convergence, however, should not be taken as a validation of the estimate. Although the authors used various methods of extrapolation, the data base was essentially the same, assumptions were similar, and all data were biased to temperate regions. Thus the autocorrelation of the estimates was very high. Difficulties encountered in extrapolating from the data base have been discussed. What are some of the potential constraints on the data base itself?

These estimates are sensitive to the assumed ratios of TOC to TSS, especially for the Asian rivers (Figure 2). If TOC/TSS is 1%, then TOC export is about 33 x 10^{12} moles C/yr; if it is 4%, then TOC export is about 66 x 10^{12} moles C/yr. One to 8% is easily within the range of values seen elsewhere, and since these regions are densely populated and heavily disturbed, and thus capable of high organic outputs, the estimates are all "possible."

Nordin (Part II) discussed the variations in discharge and TSS load, (i.e., the basis for all of the estimates). Large seasonal variations in discharge and load occur in all rivers; the most pronounced events occur in smaller rivers (which constitute about 60% of total discharge). In such systems, 90 - 99% of the total annual suspended load may be discharged during just a few days, thus vast underestimates can occur if these events are not sampled. Indeed it is often logistically impossible to obtain quantitative samples during periodsof flood, particularly of CPOC on large rivers. Further impacts of precipitation should be noted in monsoonal regions, where heavy rainfall results in overland flow, entrainment of surface material, and possibly elevated TOC levels.

Horizontal and vertical variation in both dissolved and particulate concentration is large. In the Amazon River a depth - integrated TSS value is twice that of the surface value; thus the "grab sample" method most commonly used would lead to underestimates. On the basis of these considerations, Nordin (Part II) estimated that values for sediment yield are probably low by a factor of 2. Accordingly, estimates of carbon export must be increased.

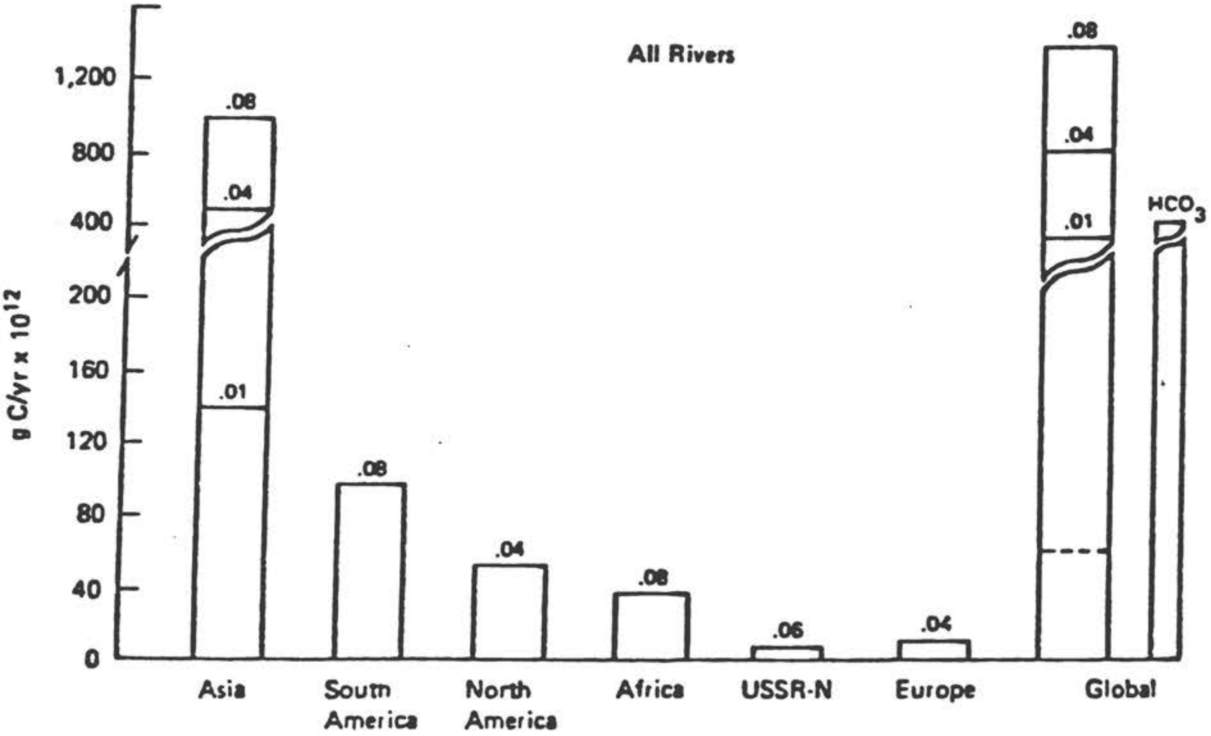

FIGURE 2 Total organic carbon export by region, calculated as a function of total suspended solids. Number over each bar is the ratio of TOC to TSS used for that region.

It should be obvious that only a range for TOC export can be established. A minimum estimate can be provided from discharge and mean TOC concentration from mostly temperate waters, and a maximum estimate can be provided from Figure 2, giving a range of 33 to 100 x 10^{12} moles C/yr. Taking a TOC/TSS ratio of 0.04 and a TSS flux of 2 x 10^{16}g/yr we determined a "best estimate" of flux for rivers to be 66 x 10^{12} moles C/yr, which is also consistent with the assumption that previous errors in estimation are symmetrical around some mean value.

THE FATE OF RIVER CARBON EXPORTED TO THE MARINE ENVIRONMENT

The organic carbon transported by rivers to the oceans is subject either to metabolic degradation or to storage in sediments. Although there is uncertainty about the amount, the storage of terrestrial carbon in nearshore sediment has been demonstrated by using both chemical and isotopic indicators (See Hedges, Spiker, and Turekian and Benoit, Part II). Perhaps the most striking evidence that the refractory organic carbon stored in many estuarine regions is soil-derived is found in data from studies in the Baltic Sea and Long Island Sound. In both of these estuaries, the dominance of ^{14}C-old carbon in the sediments prior to the industrial revolution identifies a predominant soil component in the stored carbon (Erlenkeuser *et al*., 1975, Benoit *et al*., 1979).

Determining the rate of storage of carbon from riverine sources in coastal sediments requires not only determination of the concentration of this carbon after it has been isolated from other carbon sources (such as marine plankton and salt marsh) but also determination of the rates of accumulation of the sediments. Such determinations are not easy. Although both natural (^{14}C, ^{210}Pb, ^{228}Th) and man-made (Pu, ^{137}Cs, bomb ^{14}C) radionuclides have been proposed and used to determine accumulation rates, the problems of bioturbation and physical mixing remain formidable. Rates of accumulation based on establishing a time of coastal inundation after the end of the Wisconsin glacial age may provide a suitable method, if appropriate acoustic and drilling methods are used in the survey of coastal sediments.

Although it is of some importance, for evaluation of the global carbon flux, to estimate the storage rate of terrestrial carbon in long-term, irreversible marine repositories, the large uncertainties in making such estimates must be borne in mind. The search for changes in the rate of storage caused by human perturbations of the land is subject not only to these general difficulties but also to the fact that nearshore deposits are peculiarly impacted by fossil-fuel and sewage-sludge residues that were not part of the river burden (Turekian and Benoit, Part II).

THE ROLE OF RIVER-TRANSPORTED ORGANIC CARBON IN THE GLOBAL CYCLE

The charge to this workshop was to evaluate the role of rivers in the global carbon cycle with regard to the relative magnitude of riverine fluxes to the ocean and particularly to fluxes into storage reservoirs and their change since ancient times.

The results of our deliberations are summarized in Figure 3. A number of important aspects of the global carbon cycle which are germane to the following discussion and recommendations are emphasized below:

Fluxes associated with the erosion, transport, and sequestering of organic C in marine environments are small relative to the amounts of carbon involved in photosynthesis and respiration.

There appears to be a significant flux of eroded organic carbon from upland areas to lowland areas and into temporary storage.

The estimated net flux of organic carbon from land to oceans by rivers today is about 66 x 10^{12} moles C/yr (range of estimate from 33 to 100 x 10^{12} moles C/yr). This flux of organic carbon is large enough so that increased amounts transported to and sequested in marine sediments may be an effective net sink for anthropogenic CO_2.

The accumulation of organic C in marine sediments today represents a small fraction (perhaps 0.8%) of the annual marine production of carbon by photosynthesis.

The rate of accumulation of organic carbon in coastal marine areas (including deltas, estuaries, bays, and portions of shelves) may have increased by 2 or 3-fold since ancient times but it is difficult if not impossible to measure this change, because the increase is so small relative to the amount previously accumulated with which it is mixed biologically and physically. In addition, the direct impact of fossil fuel and sewage sludge residues would obscure natural riverine and marine inputs.

The flux of organic carbon from coastal regions to the open ocean is difficult to evaluate but is known to occur. The $\delta^{13}C$ of deep sea sediments and organic matter dissolved in the sea water

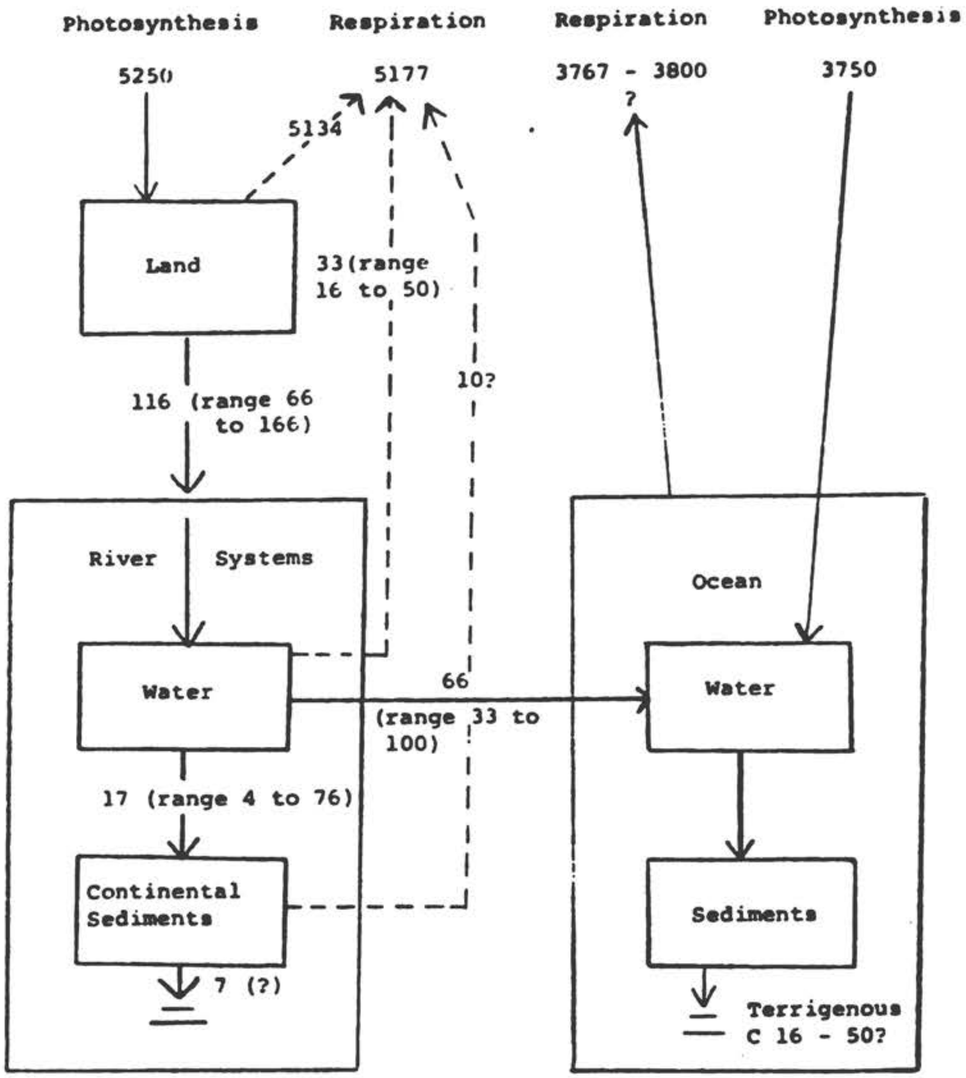

FIGURE 3 Tentative simplified model of a portion of the present-day global cycle of carbon emphasizing interactions between the riverine and ocean systems. The sum of all inputs was made to equal the sum of all outputs in this model. Fluxes are in units of 10^{12} moles C/yr. The range is given for some flux estimates. Note that organic carbon accumulation in sediments is less than 1% of total annual productivity, and thus is a difficult value to estimate. Some of today's carbon fluxes may be greater than in ancient times (prior to 1,000 years B.P.). Very tentative calculations indicate that today's fluxes of organic carbon associated with river transport and accumulation in continental sediments may be double the ancient fluxes, and present-day organic carbon storage in marine sediments may be two to three times greater than in the past. It is not known at present how to test this proposition.

Flux values are tentative estimates adapted in the main body of this report or discussed in the papers in Part II of this volume. Total organic carbon production is taken as 9000 x 10^{12} moles C/yr; 60% of this being terrestrial and 40% marine (Mackenzie, Part II). Total production is known to a precision of about + 15%. The land to river system flux of 116 x 10^{12} moles C/yr and the fluxes related to continental sediments are taken from Mulholland (Part II), Table 1 and discussions thereof. The river to ocean flux is based on the discussion in the text. Organic carbon production and accumulation fluxes in the ocean are derived from Mackenzie (Part II) and Wollast and Billen (Part II).

Care must be taken in the interpretation of this figure; note that the fluxes other than those related to photosynthesis and respiration (oxidation) are small.

implies that most of the carbon in these two reservoirs is of marine origin.

The fluxes of carbon associated with the processes shown in Figure 3 are reasonable estimates at this stage of knowledge and, within the large errors, probably provide a picture of the movement of carbon in this portion of the global carbon cycle. Organic carbon produced and eroded from uplands is transported by streams to lowland areas, and in these areas of alluvial and colluvial deposition, organic carbon is respired and decayed and returned to the atmosphere as CO_2. Additional carbon is also added to waters in their transit from upland to lowland regions by photosynthesis in stream channels, flood plains, and other areas. In the lowlands much of the organic carbon is oxidized (respired); a small part of the remainder, whose amount is poorly known, accumulates in alluvial and colluvial sediments and a larger part is carried by low order streams toward the ocean. En route, some of this carbon and carbon produced in situ, is oxidized (respired). The average annual net export of carbon from land to the marine environment (66×10^{12} moles) is a result of the complex balance between storage, release, and respiration (oxidation) of organic carbon in terrestrial and aquatic environments.

In the marine environment the exported terrigenous carbon mixes with organic carbon produced by marine organisms. Some of the terrestrial carbon is oxidized in the marine environment as it settles to the sea floor, but much of the terrestrial POC entering the oceans is deposited in coastal areas and escapes degradation. The fate of terrestrial DOC in the marine environment is not clearly understood but some of this carbon and a small amount of terrestrial POC is transported from coastal regions to the open ocean, where it is either metabolized or diluted beyond recognition by other organic carbon of marine origin.

The terrestrial carbon component appears to be of more importance in nearshore marine sediments than in open-ocean sediments, and it probably decays at a less rapid rate than the marine carbon component of marine sediments. It may be that the rate of sequestering of organic carbon in marine sediments has increased in recent times and therefore qualifies as a sink for anthropogenic CO_2. This sink may be expected to be the consequence of several complex processes resulting from human actions. Specifically, the processes are the extensive use of phosphorus and nitrogen fertilizers on land and their leaching by drainage waters, the cultivation of nitrogen-fixing crops, and the discharge of municipal wastes to aquatic systems. These processes can lead to an increased nutrient supply for coastal marine systems and result in increased organic carbon production and possible accumulation. Similarly, in terrestrial environments nutrients added by man's activities can lead to increased carbon storage in freshwater ecosystems or to increased runoff of organic carbon to marine systems. Furthermore, extensive deforestation may lead to increased nutrient losses as well as to greater loads of dissolved and particulate organic carbon in river systems (e.g., Bormann and Likens, 1979). These factors may lead to in increased burial of carbon in freshwater and marine deposits.

The burning of fossil fuels - coal, oil, and gas - and such other anthropogenic sources of CO_2 as net oxidation of the terrestrial biosphere because of deforestation, are responsible for an estimated increase in atmospheric CO_2 of about 14% during the last 100 years. The rate of increase in atmospheric CO_2 is now about 1.5 ppmv per year. However, fossil fuel burning alone over the last century is estimated to have released to the atmosphere more than twice as much CO_2 as the total atmospheric increase.

Estimates of the annual flux of CO_2 from the biosphere to the atmosphere range from about zero to values equal to that from fossil fuels; some authors have assumed that the biosphere is a net sink. Obviously the role of the biosphere during the last two decades and on into the twenty-first century is critical to models that predict future atmospheric CO_2 levels.

Whatever the case, some models have suggested that an amount equivalent to the annual increase in the atmosphere (200×10^{12} moles C/yr) may be stored in the oceans (Table 2). A recent estimate of ocean uptake based on GEOSECS data (Broecker, 1980) leaves 5 - 10% of the total fossil fuel additions of CO_2 to the atmosphere unaccounted for, but this shortfall estimate is within the range of uncertainty for the major global fluxes (Table 2). All ocean models currently assume that CO_2 simply dissolves into sea water and include no provision for CO_2 uptake as a result of reactions with carbonate solids in contact with shallow ocean waters, or for organic carbon buried in sediments.

If the most recent estimate of CO_2 uptake by the ocean is correct, then the ocean as currently modeled is at best a barely adequate sink for CO_2 from combustion of fossil fuel. If the terrestrial biosphere is a significant source of CO_2 for the atmosphere, then the problem of the ocean as the only major sink for

TABLE 2

Man-related Fluxes of CO_2 to the Atmosphere Compared with Estimates of Increases in Fluxes of CO_2 to Potential Sinks (units of 10^{12} moles C/y)[a]

Flux[b]	Source	Sink (increase since ancient times)
(1) Fossil fuel burning	412-428	
(2) Land use	0-415	
(3) Total inorganic carbon solution in the ocean		149-161
(4) Dissolution of Mg-calcites in ocean mixed layer		0-8
(5) Sequestering of organic C in continental and marine systems because of N and P additions to these systems[c]		0-60
(6) Terrestrial organic C transport to marine systems and storage in marine sediments[d]		0-18
(7) Terrestrial organic carbon storage in such continental systems as river flood plains.[e]		0-7
(8) Atmospheric increase		209-227
TOTAL RANGE	412-843	358-456

[a] Estimates adapted from Bolin, 1977; Broecker *et al.*, 1979; Garrels and Mackenzie, 1980; Walsh, 1980; Woodwell and Houghton, 1977; Mackenzie, Part II of this report.

[b] Because processes (6) and (7) are not resolvable from (5), their ranges are included in (5) and not included in the Total Range.

[c] Maximum from Walsh, 1980.

[d] See Mackenzie, Part II. All of the increased flux of organic carbon to sediments is considered to be due to this process.

[e] For minimum accumulation estimate, see page 9 of this report.

the missing CO_2 is exacerbated. Thus, it recently has become apparent that potential sinks other than the oceanic water deserve attention (Table 2).

Indirect effects also must be considered. For example, it has been assumed that disturbance of the biosphere alters only the exchanges with the atmosphere. However, if carbon is routed to sinks via other pathways, then such carbon should not be included in atmospheric exchange calculations.

CONCLUSIONS

Atmospheric carbon dioxide is currently increasing at a rate of about 200 x 10^{12} moles C/yr. Relative to this increase, it is necessary to determine not only the relative magnitude of carbon fluxes in the global carbon cycle, but also to determine whether fluxes into reservoirs other than the atmosphere have increased since ancient times. The flux and storage of organic carbon associated with the rivers of the world are summarized in Figure 3. Salient points relative to the role of rivers in the global carbon cycle are as follows:

- The flux of organic carbon by rivers to the oceans is of the same order of magnitude as various other fluxes in the global carbon cycle, but is small relative to the large amounts of carbon involved in photosynthesis and respiration (oxidation) that exchange between the earth's surface and atmosphere.

The amount of terrigenous carbon that enters the river systems is of the order of 116 (range of 66 to 166) x 10^{12} moles C/yr. Of this carbon, roughly 25-30% is oxidized within the river systems. Some organic carbon is stored in headwater regions, and there appears to be a significant flux (4 to 78 x 10^{12} moles C/yr) of eroded organic carbon from upland areas to lowland areas and into temporary storage. The net flux of organic carbon from rivers to the oceans is about 66 (range of 33 to 100) x 10^{12} moles C/yr, or about 50% of the amount that entered the riverine system.

- The storage of carbon in riverine reservoirs (continental and near-shore marine sediments) may be 10 to 15% of the annual atmospheric increase in carbon dioxide over the last two decades. The rate of accumulation of organic carbon in coastal marine areas may have increased two or three fold since ancient times, but there is great uncertainty concerning the values. This increase in accumulation could reflect carbon fixed by photosynthesis within rivers and in coastal waters through fertilization by river-borne inorganic nutrients.

- The surprisingly large flux and storage of riverine organic carbon indicates that rivers may play an important role in the global carbon cycle.

RECOMMENDATIONS FOR FURTHER STUDIES

Flux of carbon by rivers constitutes an important component of the global carbon cycle. Massive and logistically difficult field studies would be required to refine the current estimate of this flux. Thus, it is probably not feasible nor reasonable to attempt a significant refinement relative to an evaluation of the global carbon cycle. However, some further study should be done to clarify the biogeochemistry of rivers and their role in the global carbon cycle. We recognize the following as important and feasible studies:

1. Detailed, long-term studies of a few carefully chosen rivers should be done. These should include, in addition to carbon measurements, other chemical and hydrologic properties useful in modeling the carbon system. The following points should be considered in designing the sampling strategy:

- Rivers are not well mixed; therefore, representative samples should be collected.
- Large flows do not always imply large fluxes; to improve flux estimates, representative small-flow, large-flux streams should be sampled.
- Extreme events should be sampled intensively when the opportunity arises, and weighted according to the frequency of the event.
- To determine errors in mean values of fluxes, some long-time series from representative rivers are needed.
- Rivers in different parts of the world should be studied

during the same time period, and over at least a full year, to assess seasonal effects.

- Small rivers should be sampled frequently (daily, or at least weekly), whereas larger rivers may be sampled less often (weekly or monthly).
- A comparison should be made between "industrialized" rivers such as the Rhine and the Elbe, and "natural" rivers such as the Zaire, to determine the degree of chemical complexation of DOC. Studies should be extended to include such highly erosive basins of Southeast Asia as the Ganges-Brahmaputra, where extensive denudation studies have been conducted.
- A comparison should also be made between ground waters (at different depths) and river waters. Although the chemistry of ground water should reflect biological activities in the soil and sediment and the interaction with minerals, river water may have an additional imprint of primary productivity and subsequent biological consumption (grazing, bacterial action, and the like), as well as from industrial chemicals and sewage.

2. A major task is to determine the composition and origin of the bulk carbon observed in river waters and river and marine sediments. This analysis requires a sophisticated array of organic chemical and isotopic tracer techniques.

- Reliable techniques for measuring dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), and dissolved organic sulfur (DOS) should be developed, because variations in C/N, C/P, and C/S can be related to processes operating in the river systems. Identification of specific molecules and their quantification may help to interpret biologically determined elemental ratios relative to carbon.

- Molecular weight determinations of organic material are essential to understand the processes of complexation and condensation and will lead to investigations of the structure of dissolved organic matter. Two of the more critical parameters to study are the degree of mutual complexation and hydrogen bonding.
- ^{14}C and ^{13}C determinations in DOC and POC should be made throughout the river system, estuaries, and open oceans to determine the contribution of different carbon sources along the traverse.

3. Factors affecting hydrology need careful analysis.
   - Hydrologic analysis is based on field studies and can be generalized through mathematical modeling. Analysis of the relationship between sediment budgets and the geomorphology of the drainage basin is also based on field work, but mathematical models are not yet available in this domain. Quantitative estimates of various types of sediment influxes can be made and the inputs to rivers assessed as a basis for interpreting carbon measurements and for predicting the effects of perturbations on carbon mobilization or sequestering. Some of these assessments could be made on the basis of existing data; others would require field studies.

- A major uncertainty concerns routing of sediments downstream, once they have left the hillslope. For undisturbed watersheds, geologic time-scale, steady-state assumptions can be made about storage and residence times of the sediment. For disturbed watersheds and smaller time-scales, the prediction is more complicated and requires further field measurements (see Swanson et al. in press; Trimble 1974, 1975).
- Estimates of the total net rate of sediment accumulation and mean residence time in floodplains and lakes are needed.

4. Need to determine the rate of storage of organic carbon in marine sediments and whether this rate has changed with time. To determine the amount of carbon from terrestrial sources that is preserved in marine sediments per unit time, it is necessary to know the total accumulation rate of carbon in nearshore repositories and possible deep-sea repositories (including the water column) and the amount of that carbon that is of land origin. In addition, the role of river-derived nutrients in influencing coastal carbon production and preservation must be evaluated.

5. Changes resulting from anthropogenic influences should be identified and measured.

- The links between river-borne nutrients and primary production in river and marine environments should be investigated.
- The probable effects of land-use factors on runoff, sediment production, nutrient export, and, particularly, carbon export from watersheds must be identified.

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PART II

RATE OF DENUDATION IN BLACK SEA SOURCE AREA

Egon T. Degens

Excerpt from Degens *et al*. 1976 and 1978.

At present, the Black Sea is a gigantic catch basin for the river discharge of half of Europe and part of Asia (Figure 1). The source area is well defined and can be subdivided into several orographic provinces which are distinguished by geography extension, climate, and elevation. The following subdivision seems to be appropriate:

River	Size of Drainage Area (km^2)
1. Danube	836,000
2. Dnestr	61,900
3. Y. Bug	34,000
4. Dnepr	538,000
5. Don	446,000
6. Kuban	63,500
7. Caucasian Rivers	24,100
8. Rioni	15,800
9. Coruh	16,700
10. Turkish Rivers	231,500
11. Bulgarian Rivers	22,200
Total	2,290,200

These figures are accurate within a few percent; they represent only the planar projection of the individual terrain and not the actual surface area exposed to denudation.

The region under study is characterized by its diversity. We encounter all transitions between arid and humid climates and between lowlands and mountainous areas. The issue is further complicated, because the Pripjet swamps, the Panonic flatland, and the lowlands along the Black Sea coast are regions of sedimentation rather than denudation (Paluska and Degens, 1979).

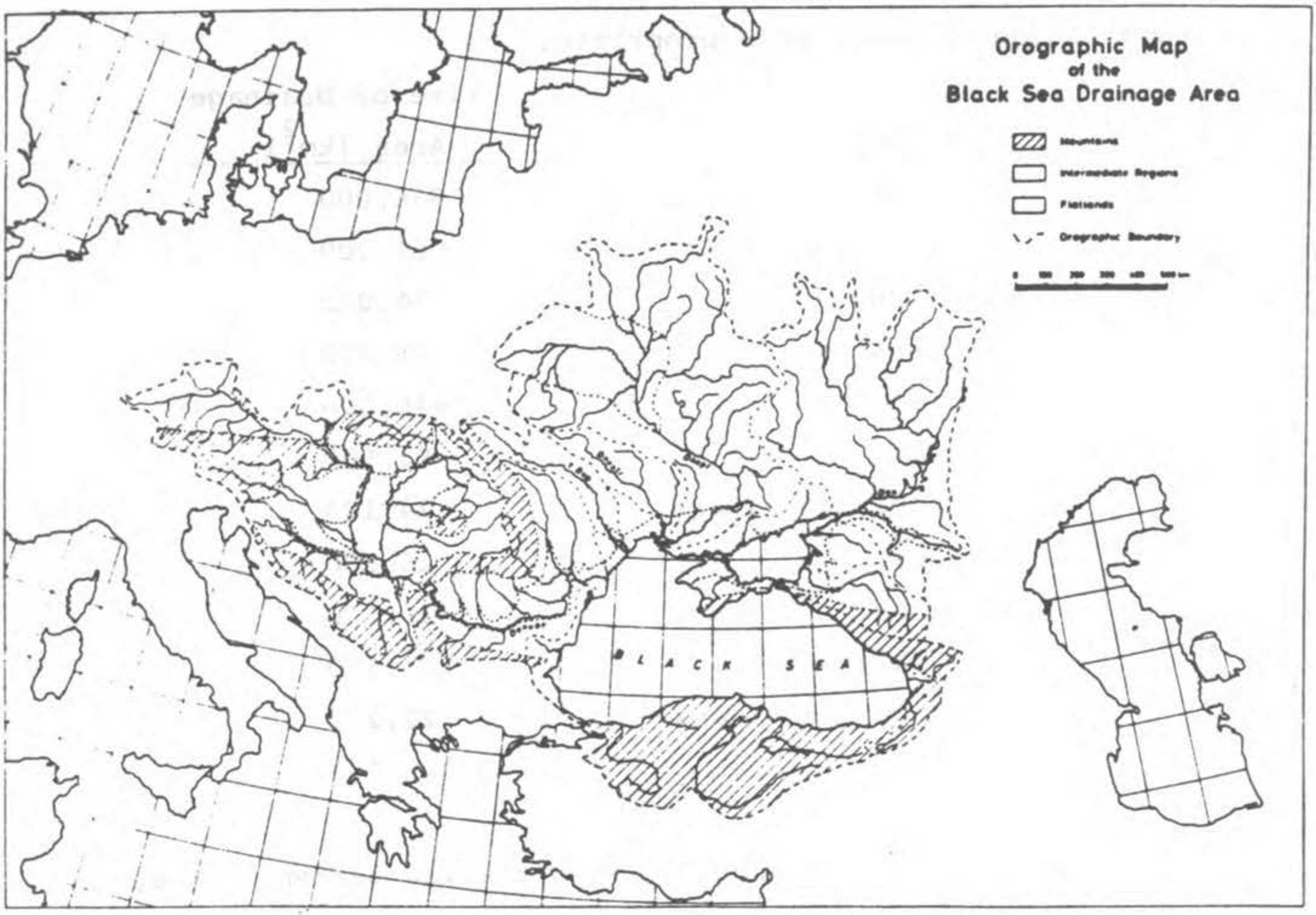

FIGURE 1 Orographic map of the Black Sea drainage area.

Shimkus and Trimonis (1974) present data on the sediment and salt load which is annually carried by the major rivers into the Black Sea basin. The total load divided by the size of the individual drainage area gives the total amount of yearly denudation in tons per square kilometer (Table 1). From these figures, Degens _et al_. (1976) derived the mean volume of eroded material, applying some "cosmetic" corrections to account for the areas of sedimentation within the Black Sea source region. The average denudation rate for the entire source is 0.063 mm/yr or about 100 $t/km^2/yr$.

From a sedimentological point of view it is of interest to know at what points most of the detritus enters the Black Sea. Figure 2 illustrates that: (1) the Danube carries about 60% of the detrital load; (2) the Don and Kuban discharge into the Sea of Asov where the material comes to rest; (3) the Caucasian Rivers, Rioni and Coruh, contribute 20% of the total detritus; and (4) Dnestr, Y. Bug, Dnepr, and the Bulgarian rivers yield very little material.

HOLOCENE VARVE CHRONOLOGY

On the basis of radiocarbon dates from the Black Sea sediments, it was concluded that the rate of deposition in the deep basin has remained fairly uniform over the past 7000 years, averaging 10 cm/1000 years (Ross and Degens, 1974). In a recent study (Degens _et al_., 1976), varve chronology was applied which put in question some of the previous interpretations. It appears that recent Black Sea sediments contain a certain amount of dead organic carbon which makes them "older" by 2,000 to 3,000 years.

TABLE 1 Denudation in Source Area of Black Sea Basin

River	Detritus[a] (10^6t/yr)	Salts[a] (10^6t/yr)	Total Load[a] (10^6t/yr)	Size of Area (km^2)	Amount of Weight (t/km^2yr)	Denudation Volume (m^3)	Denudation Rate (mm/yr)
Donau	83.00	52.51	135.51	681,000[b]	199.0	124.4	0.125
Dnestr	2.50	2.79	5.29	61,900	85.5	53.5	0.054
Y. Bug	0.53	1.35	1.88	34,000	55.4	34.6	0.035
Dnepr	2.12	10.79	12.91	383,500[b]	24.0	15.0	0.015
Don	6.40	8.43	14.83	446,500	33.2	20.8	0.021
Kuban	8.40	1.95	10.35	63,500	163.0	102.0	0.102
Caucasian Rivers	6.79		7.3	24,100	303.0	189.5	0.190
Rioni	7.08	2.16	7.6	15,800	481.0	301.0	0.301
Coruh	15.13		16.2	16,700	971.0	607.0	0.607
Turkish Coast	17.00	6.70	23.70	231,500	102.4	64.0	0.064
Bulgarian Coast	0.50	0.80	1.30	22,200	58.5	36.6	0.037

[a] Data from Shimkus and Trimonis (1974)

[b] Reduced area

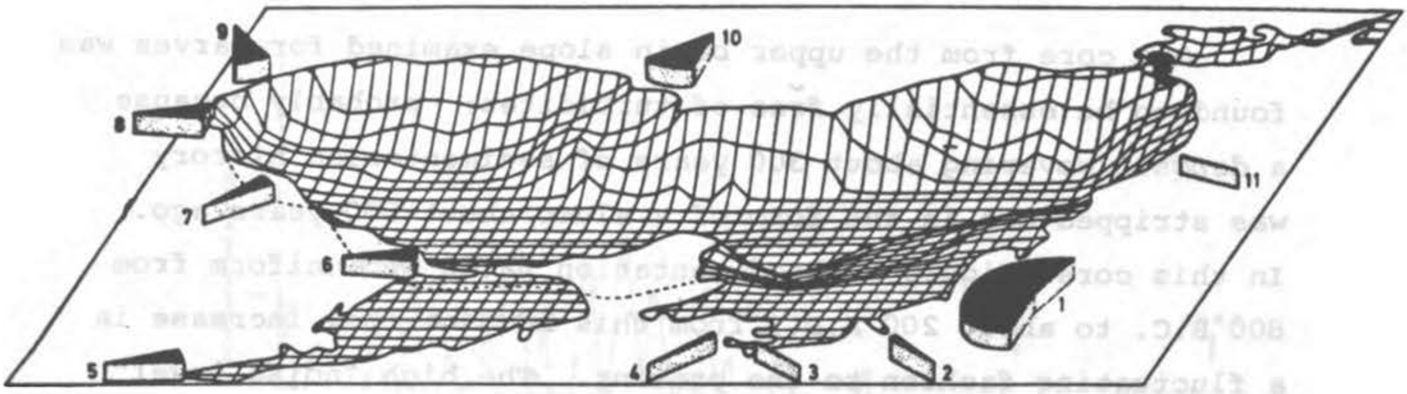

FIGURE 2 Black Sea catch basin; modern detrital flux expressed in percent of total. Danube (1); Dnestr (2); Y. Bug (3); Dnepr (4); Don (5); Kuban (6); Caucasian Rivers (7); Rioni (8); Coruh (9); Turkish Rivers (10); and Bulgarian Rivers (11).

The Holocene varves of the deep Black Sea have been described in detail (Ross and Degens, 1974). Light and dark layers alternate regularly, and the pattern is principally caused by seasonal plankton blooms which insert white coccolith bands into a darker matrix (coccolith unit), or fine, almost black bands into a dark brown matrix (sapropel unit). As many as 270 individual bands per meter of core section were counted (Degens et al., 1980), and one double layer represents one year of depositional history.

One core from the upper basin slope examined for varves was found to be essentially free of turbidites; probably because a deposit covering about 300 years of sedimentation history was stripped off in the form of a slump about 500 years ago. In this core (Figure 3), sedimentation rates were uniform from 800 B.C. to about 200 A.D., from this dateline they increase in a fluctuating fashion to the present. The high "noise level" observed for the past 1,500 years can best be accounted for by agricultural activities such as deforestation and the development of a "Kultursteppe." Episodic floods have carried higher amounts of detritus than normal to the Black Sea and have produced high peaks on the sedimentation curve.

The evolution of anoxic conditions during the Holocene is also of significance. Each gram-atom of carbon in plankton requires 1.3 moles of oxygen for its oxidation. Since the amount of organic matter that falls though the O_2-H_2S interface is fairly well known (Deuser, 1974), the decay constant of the oxygen reservoir can be calculated (Deuser, 1974). From this figure, the upward progression of the O_2-H_2S interface can be derived. Calculations show that the thermohaline boundary requires about 3,000 years to rise from the 2200-meter deep

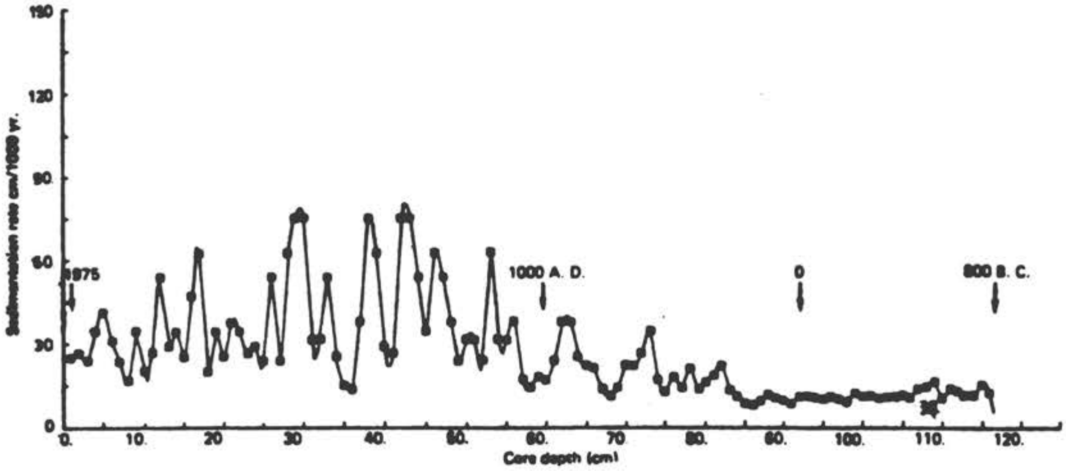

FIGURE 3 Rates of sedimentation in a sediment core from the Black Sea at a water depth of 470 meters (Core 35; Figure 4).

abyssal plain to a water depth of 500 meters. Varve-counting techniques substantiate these findings. Figure 4 (compare Cores 18 and 35) shows that finely laminated sapropels started to come in on the basin slope at a depth of 470 meters almost 2,300 years after they first appeared on the bottom of the Black Sea Basin.

In summary, during the past 5,000 years, normal rates of sedimentation in the deep basin were 10 $cm/10^3$ yr for the sapropel unit and 30 $cm/10^3$ yr for the coccolith unit. Turbidites and slumps supplied substantial amounts of detritus to the central basin and increased rates to 1 $m/10^3$ yr. In contrast, the sedimentation rate on the upper basin slope is generally three times greater than in the deep basin. There, however, submarine stripping and erosion may have removed material, thereby lowering the actual rates of accumulation. The sapropel unit has formed at times of forest vegetation, whereas the coccolith unit began when agriculture had already transformed the Black Sea source area into a steppe.

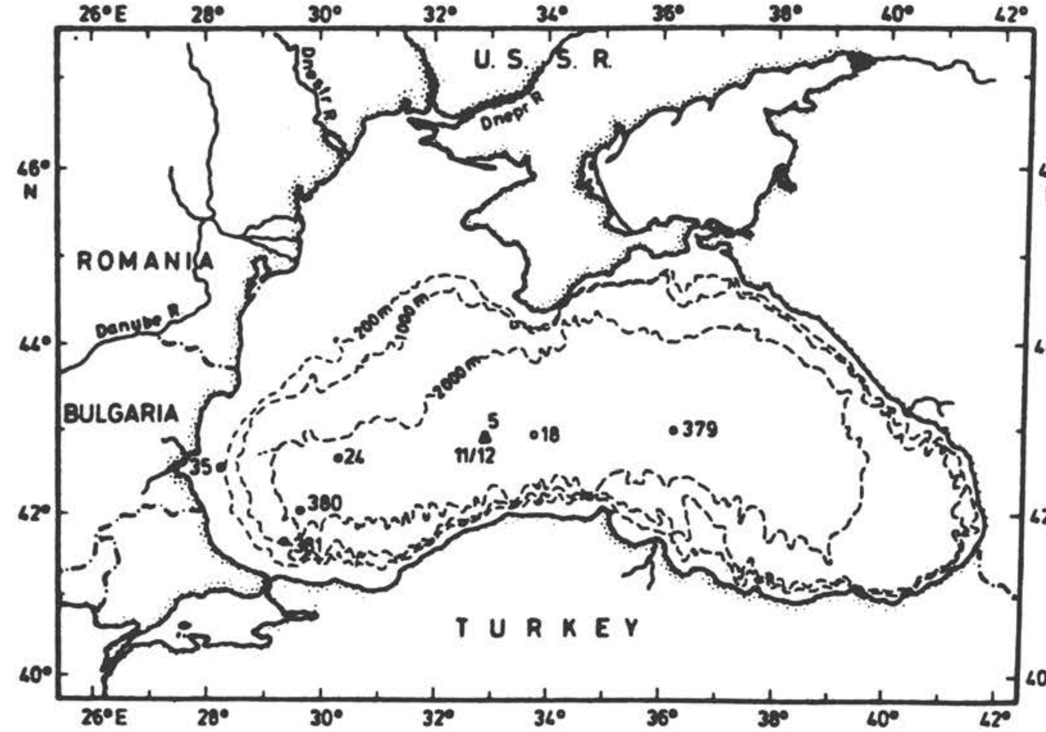

FIGURE 4a Coring sites occupied off the coast of Turkey and Bulgaria.

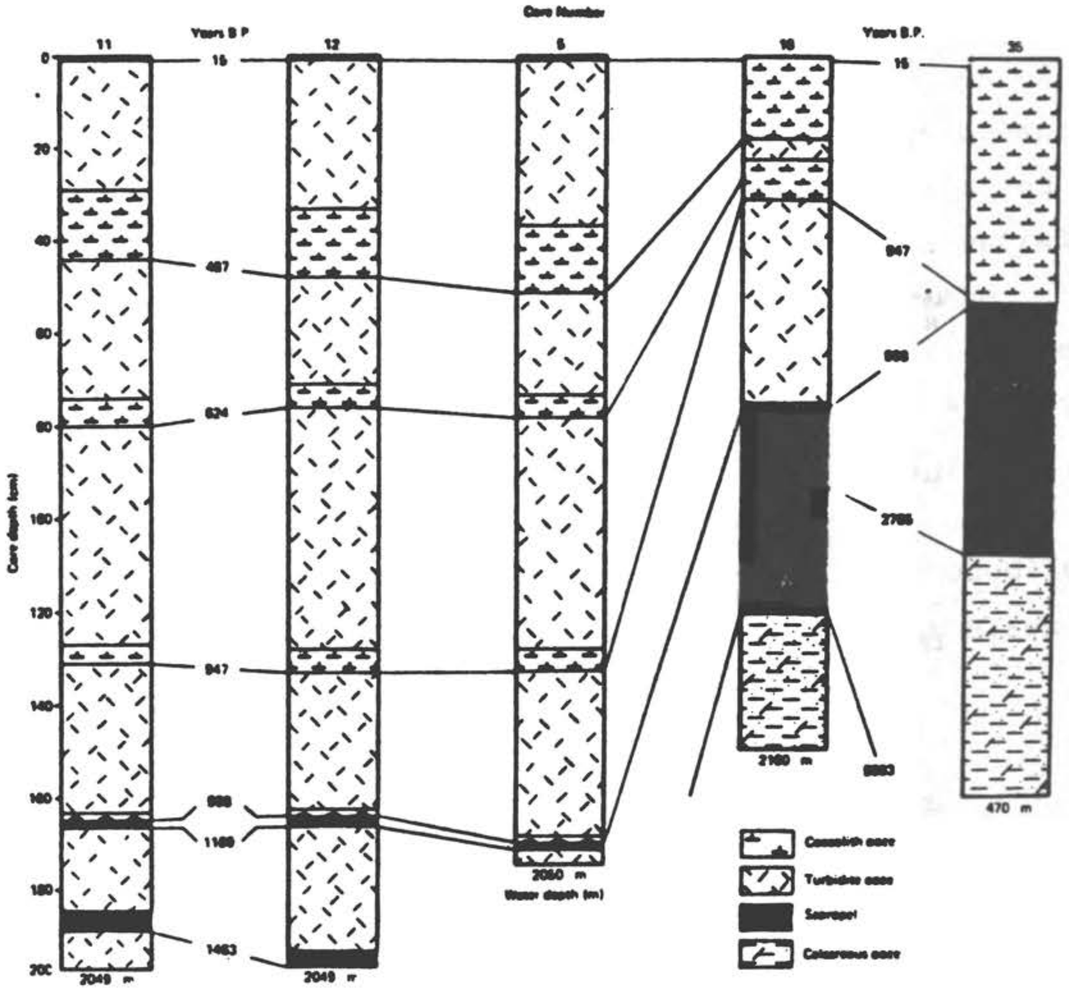

FIGURE 4b Stratigraphic correlation of short cores; coring sites depicted in Figure 4a.

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THE USE OF CARBON ISOTOPE MEASUREMENTS TO EXAMINE THE MOVEMENT OF LABILE AND REFRACTORY CARBON IN SOIL

B. J. O'Brien, J. D. Stout, and K. M. Goh

The genesis of a soil is complex. Factors contributing to the complexity include the weathered rock matrix, the overlying plant species, and the temperature regime and hydrology of the area. The soil is an ecosystem in itself, its nature depending on physical, chemical, and biological interactions. Because of these complex interactions, it has been difficult to understand in detail its genesis and dynamic steady state behavior.

Soon after carbon-14 dating was established, attempts were made to date soil charcoal. Around 1960 it was established that the ^{14}C in living plant leaf material was in equilibrium with that in the atmosphere, even though this was rising steadily because of the production of ^{14}C in the atmosphere from atmospheric nuclear tests. Studies were begun in the 1960's to use the increasing atmospheric ^{14}C to determine the turnover times of carbon in a variety of soils (Broecker and Olson, 1960; Rafter and Stout, 1970). At the same time, $\delta^{13}C$ measurements were often made on the soil carbon refractions (Stout <u>et</u> <u>al</u>., in press). Because biological processes fractionate ^{13}C with respect to ^{12}C, the juvenile CO_2, which probably had a $\delta^{13}C$ of -5%, has been fractionated into an organic pool with $\delta^{13}C$ of -25% and an inorganic pool with a $\delta^{13}C$ of 0% (Degens and Kempe, 1978).

From extensive measurements of ^{13}C and ^{14}C in soil and plant components it has become possible to model the carbon movement and turnover in soil (Rafter and Stout, 1970; Jenkinson and Rayner, 1977; O'Brien and Stout, 1978). Carbon-14 and ^{13}C measurements have also been made on carbon components in ground waters. In this report we review some data for New Zealand and indicate how carbon isotope measurements can help us to understand the movement of carbon from plant to soil to ground water.

CARBON ISOTOPES IN SOIL CARBON

Measurements of ^{14}C and ^{13}C in soils were begun in the 1960's (Rafter and Stout, 1970; Stout and O'Brien, 1973). The interpretation of these results was complicated by the fact that ^{14}C from nuclear weapons had already enriched atmospheric carbon dioxide and was beginning to penetrate the top layers of soil. The work of Rafter and Stout confirmed that ^{14}C levels in the leaves of trees and in grass were essentially the same as in atmospheric carbon dioxide. The activity in the grass grub was the same as in grass, but in earthworms it was 13% lower.

The ^{14}C levels in the atmosphere rose to a maximum in 1965, and it can be seen in Table 1 that the ^{14}C activity in topsoil under pastures increased markedly during this time. Also shown in Table 1 are the ^{14}C acitivities in the litter and soil profile of the Waipawa Forest measured in 1971. In this case the nuclear-weapon ^{14}C appears to have penetrated only the upper litter; the bottom litter layer and the soil have not been significantly affected by bomb carbon. At greater depths the measured carbon-14 is much less than expected in a modern sample; and when used to determine an age, it often gives values of thousands of years. Data on carbon content and ^{14}C and ^{13}C concentration in a soil profile at Judgeford, New Zealand, are shown in Table 2. The positive values for $\Delta^{14}C$, in the profile above 20 cm, indicate the presence of nuclear-weapon ^{14}C. Carbon-14 ages for soil carbon below this depth are given in the table and are about 9,000 years for the 80-100 cm horizon. There is need to reconcile the great ages of subsoil carbon with the turnover time of soil carbon of a hundred years or less (Baes *et al.*, 1976) as determined by respiration measurements. Jenkinson (1971)

TABLE 1 Radiocarbon in Forest and Pasture Soils[a]

Waipoua soil under Forest[b]
Sampled September 1971
Clay from basalt

Horizon	Litter	Litter	Topsoil	Subsoil
Depth (cm)	-66 to -56	-10 to 0	0 to 10	71 to 102
% C	50	44	34	2.1
δ^{13}C%	-25.2	-24.5	-24.7	-24.9
Δ^{14}C%	+208±5	-16±5	-6±5	-182±5
Age (years before 1950)				1595

Tokomaru soil under pasture[c]
Soil, silt loam from loess
Depth 0-7 cm

Δ^{14}C in %

Collection Date	Soil Under House Built 1895	Under Pasture Sown 1870	Under Pasture Sown 1945
Nov. 1962		+ 37	+ 39
Oct. 1965	- 16	+146	+135
Feb. 1969	+105	+295	+233

[a] Goh *et al.*, 1979

[b] Stout and O'Brien, 1973.

[c] Rafter and Stout, 1970.

Table 2. Carbon content and carbon isotope data of soil samples before and after acid hydrolysis.[a]

Soil depth (cm)	Sample description	% C	$\Delta^{14}C$ ‰ above oxalic acid standard	^{14}C Age before 1950	$\delta^{13}C$ wrt PDP std ‰
0-10	Whole soil	4.8	+178± 4		- 28.0
	Hydrolysate	.25	+117± 4		- 30.6
	Residue	2.9	+136± 4		- 28.6
10-20	Whole Soil	2.6	+ 2		- 27.3
	Hydrolysate	0.20			- 29.5
	Residue	1.6	- 28	210	- 28.9
20-40	Whole Soil	1.5	- 79	650	- 26.8
	Hydrolysate	0.04	-199	1810	- 30.4
	Residue	0.5	-116	990	- 28.2
40-60	Whole Soil	0.35	-280	2690	- 25.8
	Hydrolysate	0.14	-331	3300	- 28.7
	Residue	0.09	-372	3820	- 29.5
60-80	Whole Soil	0.37	-505	5300	- 25.8
	Hydrolysate	0.21	-471	5240	- 28.8
	Residue	0.08	-558	6730	- 28.9
80-100	Whole Soil	0.21	-668	9100	- 25.0
	Hydrolysate	0.08	-630	8190	- 27.9
	Residue	0.05	-679	9380	- 28.5

[a] Judgeford silt loam, sampled January 1977.

Whole soil is from one core.
Hydrolysate and residue from an adjacent core.

found that some 70% of the radiocarbon present in decomposing ryegrass was lost within the first year. One possible explanation is that soil contains biologically inert fractions that remain almost indefinitely in the soil. A number of investigators have made ^{14}C measurements on the humic acid, fulvic acid, and humin fractions of the soil organic matter, separated by using acid or alkaline extraction methods (Rafter and Stout, 1970; Scharpensel, 1972; Stout _et al._, 1977).

Although these soil fractions show differences in ^{14}C content, they are not large and the resulting ^{14}C age estimates are not very different and do not throw much light on processes occurring. The main differences in ^{14}C and ^{13}C appear to be related to the stage of decomposition (Goh _et al._, 1977).

A DYNAMIC SOIL CARBON MODEL

In order to account for the ^{14}C distribution, including the penetration of bomb ^{14}C into deeper layers of soil, O'Brien and Stout (1978) used a steady state diffusion respiration model in which it was assumed that most of the lowering of $\Delta^{14}C$ below modern was due to a small amount of very old carbon distributed throughout the soil profile. This study was made on the Judgeford silt loam under permanent pasture and the results of ^{14}C and ^{13}C measurements are shown in Figure 1. The shallow rooting of the pasture (0-10 cm) meant that soil carbon must diffuse down the profile from the surface. Such a model could account for the distribution of ^{14}C and ^{13}C down the profile as well as for the increase in 14^{C} activity in the surface soil layer due to bomb ^{14}C, which is shown in Figures 2 and 3. This model analysis indicated that about 16% of the carbon was relatively old and fairly uniformly distributed with depth (Figure 4), that the turnover periods of the modern carbon was 63 years and that the flux of carbon in the surface layer

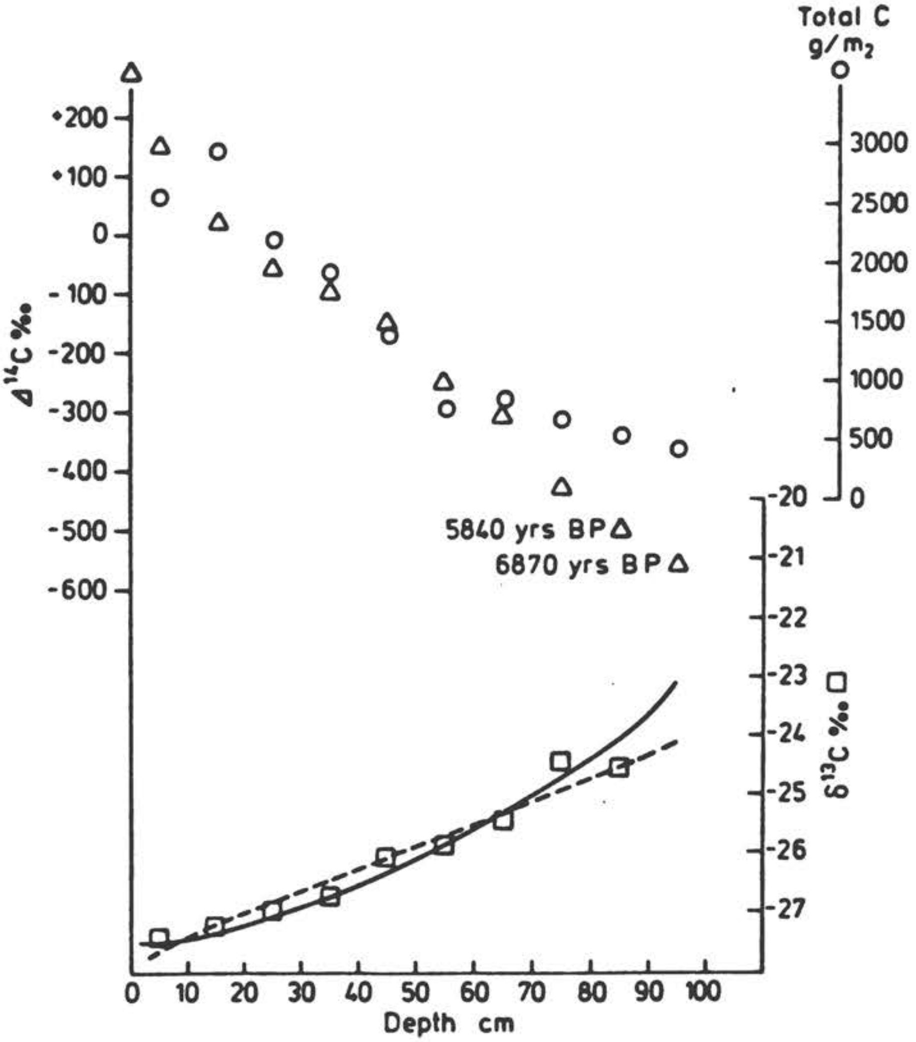


Figure 1. Distribution with depth of total carbon (circles), ^{14}C (triangles), and ^{13}C (squares) in Judgford silt loam, sampled May 1974. The solid and dashed lines fitted to the ^{13}C data are based on a steady state soil model. (O'Brien and Stout, 1978.)

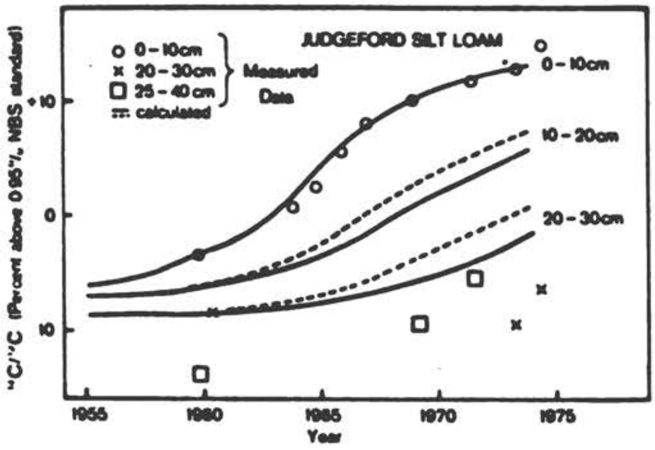


Figure 2. Radiocarbon enrichment of the atmosphere, pasture, earthworms, and soil following thermonuclear bomb testing since 1954. (O'Brien and Stout, 1978)

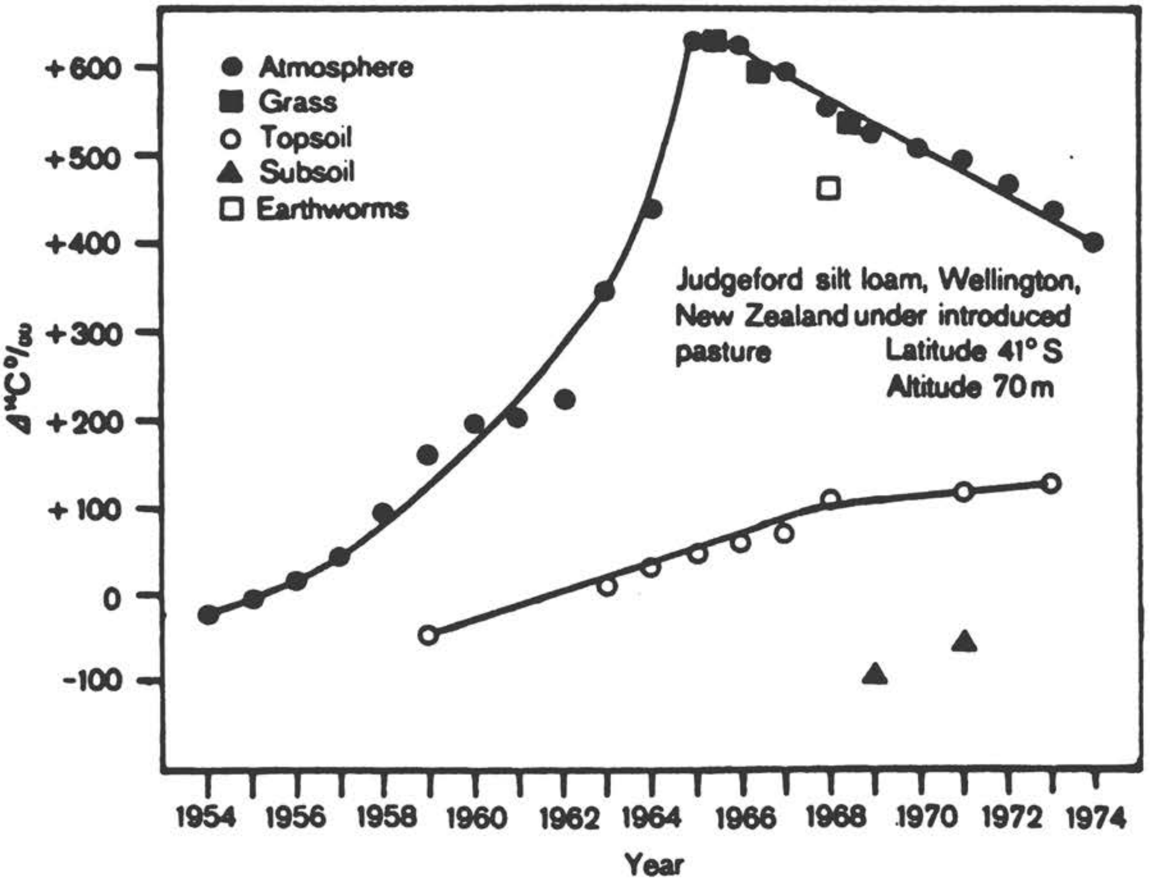


Figure 3. Measured increases in ^{14}C in Judgeford silt loam. The curves were fitted by using a diffusion carbon transport model. (O'Brien and Stout, 1978.)

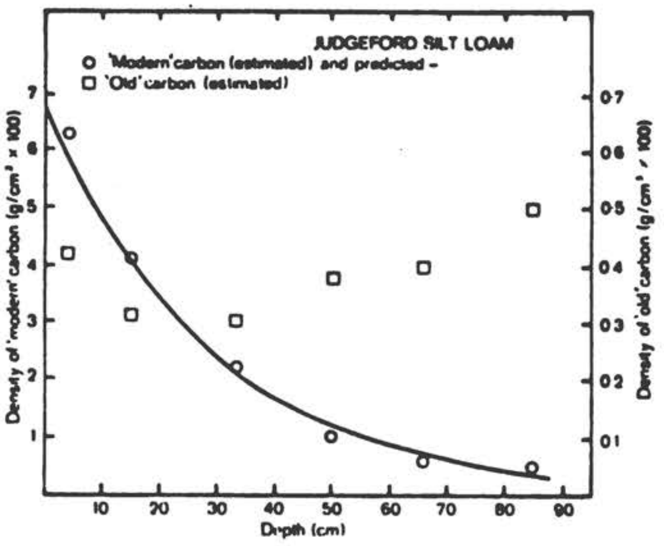


Figure 4. The concentration of "modern" and "old" carbon in soil derived from measurements. The solid line shows the concentration of modern carbon predicted from the steady state model. (O'Brien and Stout, 1978.)

of soil was 300 g carbon $m^{-2}y^{-1}$. In a steady state the last-named figure is identical with the carbon loss from the soil; it does not include respiration taking place in plants or plant litter. In Figure 1 it can be seen that the $\delta^{13}C$ values become more positive with depth, indicating that the deeper soil carbon is more enriched with ^{13}C than the top soil layer, which has about the same $\delta^{13}C$ as for grass, i.e., 27%.

DIFFERENT FRACTIONS OF SOIL ORGANIC CARBON

The Judgeford silt loam was sampled again in 1977 down to a depth of 1 m, two cores, between 1 and 2 meters apart were taken. Both cores were separated into 10 cm horizons. The total organic carbon, ^{14}C and ^{13}C concentrations were determined for each horizon of the first core. Part of each sample from the second core was separated by hydrolysis with 6N HCl and additional measurements were made on both the hydrolysate and the residue. This data is shown in Table 2.

The data in Table 2 have several features. The residue makes up the greater part of soil organic carbon in the topsoil, but only 30% in the subsoil. The concentration of carbon present in the hydrolysate is fairly constant at all depths whereas that in the residue drops by a factor of 50 between the top and bottom sections. The residue has a greater ^{14}C age at depths below 40 cm than the hydrolysate but it has more bomb ^{14}C present in the shallow soils. Values of $\delta^{13}C$ for the residue are fairly constant compared with those for the total soil and hydrolysate which appears to be less negative. The variation of ^{13}C with depth is shown in Figure 5 for the residue and hydrolysate.

Jenkinson and Rayner (1977), also found that the use of ^{14}C ages in the residue were older than in the hydrolysate, but the

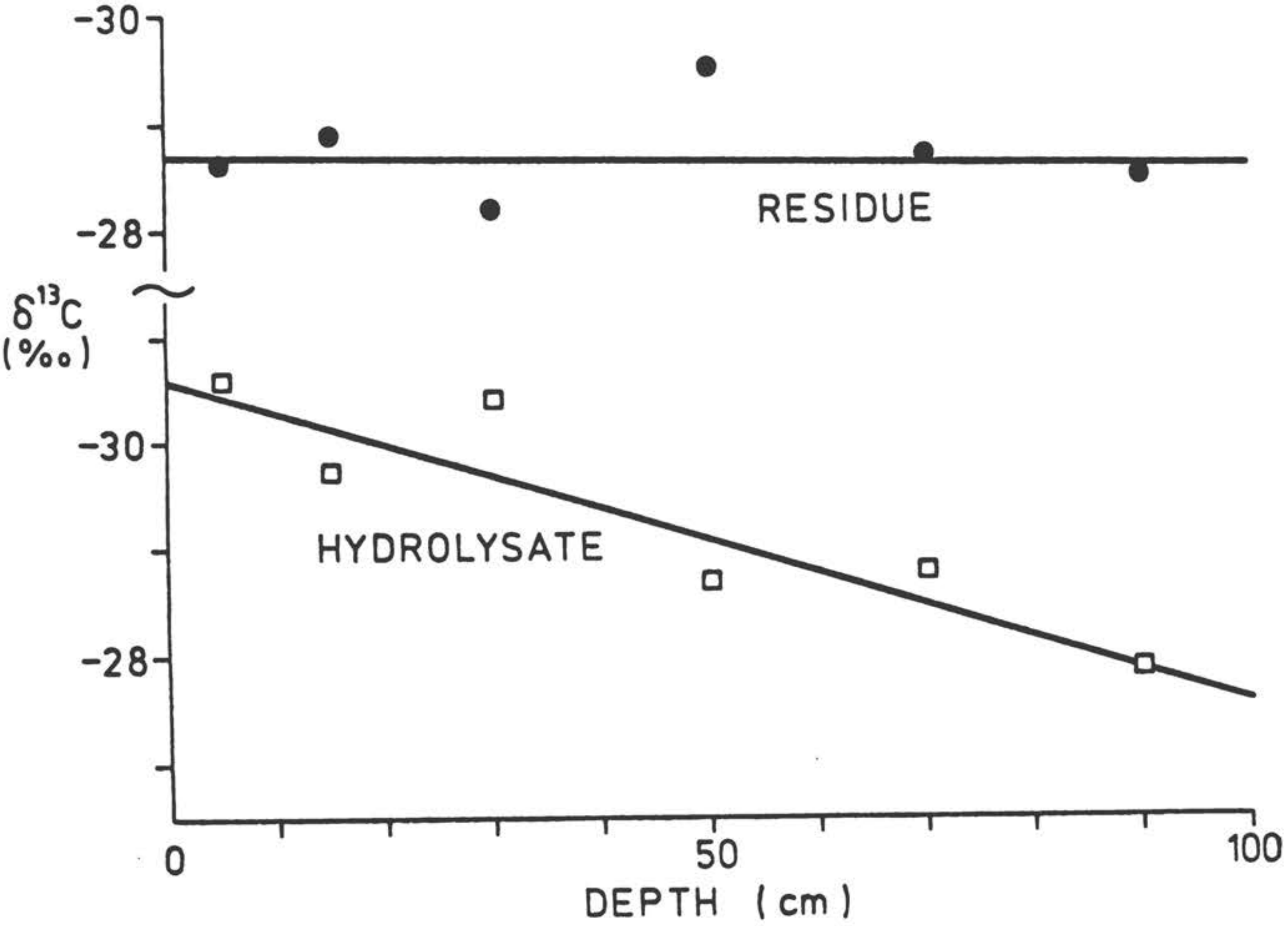


Figure 5. Distribution of ^{13}C in different organic carbon fractions of Judgeford silt loam.

differences were much greater than observed here. An increase in ^{13}C with depth was also reported in the Judgeford soil by O'Brien and Stout (1978), who interpreted this as due to fractionation during the respiration process or due to the presence of some "old" carbon fraction with more ^{13}C present. Carbon present in soil organic matter of well-drained sandy soils have also shown an increase of ^{13}C with depth (Goh _et al_., 1976). It has also been reported that ^{13}C increases with depth in soil organic carbon of well-drained soils under tussock grass in New Zealand (Stout and Rafter, 1978). However, the same authors report that in peat soils under tussock grass the ^{13}C level tends to remain constant or become lower with increasing depth. The C/N ratio in the well-drained soils range from 10 to 15, which is typical for New Zealand soils, whereas in peat soils it ranges from 20 to 30.

It is possible to interpret this information in the following way: If the residue material, shown in Table 2 and Figure 5, consists of material that has not been metabolized by decomposers, then it should have a $\delta^{13}C$ value equal to that of the parent plant material and it would be constant with depth. It would also be expected that such material would make up a large fraction of organic carbon in the topsoil layers but a much smaller fraction in the soil layers, as can be seen in Table 2 and even more clearly in Figure 6. If the soil organic material removed during the hydrolysis represents material that has been metabolized by decomposers, one would expect the ^{13}C to be fractionated and so vary with depth.

The relatively high C/N ratios observed in peat soils indicate that much of the organic matter in these soils is not decomposed (Stout and Rafter, 1978). The C/N ratios of

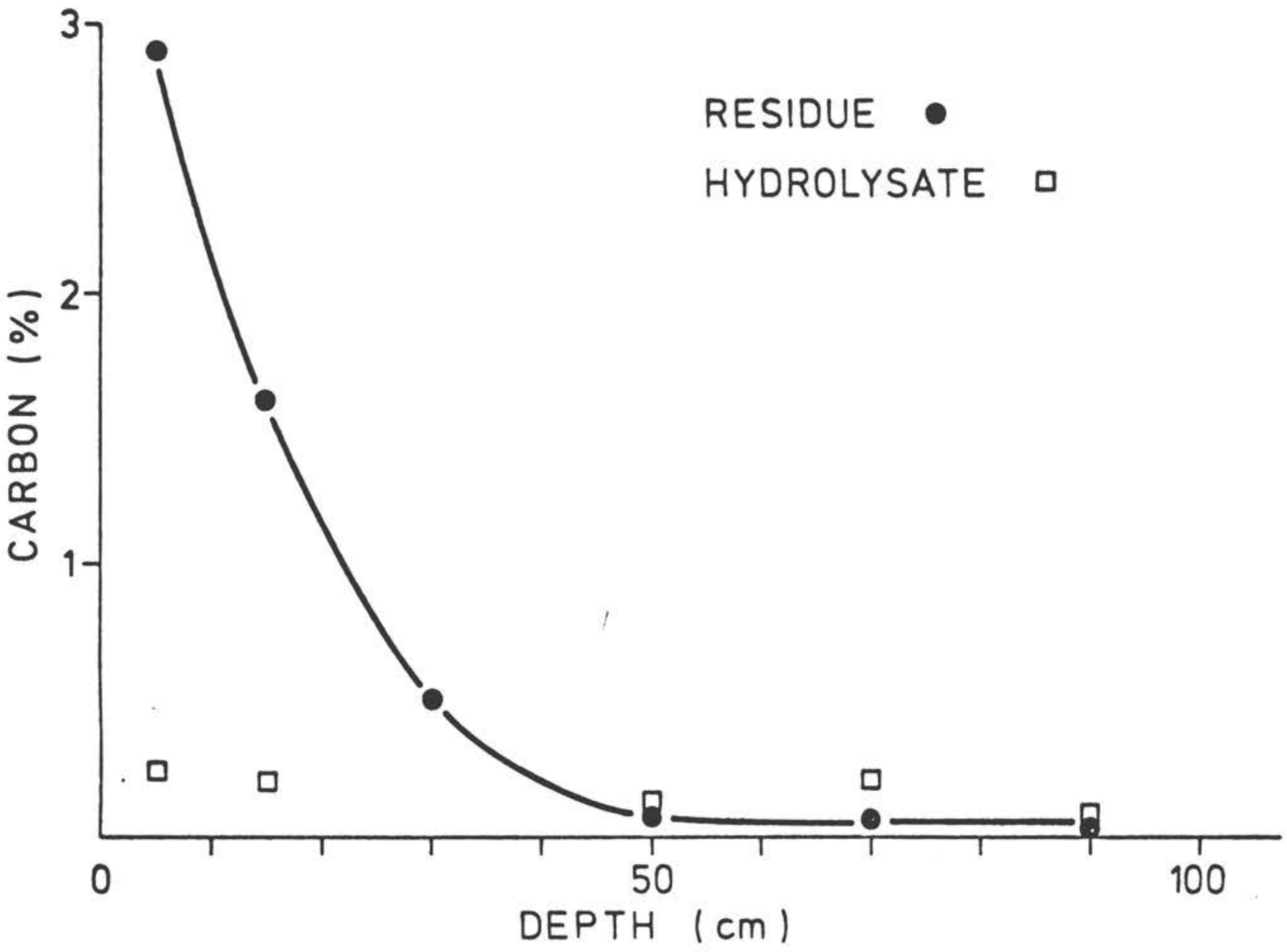


Figure 6. Distribution of organic carbon fractions with depth in Judgeford soil.

vegetation range from 10 to 200. Therefore, much of the carbon at all depths should be unfractionated, tending to make the $\delta^{13}C$ remain constant throughout the soil profile, as is observed. From the above discussion it would seem appropriate to label the residue as the un-metabolized or refractory fraction and the hydrolysis or mobile fraction as the metabolized or labile fraction.

The more uniform distribution of hydrolysate carbon with depth (Figure 6) suggests that this fraction is more mobile. This is supported also by the fact that this fraction has significantly younger ^{14}C ages than the residue at all depths, and that in the 0-10 and 10-20 cm horizons the hydrolysate has been much more enriched with bomb ^{14}C. If this fraction is more mobile and is readily separated by acid hydrolysis, one might expect that this fraction would be the most likely to give rise to dissolved organic carbon (DOC) in ground water.

CARBON ISOTOPES IN GROUND WATER

Carbon can enter the ground water as CO_2, as dissolved organic matter (DOC), or as particulate organic matter (POC). A knowledge of ^{14}C and ^{13}C concentrations in these materials is useful for understanding the movement of carbon from soil into rivers.

Hedges and Parker (1976) used ^{13}C data as an indicator of land-derived organic matter in the sediments of the Gulf of Mexico.

Lerman (1973) reported measurements of ^{13}C in soil CO_2 where C_4-type plants (with $\delta^{13}C$ values of -10 to -15%), were growing in soils with organic carbon with a $\delta\,^{13}C$ of -25 to -27%. The soil CO_2 had $\delta\,^{13}C$ values identical with the value of the plant material (15%), which indicated that the soil CO_2 was mostly derived from plant root respiration. Rubin and Spiker (1973) measured ^{13}C and ^{14}C in the dissolved organic carbon (DOC) of some rivers in the United States in 1972. Because of the very low concentration of DOC, 2-4 mg/l, very large samples were needed to determine the ^{14}C. Rock Creek had 2 mg/l of DOC, with a $\delta\,^{13}C$ of -28.2 and $\Delta\,^{14}C$ of +480%. In the Potomac River there was 4 mg/l of DOC with a $\Delta\,^{14}C$ of +350%. The ^{13}C and ^{14}C measured in the DOC of other rivers showed that there was dilution with fossil carbon. The above ^{14}C data show that the DOC originated from plant material less than 10 years old and probably came from the uppermost layer of soil.

Table 3 lists some carbon isotope measurements in New Zealand freshwaters. The dissolved carbon dioxide and carbonate ion have $\delta\,^{13}C$ values ranging from about +1 to -20. Ground water is likely to contain dissolved CO_2 with a partial pressure of several percentage points of 1 atm and with a $\delta\,^{13}C$ value of about -27. When this carbonic acid solution dissolves limestone carbonate in the soil, the resulting $\delta\,^{13}C$ value will depend on that in the carbonate and on whether it is dissolved in an open or closed system (Hendy, 1970). If calcium carbonate with a $\delta\,^{13}C$ value of +1 is dissolved in the presence of gaseous soil CO_2 (open system), the $\delta\,^{13}C$ of the inorganic carbon species in solution will be in the range of 11 to 15, but if there is no abundance of gaseous CO_2 present, it will be in the range of 15 to 18 (Hendy, 1970). Since the calcium carbonate is probably quite old, it would be depleted in ^{14}C, and for this reason it is difficult to interpret ^{14}C data in dissolved carbonates. In some soil, pedogenic carbonate is present with $\delta\,^{13}C$ values of -26 to -28% (Leamy and Rafter, 1973).

TABLE 3 Carbon Isotopes in Some New Zealand Freshwaters

Location	Collection Date	Sample Description	Concentration m mole/l	$\delta^{13}C$ %	$\Delta^{14}C$ %
Hutt Valley Silverstream[a]	11/58	CO_2	0.02	-16.5	42
		$CO_3^=$	0.40	- 9.0	-21
Hutt Valley Belmont [a]	11/58	$CO_2+CO_3^=$	-	-17.5	-75
Hutt Park aquifer[a]	11/58	CO_2	0.60	-23.5	-115
		$CO_3^=$	0.69	-16.9	-84
Lake Taupo inlet water[a]	11/58	$CO_2+CO=_3$	-	- 4.7	-336
Lake Taupo outlet water[a]	11/58	$CO_2+CO_3^=$	-	+ 1.6	-400
Lake Taupo outlet water [b]	2/78	$CO_2+CO_3^=$	0.81	+ 0.9	-174
Lake Taupo lake water[b]	2/78	$CO_2+CO_3^=$	0.85	+ 0.3	-221
Christchurch aquifer[b]	6/76	$CO_2+CO_3^=$	0.74	-16	-242
Heathcote River Mouth[c]	1/80	Particulates		-26.0	
Avon River Mouth[c]	1/80	Particulates		-24.7	

[a] Rafter *et al*., 1973.

[b] H. Jansen, personal communication, August 1980.

[c] G.L. Lyon, personal communication, September, 1980

The dissolved CO_2 and $CO_3^=$ in the Hutt Valley and Christchurch aquifers generally have $\delta^{13}C$ values consistent with carbonate being dissolved by soil CO_2, but the relatively high values for the Hutt Valley ^{14}C data indicate the presence of bomb ^{14}C. The high values for the $\delta^{13}C$ of the Lake Taupo water probably reflect the presence of CO_2 of geothermal origins (with a $\delta^{13}C$ of -3%) in this water. This would also account for the low values of $\Delta^{14}C$.

The $\delta^{13}C$ values for particulate organic matter at the outlets of the Heathcote and Avon Rivers, near Christchurch, New Zealand, in January 1980 of -26% and 24.7% reflect values expected of the soils of this area (G. L. Lyon, Institute of Nuclear Sciences, personal communication, 1980).

THE RUNOFF OF SOIL CARBON FROM JUDGEFORD SILT LOAM

A 2-year study was made of sediments and discharges into the Pauatahanui inlet in 1976-1977 (Healy, 1980). A map of the inlet and catchment area, which includes the Judgeford Valley, is shown in Figure 7. The inlet, north of Wellington, New Zealand, has only a small channel connecting with with the ocean. Details of the catchment area and sediment runoff are given in Table 4. The sediments of the inlet are deep, and Figure 8 gives data on ^{14}C age and sedimentation rate. The deepest sediment at 12-13 m was 8,360 years old and had accumulated since the last glaciation. The $\delta^{13}C$ values for the sediment carbon ranged from 25.4% to 28.8%. This would indicate that essentially all the carbon in the sediment is of terrestrial origin (Hedges and Parker, 1976). The amount of carbon in the sediment ranged from 1% at 0.65 m to 6.1% at 9-10 m, varying with the rate of sedimentation and environmental conditions, particularly climate and vegetation history.

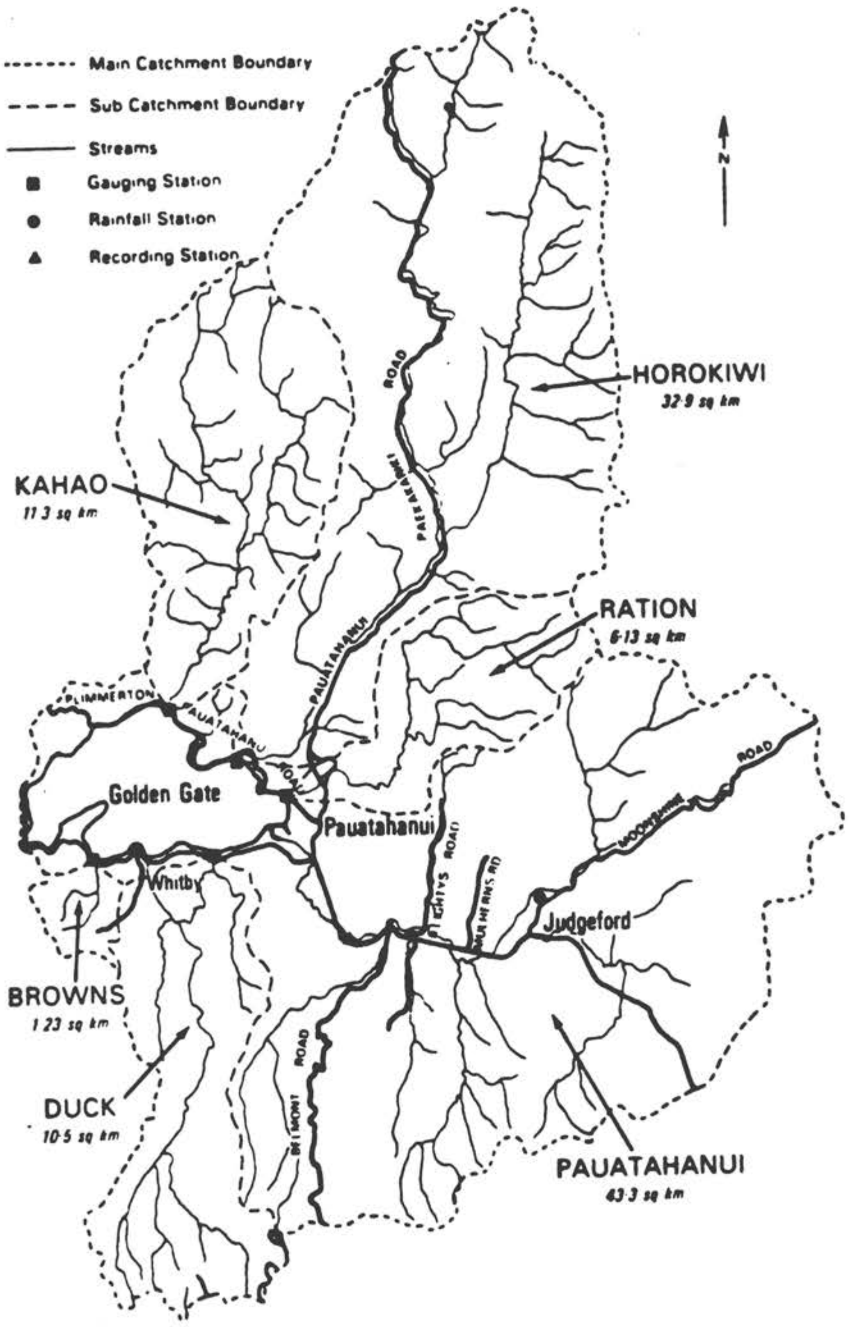
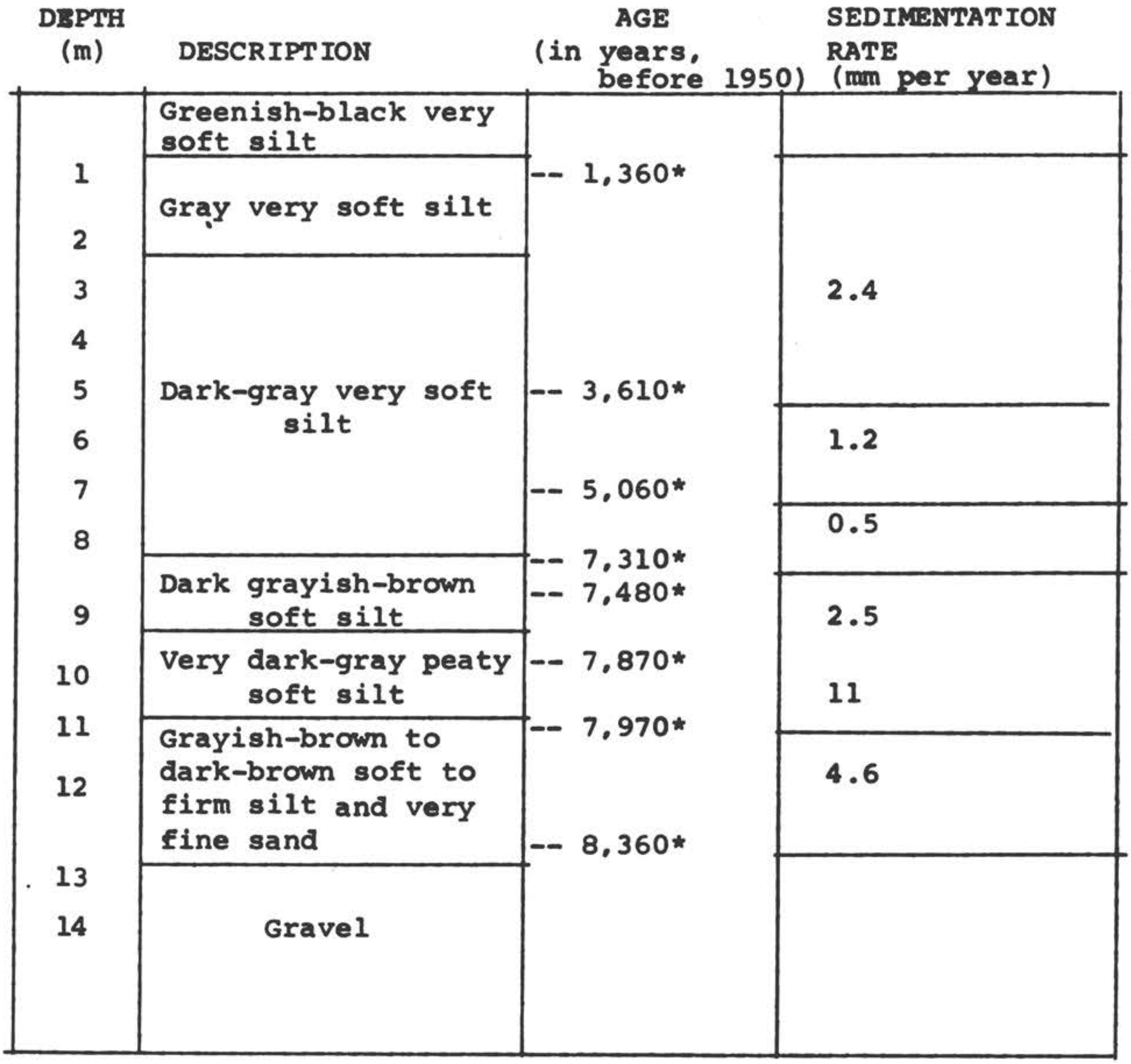


Figure 7. A plan of the Pauatahanui Inlet catchment area. (Healy, 1980.)

TABLE 4 Transport of Soil Carbon into the Pauatahanui Inlet [a]

Area of catchment	105.4 km^2
Carbon in soils of catchment, topsoils	5.6%
subsoils	1%
C/N ratio of soils of catchment, topsoils	14
subsoils	11
Carbon in inlet sediments	1-6%
C/N ratio of inlet sediments (surface)	10
Annual water discharge to inlet	$5.1 \times 10^7 m^3$
Annual sediment discharge to inlet	3,900 t
Annual nitrogen discharge to inlet	6.8 t
Annual organic carbon discharge to inlet	68 t

[a] Data from Healy, 1980.



* ± 150 years

Figure 8. Radiocarbon age in years before 1950 and rate of sedimentation in mm per year of Pauatahanui Inlet sediment. (Healy, 1980.)

The average loss of soil carbon as particulate organic carbon (POC) can be estimated from Table 4. Using the annual discharge of 68 t and the catchment area of 105.4 km^2, one finds that the annual loss (POC) from soils is 0.65 g m^{-2}. This compares with 300 g $m^{-2}y^{-1}$, which is the annual loss of soil carbon at Judgeford, as determined by modeling the ^{14}C data (O'Brien and Stout, 1978). The average loss of POC in ground water is thus only about 0.2% of the total soil loss. Moeller et al. (1979), who studied DOC transport down seven U. S. rivers found that the run off of FOC from the catchment areas was 0.083 to 0.4% of the net primary production rate. An estimate can be made of the soil carbon being carried off as dissolved bicarbonate. If the $CO_2+CO_3^=$ concentration in the river and stream waters is assumed to be 0.8 m mole/l, as given for Lake Taupo in Table 3, and if half of this is from the CO_2, then the total annual runoff of soil carbon is 24 to. This is 0.23 $gm^{-2}y^{-1}$ in the catchment area, which is 0.08% of the estimated annual loss from the Judgeford silt loam.

During the Pauatahanui study it was observed that most sediment was transported to the inlet during high-flow conditions after storms. In 1976, 20% of the annual sediment discharge was made during two storms of several days duration.

CONCLUSIONS

The ^{14}C in the upper layers of soil has increased because of the incorporation of bomb carbon. At greater depths the ^{14}C indicates ages of thousands of years. In well-drained soils the ^{13}C becomes more concentrated at depth. A carbon transport diffusion model can be used to analyze the ^{14}C

data and estimate the average annual loss, carbon turnover time, and diffusion rates in soils.

The hydrolyzed fraction of the carbon in the Judgeford silt loam showed an increase of ^{13}C, but there was no shift in the residue. This indicates that the hydrolysate is metabolized but the residue unmetabolized. From its distribution with depth and its younger age, the hydrolysate appears to be the more mobile fraction.

The measurements of carbon isotopes in soil, air, and ground water, and in the organic component of river waters, are few, but those that have been made indicate that DOC originates from fairly young soil organic matter. There is a great need for more measurements of ^{13}C and ^{14}C in ground waters and in different soil fractions. The advent of ^{14}C measurements with accelerators and the use of small counters should make this much easier, since measurements can be made on small samples.

A study of the transport of sediments to the Pauatahanui inlet over a 2-year period, and measurements of ^{13}C in the sediment, indicate that the sediment carbon is of terrestrial origin and that the loss of soil carbon as POC is about 0.2% of the net soil carbon loss.

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CARBON ISOTOPES AS INDICATORS OF THE SOURCE AND FATE OF CARBON IN RIVERS AND ESTUARIES

Elliott C. Spiker

INTRODUCTION

The riverine flux of carbon may be serving as an effective short-term sink for anthropogenic CO_2 if this carbon flux is increasing in response to human activities, and if this carbon is ultimately sequestered in sediments for several tens to hundreds of years. The source of this is of primary importance. If most of this carbon is derived from the weathering of rocks and soil humus, and only a small fraction from the atmosphere and recent vegatation, then this flux will be slow to take up anthropogenic CO_2. Likewise, the carbon preserved in sediments may be derived mostly from older refractory soil humus, while that which is re-mineralized and returned to the atmosphere may be mostly from younger labile carbonaceous material. Before an estimate can be made of the relative importance of the riverine carbon flux, the sources, sinks, and rates of biochemical processing in river-estuarine systems need to be determined.

This paper discusses the application of carbon isotopes ($^{14}C/^{13}C/^{12}C$)* to these studies. The double isotopic labeling of carbon is particularly useful for the analysis of sources and sinks of carbon. The onset of nuclear weapons testing in 1954 resulted in a large input of bomb-produced "excess" ^{14}C into the atmosphere. The ^{14}C composition of atmospheric CO_2 in the Northern Hemisphere increased nearly 100% by 1964 (Figure 1). This excess ^{14}C has been a useful tracer for studying atmospheric mixing and air-sea exchange of CO_2. The ^{14}C enrichment of soil humus has been used to study soil turnover rates (see Stout, this conference). Its distribution in rivers is discussed here.

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* The isotope compositions are expressed as the difference in parts per thousand (permil) between the sample and reference standard. $\delta^{13}C$ is referenced to the PDB standard (Craig, 1957), and $\Delta^{14}C$ is referenced to the oxalic acid standard (Stuiver and Polach, 1977).

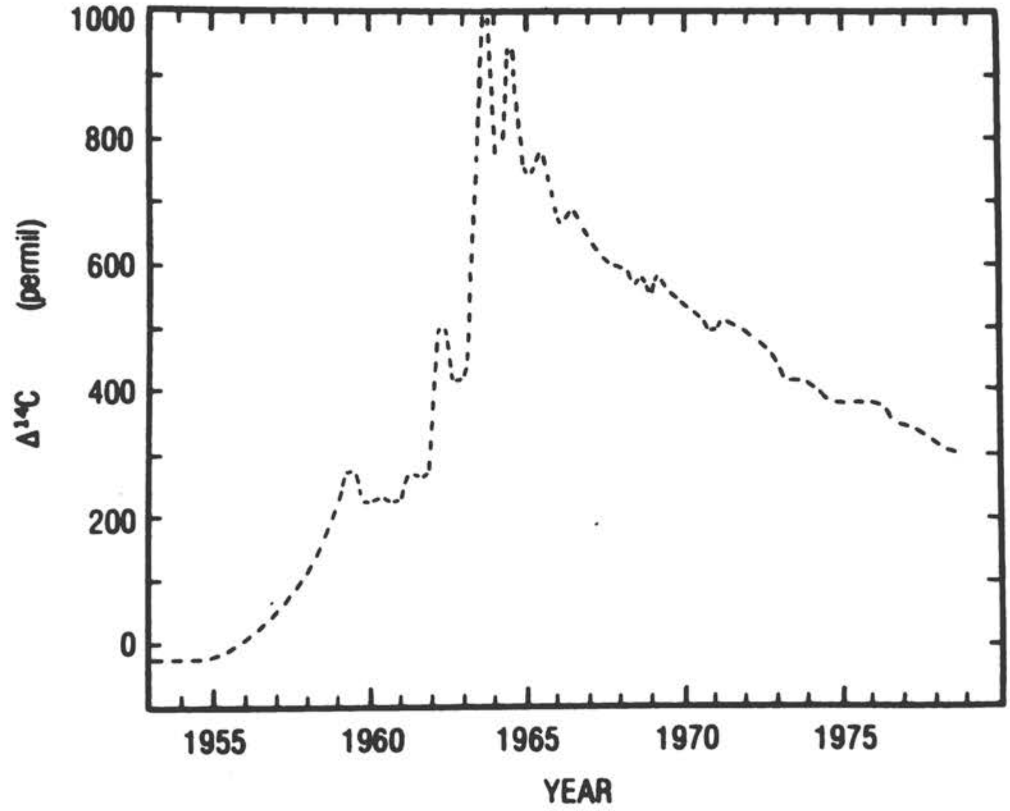


FIGURE 1 ^{14}C concentration of tropospheric CO_2 in the Northern Hemisphere since 1953 (Levin _et_ _al_., 1980; Druffel, 1980).

RIVERINE INORGANIC CARBON

Chemical weathering is primarily due to the reaction between carbonic acid and rocks. The dissolution of carbonate-bearing minerals is the primary source of most of the inorganic carbon (and alkalinity) in natural waters. In nearly all natural weathering situations, carbonate dissolution produces two bicarbonate ions formed from one carbonate molecule and one CO_2 molecule. In a system isolated from exchange with other sources of carbon, the carbon isotope composition of the resulting solution is expected to be intermediate between that of the carbonic acid and the carbonate mineral (Figure 2). In contrast, the solution resulting from silicate weathering under similar conditions would have a carbon isotopic composition equal to that of the carbonic acid. On the basis of the SiO_2 river flux, Kempe (1979) estimated that the weathering of silicates accounts for about one quarter of the DIC in rivers.

Although some CO_2 is dissolved in rain water, most carbonic acid is derived from root respiration and humus decay in the soil zone. The isotopic composition of soil CO_2 should reflect the relative contribution from root respiration ($\delta^{13}C \approxeq -25$; $\Delta^{14}C \approxeq +400$, $\approxeq$ atmospheric CO_2) and from the decomposition of humus, which may be at least hundreds of years old ($\delta^{13}C \approxeq -25$; $\Delta^{14}C \approxeq -200$ to zero). Thus, assuming values for soil CO_2 ($\delta^{13}C \approxeq -25$; $\Delta^{14}C \approxeq +100$) and for carbonate minerals ($\delta^{13}C \approxeq 0$; $\Delta^{14}C \approxeq -1000$), the $\delta^{13}C$ and $\Delta^{14}C$ compositions of the DIC resulting from closed system carbonate weathering are estimated to be about -12.5 and -450 permil, respectively. This is the simplest case. If little organic matter is present, carbonate dissolution primarily by reaction with CO_2 in rain ($\delta^{13}C \approxeq -7$;

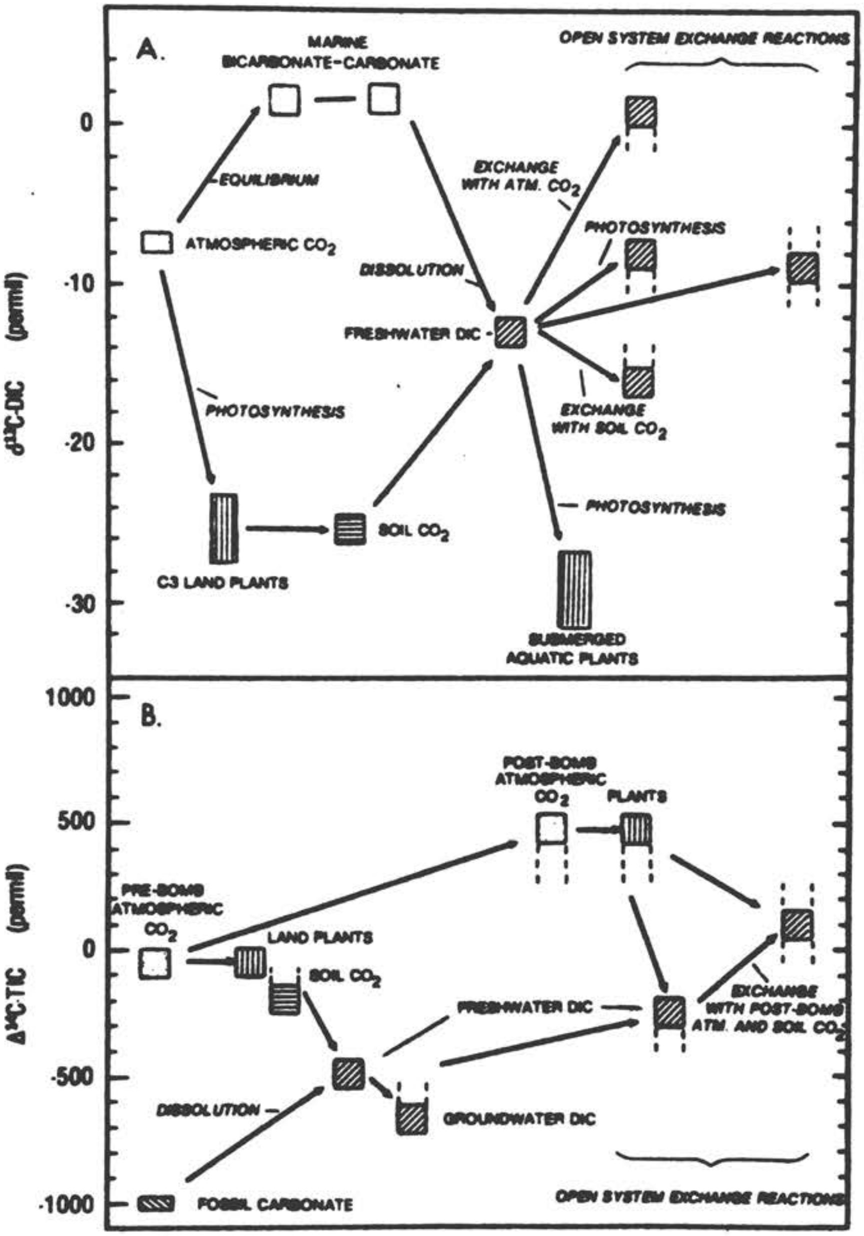


FIGURE 2 The carbon isotopic composition of various compounds in nature.

$\Delta^{14}C$ ≅ +300) will produce somewhat more positive values. In soft water, most carbon will be derived from organic matter, yielding more negative $\delta^{13}C$ values, and probably more positive $\Delta^{14}C$ values for the DIC.

Weathering in a system open to exchange with the atmosphere or other sources of carbon will result in higher or lower values, depending on the sources and extent of exchange. In any case, the initial isotopic composition of the DIC is expected to be altered as a result of various inputs and outputs of carbon and isotopic exchange (Figure 2). Seasonal trends may be expected to be related to variations in biological processes, atmospheric exchange, and surface and ground water runoff. More negative $\delta^{13}C$ values result from the input of biogenic CO_2 from oxidation and respiration processes, and more positive values generally result from atmospheric exchange and preferential ^{12}C utilization during photosynthesis (Broecker and Walton, 1959; Oana and Deevey, 1960; Parker and Calder, 1970; Mook, 1970; Spiker and Schemel, 1979; Spiker, 1980). In lakes with sufficient water residence times, atmospheric exchange may result in a ^{13}C enrichment toward equilibrium values of about +2 permil, as in the surface ocean.

The ^{14}C effect of biogenic CO_2 input will depend on its source and ^{14}C content or apparent "age" (Figure 2b). Sources are the oxidation of older soil humus or benthic sediment organic carbon, or recent post-bomb era plant material ($\Delta^{14}C$ ≈0 to + 800). Municipal sewage effluent can be a significant source of ^{14}C- enriched DIC and DOC from post-bomb era vegetation. Atmospheric exchange may also result in ^{14}C enrichment of the DIC toward atmospheric levels. Although the effect of respiration and remineralization of algal carbon can dominate the $\delta^{13}C$-DIC, the effect on $\Delta^{14}C$-DIC is minimal compared with other effects. Algae may be expected to be about 20 permil depleted in ^{13}C and 40 permil depleted in ^{14}C relative to the DIC.

Values for $\delta^{13}C$-DIC and $\Delta^{14}C$-TIC (total inorganic carbon: unfiltered water was acidified and the CO_2 collected for ^{14}C analysis; see Spiker, 1980) from four rivers are given in Table 1. The most striking aspect of these data is the high ^{14}C values relative to that predicted for closed system weathering. The inorganic carbon is apparently dominated by post-bomb era carbon, indicating significant inputs from the oxidation and respiration of post-bomb plant material and possibly atmospheric exchange. Sewage effluents may also be an important source. The DOC in Baltimore effluent, sampled in June 1972, had $\Delta^{14}C \approx +502$, similar to atmospheric CO_2 in 1972 (Spiker and Rubin, 1975). The $\delta^{13}C$-DIC is apparently maintained in the -7 to -11 permil range by the coupled effect of respiration, photosynthesis, and atmospheric exchange (Spiker, 1980).

Also interesting is the apparent difference between the east coast and west coast rivers, possibly due to control by rock type. The lower $\Delta^{14}C$ values in the East may be due to carbonate weathering in the Appalachian Mountains, as well as greater ground-water discharge. Weathering of silicates and argillaceous sediments dominates in the Sacramento River watershed. Thus, the $\Delta^{14}C$-TIC appears to reflect both geologic province and biochemical processing in the river.

TABLE 1 δ^{13}C-DIC and Δ^{14}C-TIC from Several Rivers in the United States

River	Date	δ^{13}C-DIC (permil)	Δ^{14}C-TIC (permil)
Sacramento River at Rio Vista, Calif.	September 1975	-11.4	+284
	March 1976	-12.0	+255
James River at Hopewell, Va.	July 1976	- 9.1	+ 21
Susquehanna River at Port Deposit, Md.	April 1977	- 9.5	+ 47
	September 1978	- 8.3	+ 82
	June 1979	- 8.8	- 40
Potomac River at Great Falls, Va.	August 1978	- 7.5	+ 16

If these data are representative of other major rivers, post-bomb atmospheric CO_2 is a major component of the inorganic carbon. Assuming values for $\Delta^{14}C$-TIC = +100 and atmospheric CO_2 = +400, it appears that as much as 80% is derived from post-bomb atmospheric CO_2, due to carbon exchange in the river, and only 20% from fossil carbonate minerals. If we assume a total inorganic carbon flux of 530 x 10^{12} grams C/year (Meybeck, this workshop), the flux of post-bomb inorganic carbon in rivers is as much as 424 x 10^{12} grams C/year, or about 46% of the total carbon flux in rivers. Thus, the riverine flux of inorganic carbon appears to be a significant component of the atmospheric CO_2 cycle, as much as 9% of the yearly fossil fuel CO_2 input to the atmosphere. Note, however, that this riverine flux can be an effective sink for anthropogenic CO_2 only if this flux is increasing in response to human activities and if the bulk of it is sequestered in sediments.

DISSOLVED ORGANIC CARBON

The principal sources of DOC in rivers are soil humus, land=plant detritus, and aquatic productivity. Land plants have atmospheric ^{14}C values, while soils are deficient, reflecting their mean residence time. The ^{14}C composition of algae will reflect that of the DIC.

$\Delta^{14}C$-DOC data from six rivers are given in Table 2. These data are mostly from Spiker and Rubin (1975). Except for the one high value from the Potomac River during Hurricane Agnes (April 17, 1972), the $\Delta^{14}C$-DOC values were typically intermediate compared with the sources, thus probably reflecting a mixture of these sources. The high value during the Agnes flood is especially interesting, since it indicates that the increased flux of DOC during the flood was derived from post-bomb era carbon ($\Delta\ ^{14}C \approx +500$). Apparently, plant debris that grew since 1954 was preferentially washed into the river, as opposed to older soil carbon.

Although the relationship between POC and DOC in fresh water is uncertain, their $\delta^{13}C$ Compositions appear to be similar. Williams and Gordon (1970) reported values of -28.5 and -29.4 permil for DOC and POC in the Amazon River. Shultz (1974) and Eadie _et_ _al_. (1978) found values for DOC in the Mississippi to range from about -25 to -28 permil. Nissenbaum and Kaplan (1972) found similar values for soil humic and fulvic acid. The behavior of $\delta^{13}C$-DOC in the river-estuarine environment and its relationship to aquatic productivity are not yet known.

TABLE 2 $\Delta^{14}C$ Value of Dissolved Organic Carbon from Several Rivers in the United States

River	Date	Water Discharge (m^3/sec)	DOC (mg/l)	$\Delta^{14}C$ (permil)
Potomac River, upstream of Washington D.C.	April 17, 1972	1,531	4.0	+365
	December 4, 1972	492	4.5	+ 28
	March 7, 1973	546	4.6	+ 91
Susquehanna River, at Port Deposit, Md.	September 21, 1972	320	3.5	- 81
Rappahannock River, upstream of Fredericksburg, Va.	February 1, 1973	91	1.5	- 91
James River, upstream of Richmond Va.	February 22, 1973	308	2.0	+ 42
Brandywine Creek, at Dowlan, Pa.	August 22, 1973	1	2.5	+ 63
Sacramento River, at Rio Vista, Calif.	1974		3.5	- 31

PARTICULATE ORGANIC CARBON

This section discusses the use of $\delta^{13}C$ as an indicator of the source and fate of particulate organic carbon. We have as yet no ^{14}C data for POC. $\delta^{13}C$ distributions in San Francisco Bay and in the Potomac River and its estuary are discussed as case studies. A comparison of these two systems, which differ considerably with respect to their hydrodynamics and biochemical cycling, provides added perspective on estuarine carbon dynamics.

The carbon isotope composition of organic matter in estuarine and coastal regions has been extensively used as a relatively simple and reliable source indicator that can discriminate between terrestrial and marine organic carbon. Consistent increases in the $\delta^{13}C$ from riverine values (about -25 to -30 permil) to marine values (about -18 to -22 permil) are generally interpreted as indicating mixing between land-derived carbon and marine carbon (Sackett and Thompson, 1963; Calder, 1969; Hunt, 1970; Eadie and Jeffrey, 1973; Shultz, 1974; Hedges and Parker, 1976; Shultz and Calder, 1976; Gearing et al., 1977; Spiker and Schemel, 1979; Tan and Strain, 1979).

Terrestrial carbon is apparently limited more or less to estuarine and near-coastal marine waters and sediments. In general, the extent of riverine values offshore is dependent on local river discharge and the width of the continental shelf. A wide shelf or large estuary is an efficient trap for land-derived material. The implication is that terrestrial carbon is probably not a significant source of organic carbon to the open ocean.

Although this simple two-endmember (terrestrial versus marine) model is clearly useful, there are several factors that limit its resolution and applicability. First, it is often difficult to estimate low levels of terrestrial carbon in coastal areas precisely because of the several-permil range of $\delta^{13}C$ commonly observed in both riverine and marine organic matter. Second, this model does not consider the effect of estuarine and fresh water aquatic productivity. This may be a dominant source of organic carbon, especially in areas enriched with nutrients as a result of man. Third, the isotopic composition of the more refractory organic matter preserved in sediments may differ from the bulk source material.

Unless the $\delta^{13}C$ composition of the marine endmember can be narrowly defined, estimates of the terrestrial input to coastal marine water and sediments can only be approximate. For example, outer-shelf sediments often have a $\delta^{13}C$ value of about - 21 permil. The estimate of the terrestrial carbon component could range from zero to about 50%, the range depending on the $\delta^{13}C$ values assumed for the marine and riverine sources.

The range of $\delta^{13}C$ values for marine organic matter may be due to several factors. The isotopic composition of plant carbon is a function of fractionation during carbon metabolism and the $\delta^{13}C$ of the inorganic carbon source utilized. Most temperate open-ocean marine plankton typically have values in the range -18 to -21 permil. The apparent photosynthetic fractionation varies as a function of pH, growth-rate, temperature, and species (Degens, 1969; Wong and Sackett, 1978).

Much of the range in values reported for marine plankton in coastal waters could conceivably be related to seasonal variations in primary productivity, although insufficient carbon isotope data exist to test this. At high latitudes, the $\delta^{13}C$ of marine plankton decreases, approaching values more typical for riverine carbon (Sackett _et_ _al_., 1965; Eadie _et_ _al_., 1978). These patterns definitely limit the applicability of the $\delta^{13}C$ technique in these areas.

It is important to distinguish between marine plankton and the large reservoir of deep-ocean dissolved organic carbon(DOC) and particulate organic carbon(POC). DOC and POC in most temperate open-ocean waters have $\delta^{13}C$ values in the range of -20 to -24 permil, significantly lower than values for surface water plankton (Williams and Gordon, 1970; Eadie and Jeffrey, 1973; Eadie _et_ _al_., 1978). Although it may be argued that this deep-ocean carbon contains a significant terrestrial component, it probably consists of biochemically resistant fractions that have been stripped of ^{13}C-enriched amino acids and sugars. This deep-ocean organic matter is probably not representative of larger, faster sinking particles, such as fecal pellets, which originate in the surface water and are the dominant source of sedimentary carbon (Bishop _et_ _al_., 1977). This would explain why the $\delta^{13}C$ of open-ocean benthic sediments more closely reflects the $\delta^{13}C$ of surface water POC (Eadie and Jeffrey, 1973; Tan and Strain, 1979).

Another factor that probably contributes to $\delta^{13}C$ variations in shelf sediments is the nature of the refractory carbon preserved there. Some may be older recycled kerogen (Sackett et al., 1974). Kerogen in modern sediments is at least 1 permil lighter than the assumed bulk plant carbon precursor (Nissenbaum and Kaplan, 1972; Stuermer et al., 1978). Varying amounts of land-plant fragments may also be significant. Hedges and Parker (1976) found a good correlation between $\delta^{13}C$ and the relative concentration of lignin compounds in sediments from the western Gulf of Mexico. However, they conclude that most of the lignin occurs as plant fragments and not in the form of humic acids or simple phenols. Similar results were obtained from surface sediments and cores from the southern Washington State continental shelf and slope (Hedges and Mann, 1979). Gearing et al. (1977) noted that the organic carbon in the coarse fraction was about 1 permil less than that associated with the fine fraction of Mississippi Delta sediments. This coarse fraction consisted of woody flakes and plant fibers mixed with sand. This suggests that terrestrial carbon in outer-shelf sediments may be mostly in the form of refractory woody detritus. Thus, the range of $\delta^{13}C$ values observed in coastal ocean waters and sediment appears to be due to factors in addition to low levels of modern terrestrial carbon, such as fractionation effects during photosynthesis and decomposition, and possible recycling of older refractory material.

The relatively wide range of $\delta^{13}C$ values for riverine organic matter (about -25 to -30 permil) is indicative of its heterogeneity also. POC in rivers and estuaries includes both living and dead organisms, detrital land-derived material, and organic carbon resuspended from benthic sediments. We may expect at least a several-permil range for most land-plant detritus because of a variety of factors related to species and environment. Most plants use the C3 (Calvin) photosynthetic pathway, and typically have values ranging from -25 to -27 permil (Degens, 1969). Plants that use the C4 (Hatch-Slack) pathway have a mean $\delta^{13}C$ of about -13 permil (Smith and Epstein, 1970). These plants include some desert and salt marsh plants and tropical grasses.

Floating pondweeds that utilize atmospheric CO_2 (about -7 permil) have values similar to those of land C3 plants. However, the $\delta^{13}C$ of submerged aquatic plants may be different because of their utilization of freshwater dissolved inorganic carbon (DIC) (typically about -10 permil), which may vary in isotopic composition in response to photosynthetic utilization, respiration, and mineralization (Oana and Deevey, 1960; Stuiver, 1975). Various species and growth-rate effects also are important (Degens, 1969; Wong and Sackett, 1978). Fresh water algae typically have values of about -30 permil. Values in the range -25 to -30 permil are common for organic carbon in lake sediments.

The $\delta^{13}C$ of estuarine algae is probably primarily related to that of the DIC, which typically increases systematically with salinity, approaching marine values of about ±2 permil (Sackett and Moore, 1966; Mook, 1970; Strain and Tan, 1979; Spiker and Schemel, 1979; Spiker, 1980). Thus the $\delta^{13}C$ of estuarine algae is expected to vary (river to ocean) from about -30 to -18 permil, assuming a mean photosynthetic fraction of about 20 permil.

Another possible source of estuarine detritus is marsh-grasses such as C4-pathway Spartina alterniflora (about -12 permil) from bordering tidal salt marshes. However, since the δ^{13}C of estuarine and coastal POC and sediment mostly reflects algal sources, salt-marsh grasses are probably not a large net source of detritus (Haines, 1977; Hackney and Haines, 1980).

THE SAN FRANCISCO BAY - A CASE STUDY

Fresh water enters the San Francisco Bay system principally in the northern arm (North Bay), a partially-to-well-mixed estuary of the Sacramento and San Joaquin rivers. River inflow remained low during the study period (1976-1978) and water replacement time in North Bay was 6 to 12 weeks. Spiker and Schemel (1979) discussed the distribution of carbon and $\delta^{13}C$ in the water and sediments. Some of their results are shown in Figure 3 and Figure 4 (top).

The observed distributions appear to be consistent with a simple conceptual model shown in Figure 4 (bottom). In the outer estuary, the distribution of $\delta^{13}C$-POC resulting from dilution is a concave-upward curve because of the high POC concentration at low salinity. Alternatively, the distribution that would result from <u>in situ</u> algal production alone is estimated from the $\delta^{13}C$-DIC distribution and an average photosynthetic fractionation ($\Delta\delta^{13}C$). Values in the turbidity maximum may be related to riverine values upstream, if flocculation is the dominant process, or possibly to estuarine values downstream, if landward transport by estuarine circulation is more important. Of course, resuspension of benthic carbon and phytoplankton production in the turbidity maximum zone may also be significant sources.

The observed distributions of $\delta^{13}C$-POC and sediment TOC in the outer estuary appear to be generally the result of dilution, approaching marine values at Golden Gate. However, during March 1977 a $\delta^{13}C$-POC maximum, coincident with increased

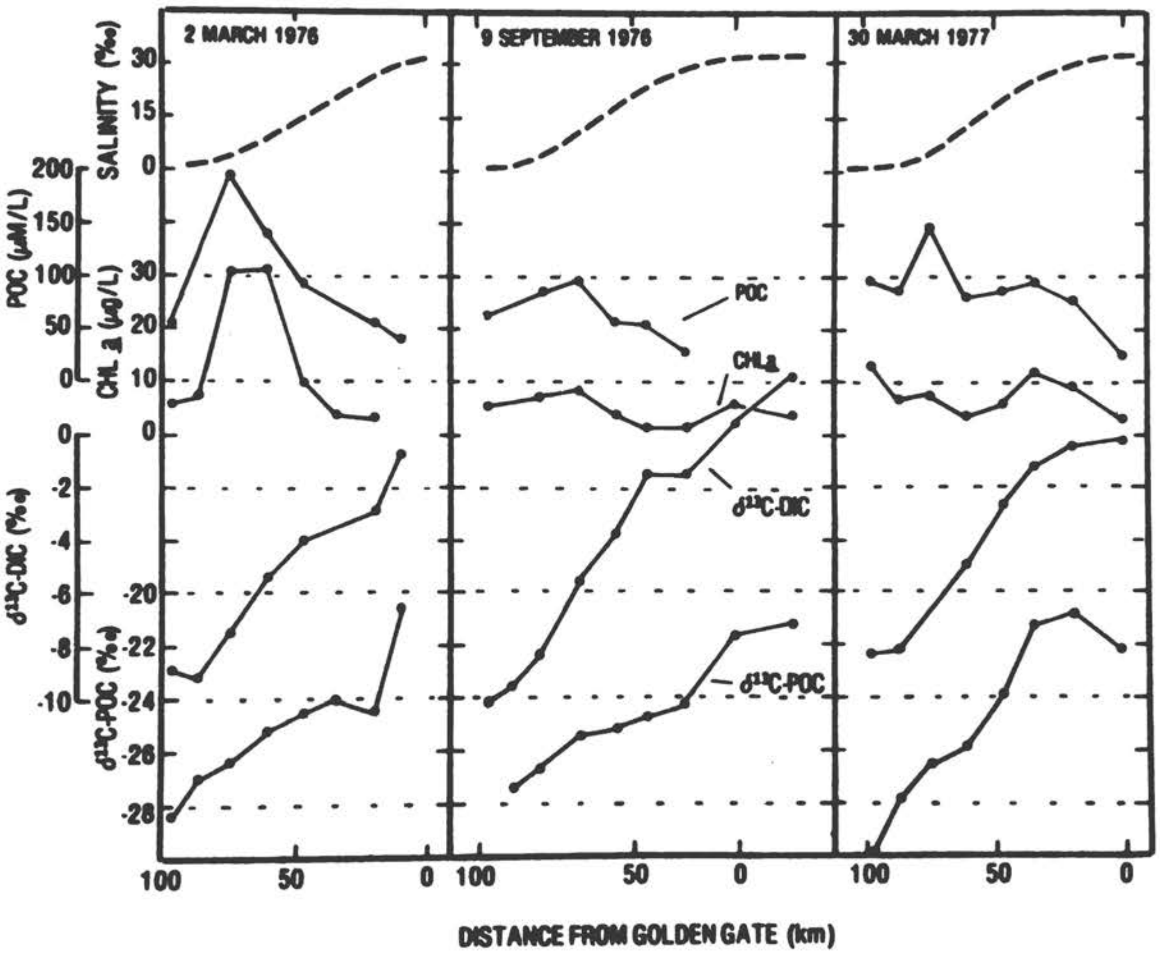
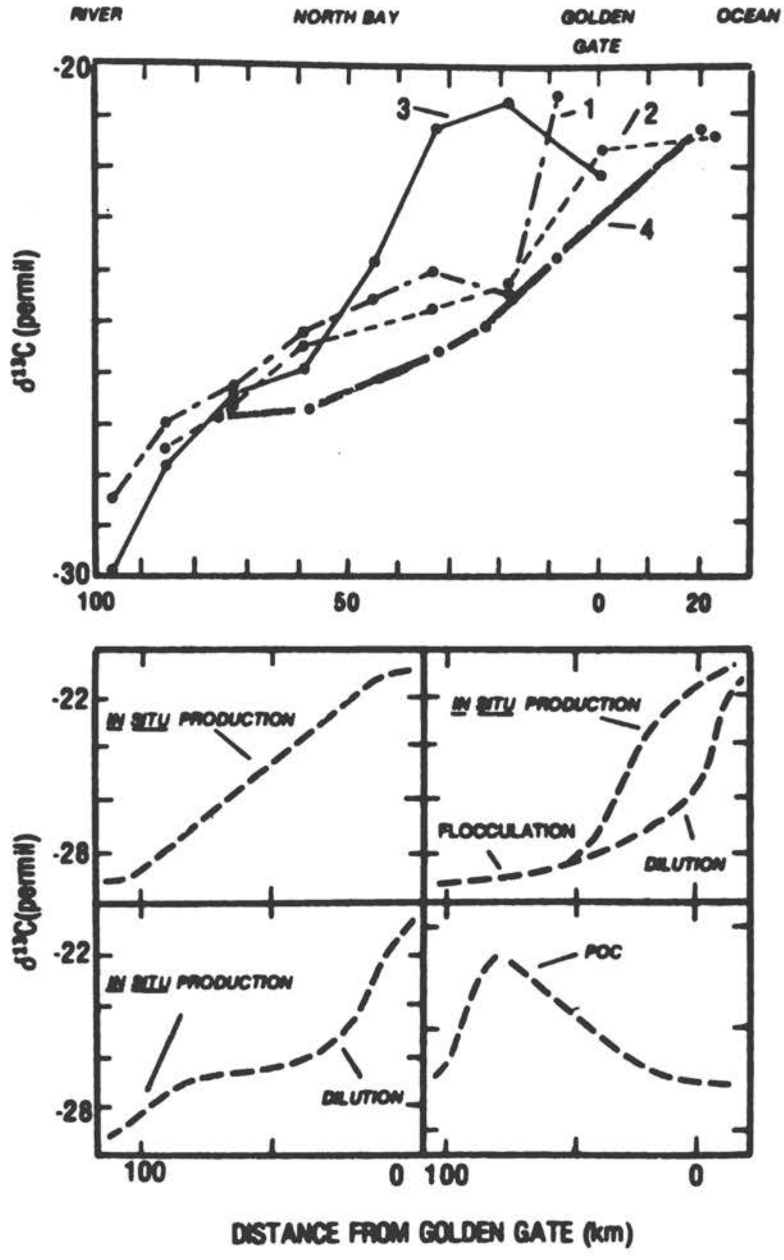


FIGURE 3 Salinity, particulate organic carbon (POC), chlorophyll a (CHL a), δ^{13}C-DIC, and δ^{13}C-POC in the North San Francisco Bay.



Above:

FIGURE 4 δ^{13}C-POC: March 2, 1976 (1); September 9, 1976 (2); March 30, 1977 (3); and δ^{13}C-TOC August 1973 (4) in North San Francisco Bay.

Below:

Theoretical δ^{13}C-POC and POC distributions (see text).

chlorophyll _a_ and POC and pCO^2 depletion (see Spiker and Schemel, 1979), approached values predicted for _in situ_ algal production. This was not observed when phytoplankton were less abundant.

The value in sediment 16 km seaward of Golden Gate (-21.2‰) is within the range of midlatitude marine POC, indicating that less than 10% of the carbon in these sediments is land derived. If this offshore carbon is considered as a mixture of three sources (marine, land-derived, and estuarine phytoplankton), then the fraction of land-derived carbon is probably even smaller.

The δ^{13}C-POC values in the river were several permil lower than usual for land plants, indicating that algal production (about -29 permil) was an important source in the river during all our samplings. The values in the turbidity maximum were several permil higher than the riverine values, but were similar to the δ^{13}C-TOC in the benthic sediments. This indicates that, at least during low river-flow conditions, less than two thirds of the POC in the turbidity maximum was derived from upstream POC and, therefore, that the remainder was derived from the estuary (i.e., landward transport or phytoplankton production) or from resuspended benthic sediments.

The δ^{13}C-TOC in the benthic sediments was generally more negative than the suspended POC. This could be due to a larger fraction of riverine or land-plant carbon in the sediments, reflecting deposition predominantly during periods of high-river discharge. Alternatively, selective preservation of the more refractory land-plant material and isotopic fractionation effects related to decomposition could account for the low TOC values.

THE POTOMAC RIVER AND ESTUARY - A CASE STUDY

In its lower reach, the Potomac River is a partially mixed estuary of the Chesapeake Bay. It is the second largest tributary of that system, having average river discharge of about $300 m^3/sec$. River flow is typically highest in March (about $500 m^3/sec$) and declines through September (about $50 m^3/sec$). Carbon isotope data were collected during 1977 and 1978 in conjunction with water-chemistry studies (Smith and Herndon, 1979, 1980 a,b,c) and benthic sediment studies (J. Glenn, U.G. Geological Survey, unpublished data). Some of the preliminary results are shown in Figures 5 and 6.

Perhaps the most striking feature of the carbon isotope distributions is that the $\delta^{13}C$ of the DIC and POC were covariant throughout the system during the spring, summer, and fall. This correlation indicates that in situ phytoplankton production was the dominant source of POC. The apparent fractionation ($\Delta\delta^{13}C = \delta^{13}C\text{-DIC} - \delta^{13}C\text{-POC}$) ranges between about 17 and 21 permil. During the dry late-summer of 1977, a large algal bloom in the river produced a 3-permil enrichment in the DIC as a result of the preferential photosynthetic utilization of ^{12}C. This effect is also seen in the $\delta^{13}C$-POC. High phytoplankton biomass is common in the Potomac. This is due, at least in part, to the relatively large anthropogenic nutrient sources.

By contrast, the $\delta^{13}C$-POC during January 1978 decreased from about -26 permil in the river to -27 permil in the lower

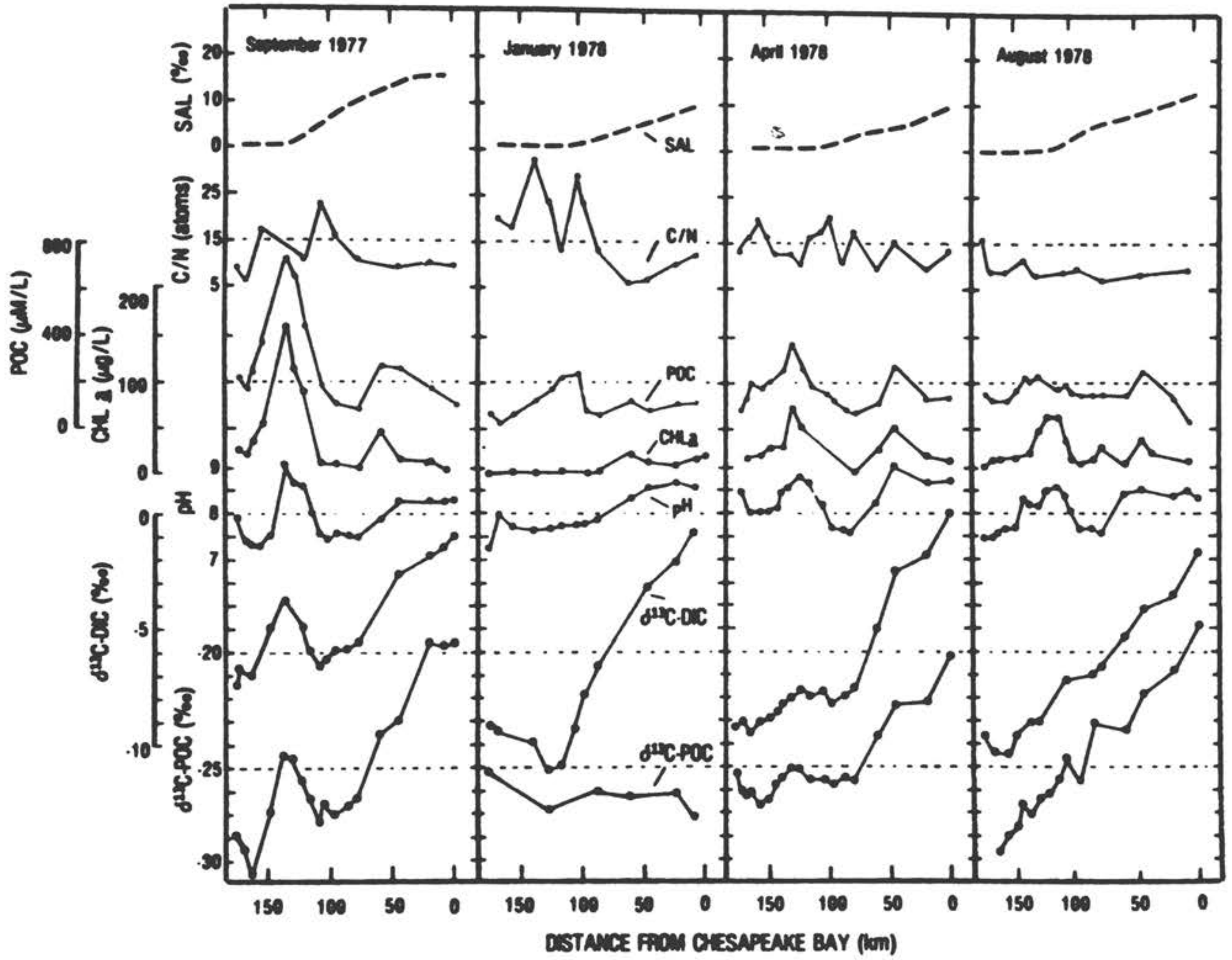


FIGURE 5 Potomac River estuary profile data: salinity (SAL), particulate C/N ratio, chlorophyll a (CHL a), pH, δ^{13}C-DIC, and δ^{13}C-POC.

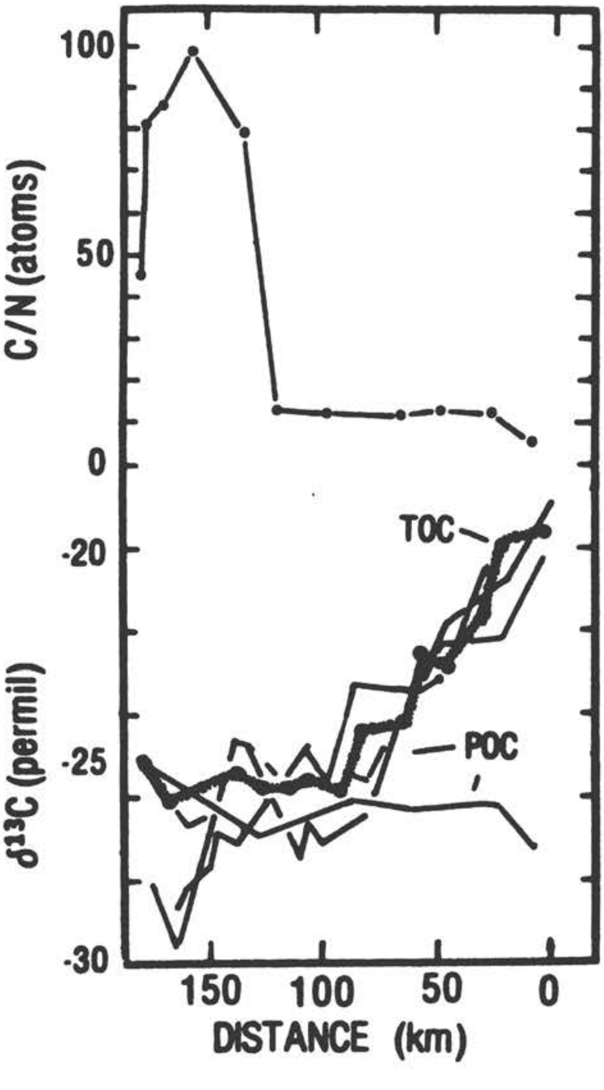


FIGURE 6 Potomac River estuary sediment data: C/N ratio, δ^{13}C-POC, and the δ^{13}C of sediment TOC.

reach of the estuary, and showed no relation to the DIC. From this it appears that land-plant detritus was dominant in the river and estuary during the high winter discharge. However, an increase in chlorophyll a and low C/N ratios in the lower estuary suggest algal production is also an important component of the POC. The low δ^{13}C-POC values in the lower estuary may be reconciled by considering the low water temperature (1°C) and the temperature dependence of the photosynthetic isotope effect (Sackett et al., 1965). Cold-water marine plankton typically have values of about -25 to -27 permil.

The δ^{13}C of the benthic sediment TOC remained relatively constant in the river section, at about -26 permil. TOC values increased abruptly in the estuary following the trend of the POC during spring and summer. Apparently, the benthic sediment TOC is dominated by algal production, at least in the estuary. The δ^{13}C-TOC distribution may also be partly controlled by estuarine circulation, since the point where TOC values begin to increase approximately marks the upstream limit of landward transport of estuarine POC by the salt-wedge circulation cell.

CONCLUSION

The transport of carbon by the world's rivers is a significant global process. The extent to which it is a sink for anthropogenic CO_2 is dependent on the source and fate of this carbon. An increase in this riverine flux might be due to increased photosynthetic activity in the river or on land, or to increased soil erosion. The spread of bomb ^{14}C through the terrestrial carbon pool offers considerable potential in resolving these two alternatives, by determining the time of fixation by photosynthesis.

$\delta^{13}C$ is a relatively simple and reliable source indicator that can discriminate between terrestrial and marine organic carbon. However, since estuarine phytoplankton have intermediate $\delta^{13}C$ values, this two-endmember (terrestrial versus marine) model may lead to an overestimate of the terrestrial component in estuarine and coastal marine water and sediments. This two-endmember model also overlooks this potentially important source of organic matter to the ocean. A comparison of $\delta^{13}C$ distributions in the San Francisco Bay and the Potomac River estuary demonstrates the varying importance of estuarine primary production in different systems.

The analysis of both ^{14}C and ^{13}C provides unique information about the derivation and processing of carbon in rivers. The usefulness of these techniques is of course greatly enhanced when applied in conjunction with other tracers, such as ^{15}N (Peters <u>et</u> <u>al</u>., 1978; Stuermer <u>et</u> <u>al</u>., 1978), C/H/N ratios, and various organic compounds. $\delta^{15}N$ may be very useful if it can distinguish between fresh-water aquatic plants and land plants (nitrate uptake versus nitrogen fixation). The new solid-state ^{13}C NMR techniques (Hatcher <u>et</u> <u>al</u>., 1980) should provide a powerful tool that can descriminate between algal and vascular plant carbon.

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CHEMICAL INDICATORS OF ORGANIC RIVER SOURCES IN RIVERS AND ESTUARIES

John I. Hedges

Following are some of the questions that arise when the broad topic of riverine carbon fluxes to the ocean is considered.

How much organic carbon is being introducted in dissolved and particulate form by rivers to the ocean?

Where in the drainage basin or river itself does the organic material originate?

What organisms and tissues are the sources of this organic material?

What is the fate of organic matter undergoing riverine transport to the ocean? Is it remineralized in the river, trapped in the estuary, dispersed at sea, degraded at the sea-sediment interface, or preserved in forming marine sedimentary deposits? What are the proceesses at work?

I will address primarily the question of the geographic and biological sources of organic carbon in rivers, estuaries, and coastal marine environments, focusing upon chemical means for source identification.

For our purposes, information concerning organic carbon sources can be though of as existing in shells of different scale (Figure 1). The innermost shell or core of information is isotopic composition, the smallest-scale distinction in

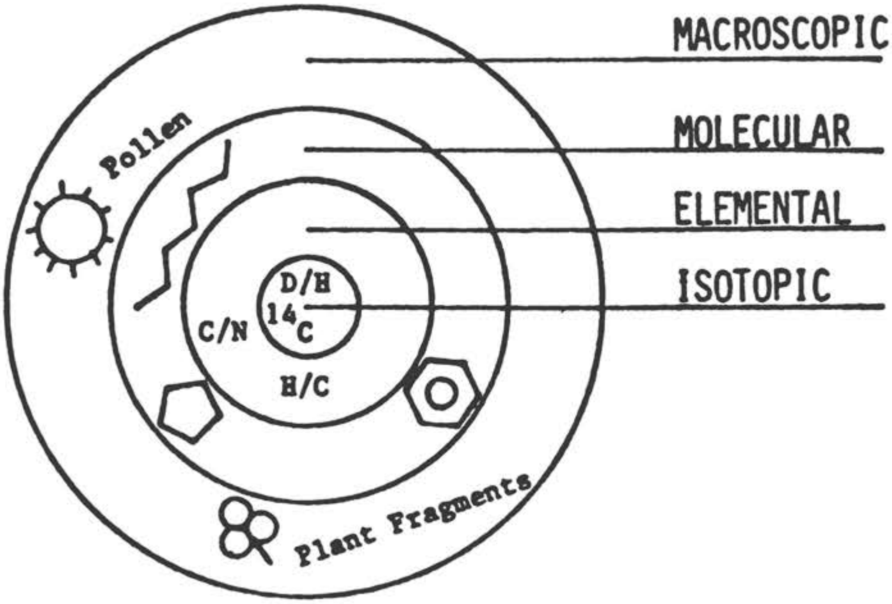


FIGURE 1 Scales of geochemical information.

organic content that we are presently able to make for geochemical purposes. A major advantage of isotope analyses for source discrimination is that isotopic measurements are usually comprehensive for a specific element (C, N, H, or S) in a sample. For example, in stable carbon isotope analyses, all carbon except C-14 is accounted for, and errors involved with treating a possibly nonrepresentative fraction of the total sample are avoided. Common disadvantages of isotopic analyses are that the informational yields are typically small (one or two compositional parameters per element) and that the isotopic contents of some organic sources may not be significantly different.

The next largest scale of information is the elemental composition of organic materials, the relative abundances of the major component elements C, O, H, N, S, and P. Different types of organic material often have characteristic elemental ratios (e.g., C/N or H/C) that can be readily measured and bear information concerning biological or geographic sources. Elemental measurements share the advantage of often being possible for entire plant or sediment samples, but are generally more susceptible to diagenetic influence than isotopic source labels.

The third scale of geochemical information occurs at the molecular level and is obtained by isolating and quantifying types of organic molecules. The advantage of organic molecules as source indicators is the immense informational potential afforded by the diversity and structural complexity of the available molecules. Carbon skeleton forms, points of unsaturation, stereochemical characteristics, and differences in functionality may all carry clues concerning biological sources and diagenetic history. The major disadvantage of molecular analyses is that they are intrinsically selective and, as a result, only a small portion of the total organic matter in a sample typically is represented. Thus, serious questions often arise as to the quantitative validity of a particular molecular tracer versus the organic fraction it supposedly represents.

The fourth and largest-scale source indicators are macroscopic materials such as pollen and recognizable remains of living organisms. This scale is the realm of the botanist, zoologist, paleontologist, and palynologist, and, unfortunately, is too often overlooked in geochemical studies. Pollen in particular offers a detailed and long-lasting record of the distributions of a wide variety of vascular plant species within a river drainage basin.

MOLECULAR ORGANIC TRACERS

I am by training an organic geochemist, representing a guild that has given little attention to rivers but much to rocks, soils, and sediments from lakes and oceans. Thus, I cannot present volumes of data on the sources and chemical composition of riverine organic matter, and will have little to report about actual applications of source indicators in rivers. Rather, I will try to present a "shopping list" of organic molecules that have proven useful in the past as source indicators and show promise for tracing particular types of organic matter down rivers and into the marine environment.

Although most of the tracers to be discussed are theoretically applicable either to particulate or to dissolved organic materials, dissolved substances present special analytical problems that will be discussed later.

Almost all molecular tracers used to distinguish the geographic or biological sources of organic matter in natural environments are derived from photosynthetic plants. This selectivity results from the fact that photosynthetic plants are the ultimate carbon source and typically the major biomass constituent. Animals are usually of minor quantitative importance, and are composed primarily of proteins that are compositionally similar at the molecular level.

Lower plants, such as fungi, bacteria, and phytoplankton are ubiquitous, while higher (vascular) plants are confined almost exclusively to land. Almost all distinction between marine- and land-derived organic matter currently made at the molecular level are accomplished, in fact, by identifying biochemicals characteristic of higher land plants. It is relatively difficult to distinguish the geographic sources of animal or lower-plant remains at the molecular level. Luckily, it is intrusions of land-derived organic matter into marine environments that are most often encountered.

Molecular organic indicators can be classified in terms of the four major categories of plant natural products: carbohydrates, proteins, phenolics (primarily lignins), and lipids. For illustrative purposes, the relative proportions of these four biochemical classes in selected higher plant tissues and marine plankton are given in Table 1. As can be

TABLE 1 Weight Percentages of Major Biochemical Classes in Selected Organisms

	Higher Plants		Marine Plankton	
Biochemical Type	Conifer Wood[a]	Wheat Straw[b]	Diatoms and Dinoflagellates[b]	Copepods[b]
Carbohydrate	56-65	75	0-36	0-4
Protein	([c])	2-5	24-48	71-77
Lignin	28-34	18	0	0
Lipid	([c])	([d])	2-10	5-19

[a] Whistler and Smart, 1958

[b] Tissot and Welte, 1978.

[c] Trace.

[d] Unreported.

seen, carbohydrates are the predominant biochemicals in higher plants, followed by lignins; very little protein or lipid is present. Marine plankton contain primarily protein, some carbohydrate and lipid, but no lignin.

There are a variety of criteria for selecting an organic tracer. An "ideal" tracer has the following general attributes:

> It occurs only in the class of organic matter that it is being used to tag or (second best) has a characteristic abundance pattern in the class of interest although it occurs elsewhere.
>
> It is abundant in the designated fraction and occurs in a constant weight ratio to it.
>
> It is chemically stable.
>
> It carries additional information about specific geographic or biological sources.
>
> It is easily analyzed with inexpensive equipment.

I would now like to discuss specific molecular tracers from the previously mentioned four natural product classes that might prove useful in a study of the fluxes of riverine organic matter to the ocean. In this context, only organic indicator molecules that can be recognized as being land derived will be considered since a major scientific goal of river-flux studies is to trace terrigenous organic materials into the marine environment.

Proteins

Proteins and their molecular components, amino acids, occur in all living organisms. Although characteristic differences may occur between the amino acid compositions of marine- and land-derived organic materials, they are difficult to sort out at the molecular level (Kvenvolden, 1975; Degens and Mopper, 1979). However, at the elemental level, organic materials from these two sources often can be distinguished by the characteristically low C/N of marine plankton. This elemental difference results in part from the higher levels of protein in mixed marine plankton, a significant portion of which typically are amino acid-rich zooplankton (Table 1). Higher land plants, which are composed primarily of cellulose and lignin, contain relatively little organic nitrogen.

C/N ratios have been used to establish the presence of land-derived organic matter in sediments and suspended particulate material from the St. Lawrence estuary (Pocklington, 1979; Pocklington and Leonard, 1979; Tan and Strain, 1979). The main disadvantage of this method in quantitative applications is the wide range of C/N values observed in different higher plant tissues (Tan and Strain, 1979) and the susceptibility of this ratio to diagenetic alteration, primarily due to preferential biodegradation of nitrogen-containing biochemicals in marine plankton (Knauer _et al_., 1979; Suess and Muller, in press). Inasmuch as many organic carbon analyses are currently made with elemental analyzers, C/N ratios are often obtained as "free" parameters that should be taken advantage of when available as a potential source indicator.

Carbohydrates

Carbohydrates are the most abundant class of natural products. They occur in myriad forms, including celluloses, starches, and nucleic acids (Pigman, 1957). The most common molecular constituents of carbohydrate natural products are neutral sugars such as glucose, galactose, and ribose, which are released by hydrolysis and can be analyzed by a variety of techniques (Swain, 1969; Dutton, 1973; Mopper, 1977).

Neutral sugars are attractive candidates as terrestrial tracers owing to their great overall abundance. However, no individual neutral sugars are known to be unambiguously terrestrially derived. Recent studies (Degens and Mopper, 1979) do indicate that the ratio of glucose to ribose in organisms and sediments increases with terrestrial influence (Figure 2). This trend results in part from the high relative abundance of α-cellulose (a glucose polymer) in most tissues of vascular land plants (Whistler and Smart, 1953). In comparison, marine plankton have less glucose and relatively high ribose levels (Degens and Mopper, 1979).

Carbohydrate stabilities vary considerably because of differences in form and environmental conditions. A pertinent consideration for the glucose/ribose compositional parameter is that ribose is relatively susceptible to biodegradation, probably because of significant contribution of this sugar by labile nucleic acids (Degens and Mopper, 1979). Thus, this parameter may be sensitive to digenetic alteration.

A second, less abundant class of carbohydrates is the uronic acids. These compunds are structurally identical to

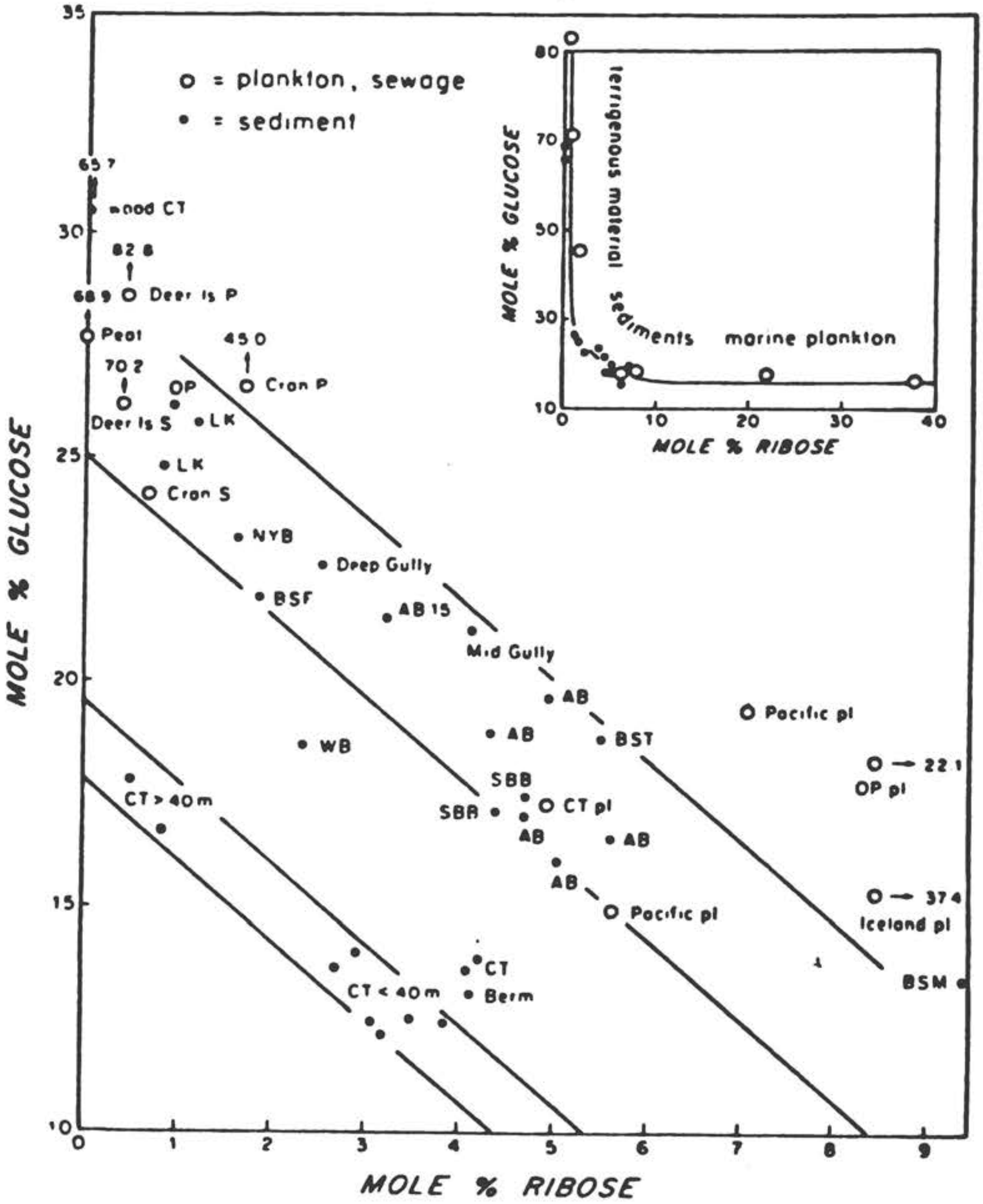


FIGURE 2 Relationship (inverse) between glucose and ribose contents of marine sediments. Terrigenous material is enriched in glucose and depleted in ribose, whereas the marine plankton shows the reverse trend. AB = Argentine Basin; CT = Cariaco Trench; NYB = New York Bight; OP = Oyster Pond; BSF, T. M = Black Sea freshwater, transition, marine; Berm = Bermuda; WB = Walvis Bay; SBB = Santa Barbara Basin; LK = Lake Kivu; Cran = Cranston sewage sludge; Deer Is = Deer Island sewage sludge; P = primary sludge; S = secondary sludge; pl = plankton. (From Degens and Mopper, 1979.)

reducing sugars except that the aldehyde is replaced by a carboxyl group. Uronic acids are found in both higher and lower plants where they occur in polysaccharides having structural and ion regulatory roles. Like the neutral sugars, uronic acids are released from polysacchárieds by acidic hydrolysis and can be separated from neutral sugar counterparts by ion exchange prior to chromatographic analysis (Mopper, 1977).

As with neutral sugars, no common uronic acids are presently recognized to have only a terrestrial (higher plant) or marine (other) origin. However, galacturonic acid, 2-0(4-0-methyl-α-D-glucopyranosyl-uronic acid)-D-xylose, and 4-0-methylglucuronic acid have characteristically high concentrations in some higher-plant tissue hydrolysates and may have potential as terrestrial tracers (Mopper and Larsson, 1978).

Lignins

Lignins are phenolic polymers that occur exclusively in vascular plants (Table 1), being essentially absent from all other living organisms (Sarkanen and Ludwig, 1971). Thus, lignins are the only major biochemicals to have an unambiguous terrestrial origin. Weight percentages of lignins in vascular plants range up to 40% (Sarkanen and Ludwig, 1971; Whistler and Smart, 1953) and are second only to carbohydrates in overall abundance (Table 1). Lignins have intrinsically stable cross-linked aromatic structures and are thought to be among the biopolymers most resistant to microbial degradation (Flaig, 1964; Christman and Oglesby, 1971).

Analyses of lignin compounds in plant and sediment samples for geochemical purposes are usually carried out with either nitrobenzene (Gardner and Menzel, 1974; Pocklington

and MacGregor, 1973) or cupric oxide (Hedges and Parker, 1976; Hedges and Mann, 1979a, b), which are used to partially degrade the polymers releasing simple phenols which can be analyzed by gas chromatography. In our laboratory, eight simple phenols (Figure 3) are being used as lignin indicators. These compounds belong to three chemical families: (1) vanillyl phenols having one methoxyl group substituted on the aromatic ring, (2) syringyl phenols with a pair of methoxyl groups flanking the *para*-hydroxyl, and (3) cinnamyl phenols with propylphenyl carbon skeletons. Vanillyl and syringyl oxidation products occur as aldehydes, ketones, and carboxylic acids, whereas the two cinnamyl compounds occur only as carboxylic acids. None of the eight phenols is known to have a quantitatively significant source other than vascular plant lignins.

One application of these eight lignin-derived phenols is to estimate quantitatively the relative amount of total vascular plant remains in suspended particulate or sedimentary materials. Such an estimate is made by determining the total yield in milligrams of the eight phenols obtained from 100 mg of total organic carbon in the sample (Hedges and Mann, 1979b). The validity of this quantitative tracer technique has been tested in the Gulf of Mexico and Washington State coastal regions by comparing total yields of lignin-derived phenols with stable carbon isotope compositions from sediments from the same depositional regime (Hedges and Parker, 1976; Hedges and Mann, 1979b). The two parameters generally show good correlation, indicating that in these instances lignins serve as reliable indicators of land-derived organic matter in general. A particular advantage of lignin tracers for river applications is that estimates of relative levels of vascular plant remains are possible within the river itself even when

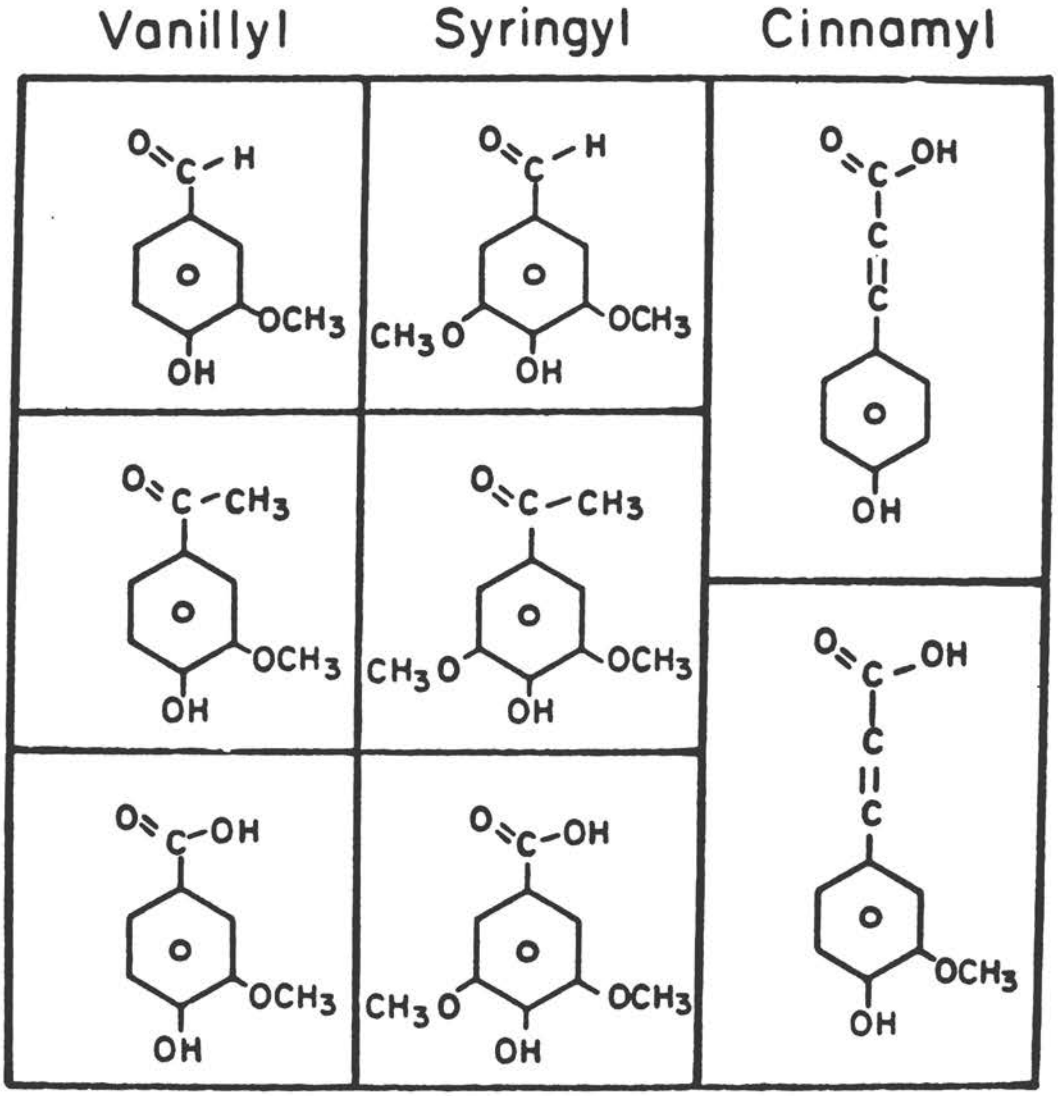


FIGURE 3 Chemical structures of lignin-derived phenols. Names (reading from top to bottom in individual columns): vanillin, acetovanillone, vanillic acid; syringealdehyde, acetosyringone, syringic acid; p-coumaric acid, ferulic acid.

other forms of organic matter such as freshwater plankton are present, often with similar carbon isotope compositions (Pocklington and MacGregor, 1973; Turin, 1980).

A second application of the eight lignin-derived oxidation products is to obtain additional information concerning the taxonomic and tissue sources of lignin mixtures in soils and sediments. Such distinctions are possible because the lignins of the woody and nonwoody tissues and of flowering (angiosperm) and nonflowering (gymnosperm) plants are compositionally distinct. These relationships are illustrated in Figure 4, where weight ratios of total syringyl phenols to total vanillyl phenols (S/V) are plotted against ratios of total cinnamyl phenols to total vanillyl phenols (C/V) for representative vascular plant tissues. As can be seen, the lignin of angiosperm plants (such as hardwood trees, herbs, and grasses) can be readily distinguished from the lignin of gymnosperm plants (such as coniferous trees) because only angiosperms produce syringyl phenols and, thus, have S/V ratios >0. Likewise, woody and nonwoody tissues (such as tree leaves, pine needles, and annual plants) can be distinguished because only nonwoody tissues produce appreciable amounts of cinnemyl phenols among their oxidation products (Hedges and Mann, 1979a). Applications of these characteristic compositional relationships for estimating the relative concentrations of these four basic types of lignified tissues have been made by our research group for marine (Hedges and Mann, 1979b) and riverine (Turin, 1980) sediments. Similar applications for suspended particulate materials in rivers and estuaries are entirely feasible.

Lipid Tracers

Lipids are, by definition, those organic substances that are soluble in nonpolar organic solvents such as chloroform.

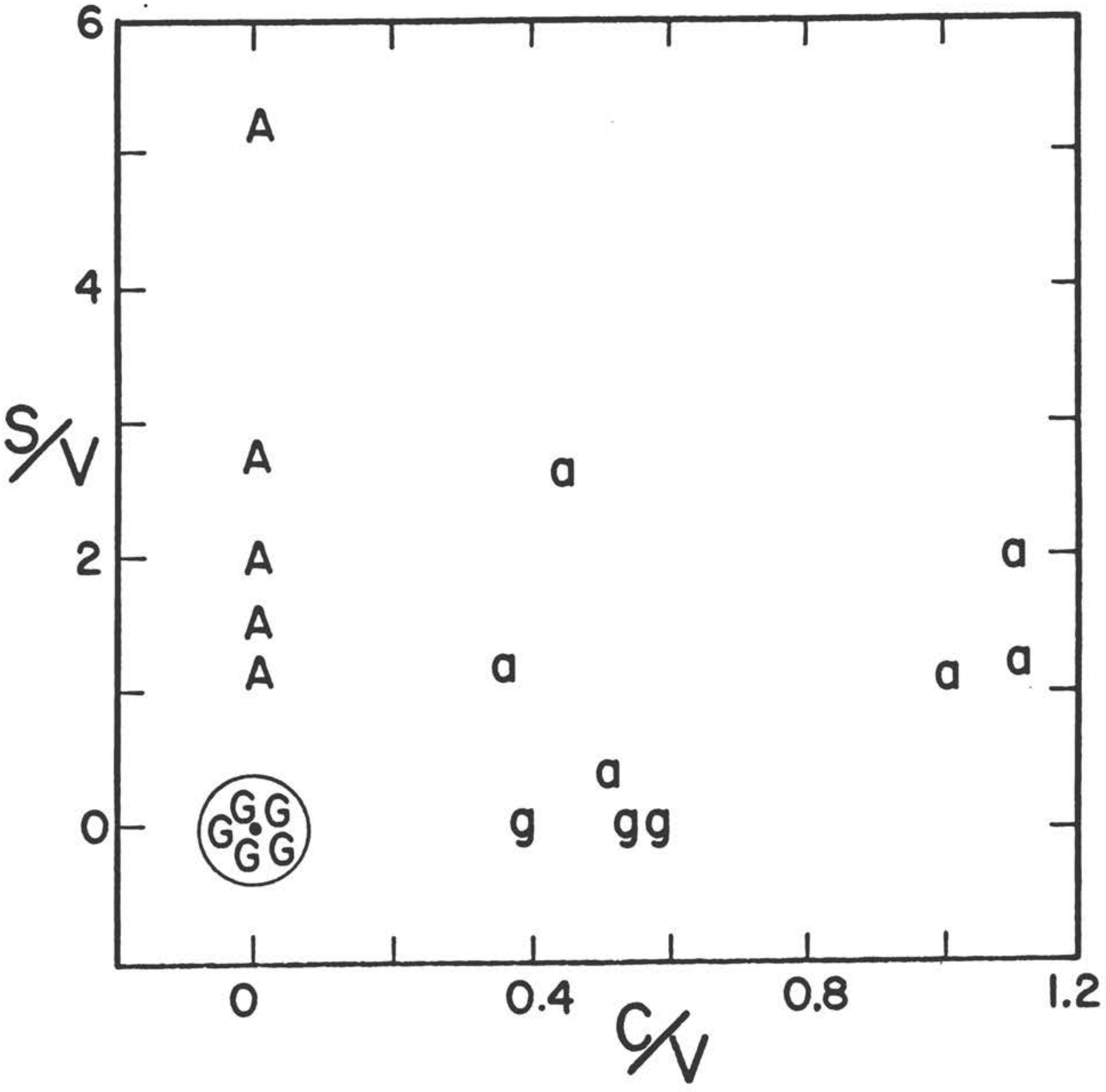


FIGURE 4 Plot of lignin compositional parameters for individual plant tissues. G = gymnosperm woods; g = nonwoody gymnosperm tissues; A = angiosperm woods; a = nonwoody angiosperm tissues; s/v = weight ratio of syringyl phenols to vanillyl phenols; c/v = weight ratio of cinnamyl phenols to vanillyl phenols. All circled letters plot at the origin.

This class of hydrophobic substances includes a variety of molecular types that can be applied as terrestrial tracers. Major advantages of lipid tracers in general are that methods for extraction and analysis are generally straightforward and that the geochemistry of this compound class is worked out in relatively good detail (Eglinton and Murphy, 1969). A major disadvantage of many lipid tracers is that, because of their low abundances and hydrophobicity, it is questionable whether they are dependable indicators of the sources and pathways of organic matter in general.

Hydrocarbons

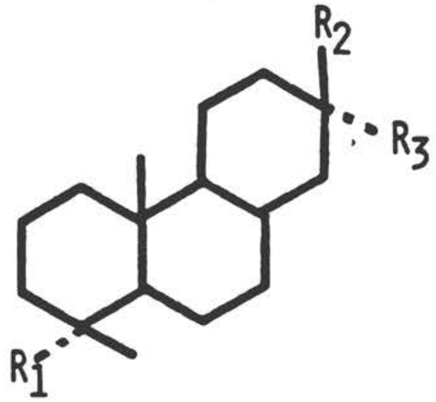
A major form of nonaromatic hydrocarbons in most higher plants is as components of cutin waxes that coat leaves and stems. Plant wax hydrocarbons occur in homologous series characterized by: (1) high molecular weight (25 to 35 carbon atoms in linear molecules without carbon-carbon double bonds) and (2) a great predominance (about 5-10/1) of odd-numbered carbon molecules to even carbon numbered molecules within this series (Caldicott and Eglinton, 1973). Most other living organisms produce molecules of lower molecular weight, often without distinct predominance of odd-carbon forms (Farrington and Meyers, 1975; Brassell et al., 1977). Petroleums and their refined products may also contain the same hydrocarbons found in higher-plant leaf waxes, but usually do not exhibit a strong predominance of odd-numbered carbon molecules.

Leaf wax hydrocarbons have been used extensively to trace higher-plant lipids in rivers (Peake et al., 1972; Hamilton, 1980), estuaries (Hurtt and Quinn, 1979; Barrick et al., 1980), and the open ocean (Gearing et al., 1976; Farrington et al., 1977; Farrington and Tripp, 1977; Keizer et al., 1978). Hamilton's seasonal study of the aliphatic hydrocarbon composition of suspended particulate material in the Green River (Washington State, U.S.A.) clearly demonstrates both geographic and temporal changes. Plant wax hydrocarbons predominate in the underdeveloped upper reaches of the river, but are diluted downstream by petroleum-derived compounds. Low molecular weight _n_-alkanes with 15 and 17 carbon atoms typical of phytoplankton are evident during warmer months but are greatly diminished in relative abundance during the winter. In this and other applications, a major advantage of aliphatic hydrocarbon analysis is that in addition to plant wax _n_-alkanes a variety of other compositionally distinct suites may be recognized and attributed to other sources such as bacteria, blue-green algae, zooplankton, and petroleum (Brassel _et al._, 1977).

Certain tricyclic diterpenoid hydrocarbons are also used as terrestrial source indicators (Figure 5). Hydrocarbons in this category usually contain 19 or 20 carbon atoms. Both aliphatic and aromatic hydrocarbons of this general structure are found in soils and marine sediments (Simoneit, 1977a,b); LaFlamme and Hites, 1978; Barrick and Hedges, in press). Although some 20-carbon diterpenoid hydrocarbons are directly synthesized by vascular plants, most diterpenoid hydrocarbons found in soils and sediments are apparently diagenesis products of higher-plant resin acids that are most abundant in angiosperms and gymnosperm trees from tropical and temperate climates, respectively (Thomas, 1969). Compounds of this structural type are not known to occur in marine organisms (Fujita _et al._, 1979).

Carboxylic Acids

Fatty acids consist of hydrocarbon chains with a terminal carboxyl group. In living organisms fatty acids occur primarily in ester form in fats (linked to glycerol) and waxes



I. ABIETIC ACID
$R_1 = \mathrm{COOH}$
$R_2 = \mathrm{H}$
$R_3 = \mathrm{CH(CH_3)_2}$

II. ISOPIMARADIENE
$R_1 = \mathrm{CH_3}$
$R_2 = \mathrm{CH_3}$
$R_3 = \mathrm{CH_2CH_3}$

III. FICHTELITE
$R_1 = \mathrm{H}$
$R_2 = \mathrm{H}$
$R_3 = \mathrm{CH(CH_3)_2}$

FIGURE 5 Carbon skeletons of some diterpenoid lipids.

(linked to a long chain alcohol). Most analytical procedures for fatty acids involve saponification of these esters to produce free acids that are subsequently methylated and analyzed by gas chromatography (Parker, 1969).

Linear, unsaturated fatty acids (n-alkanoic acids) are a major lipid component of higher plants, typically occurring in greater abundance than plant wax n-alkanes. These acids are compositionally distinct from those produced by most other living organisms, being characterized by high molecular weight (22 to 30 carbon atoms per molecule) and by a strong predominance of even-numbered carbon chains. The absence of carbon-carbon double bonds imparts a high chemical stability to these molecules (as is true of the plant wax n-alkanes), which enhances their potential as molecular source indicators. Higher-plant fatty acids have been utilized as indicators of land-derived lipids in freshwater (Cranwell, 1974; Matsuda and Koyama, 1977) and marine (Simoneit, 1977b) sediments. Simoneit (1977b) reports good correlation between fatty acid and leaf wax hydrocarbons of higher plants found in sediment cores from the Black Sea, suggesting that these two lipids follow similar geochemical pathways.

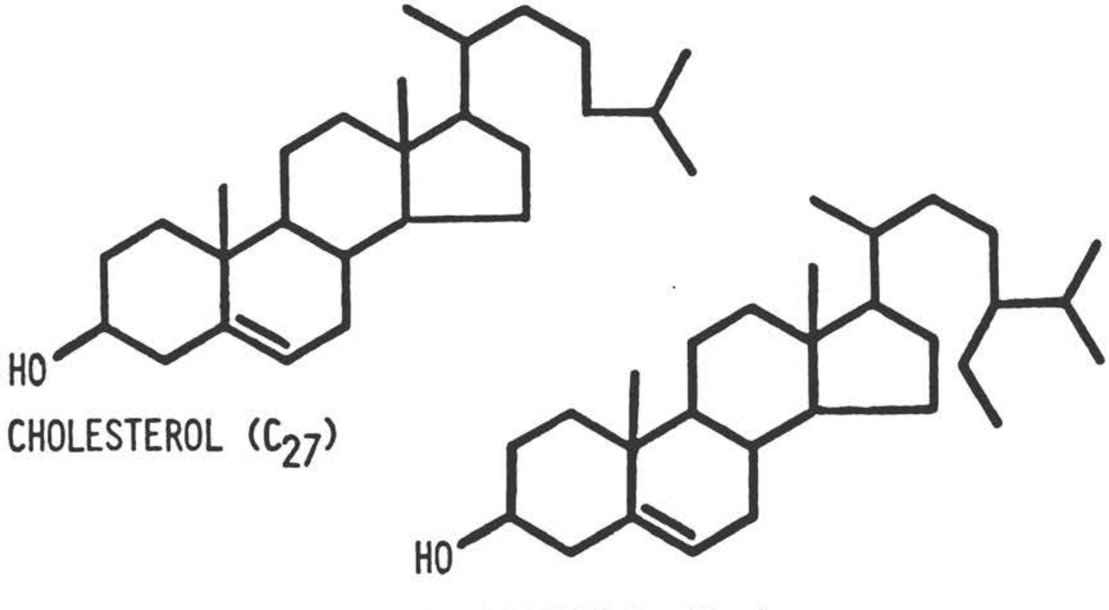
Diterpenoid resin acids having carbon skeletons similar to that shown in Figure 5 (with a carboxyl group at C-4) are also useful terrestrial source indicators. These compounds are found in soils (LaFlamme and Hites, 1978) and marine sediments (Simoneit, 1977a), often at higher concentrations than the corresponding hydrocarbons. Simoneit (1977a) reported a positive correlation between diterpenoid acid and pollen distributions in recent sediments from the open ocean.

Sterols

Sterols are tetracyclic alcohols that usually contain

27 to 29 carbon atoms, with most structural variations occurring in the long alkyl side chain (Figure 6). These alcohols occur in all eucaryotic organisms thus far examined and in many procaryots as well (Morris and Culkin, 1977). In spite of their low average concentrations ($\approx$ 0.1 wt %), sterols are useful geochemical tracers because of their relatively high chemical stability and taxonomically related structural diversity (Morris and Calkin, 1977).

Most applications of sterols as terrestrial indicators have been based on the relatively high abundance of the C-29 sterol B-sitosterol, along with stigmasterol and campesterol in higher plants (Figure 6). Plankton and marine invertebrates contain distinctly different sterol distributions in which C-27 and C-28 sterols typically predominate (Huang and Meinschein, 1976; Gagosian and Stuermer, 1977). Huang and Meinschein (1976) utilized compositional plots of percent chloresterol versus percent B-sitosterol in total sterol extracts of estuarine and coastal marine sediments to estimate the percentage of marine and terrestrial input. In a more recent paper (Huang and Meinschein, 1979) this type of approach was generalized by presenting percentages of C-27, C-28, and C-29 sterols in a ternary plot (Figure 7). In this presentation, plankton and higher-plant sterol compositions are completely resolved with open ocean, estuarine, and terrestrial sediments plotting sequentially between these two endmembers. Estimates of sterol sources based on carbon number analyses are particularly useful because the carbon skeletons are apparently not altered appreciably during catabolic or chemical processes (Huang and Meinschein, 1979).



CHOLESTEROL (C_{27})

B-SITOSTEROL (C_{29})

FIGURE 6 Chemical structures of cholesterol and B-sitosterol.

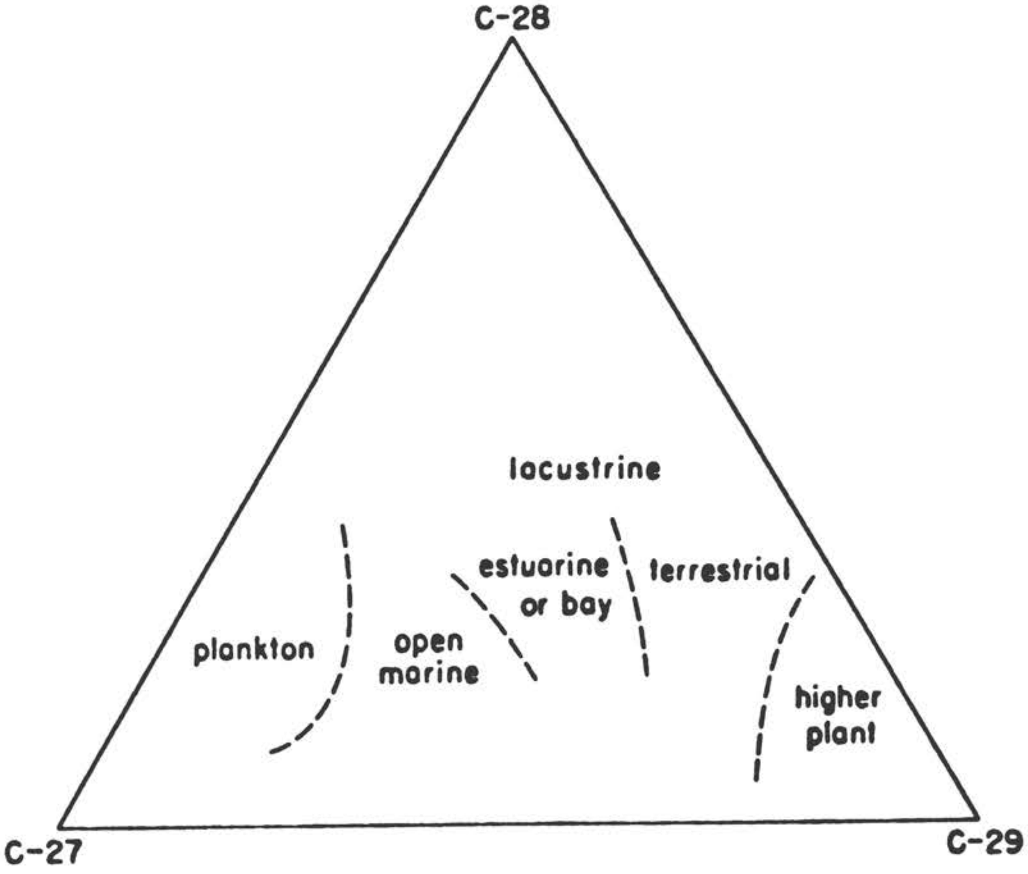


FIGURE 7 Relationship between the sterol compositions in biological sources and in open marine, estuarine or bay, lacustrine, and terrigenous ecosystems. (From Huang and Meinschein, 1979.)

APPLICATIONS OF MOLECULAR TRACERS TO DISSOLVED ORGANIC MATTER

Most of the previously discussed molecular tracers have been applied predominantly to particulate samples from soils, sediments, or natural waters. Since most of the organic material carried by rivers is usually in dissolved form (Menzel, 1974; Duce and Duursma, 1977), applications of chemical methods for identifying the biological and geographic sources of this material are of interest.

The bulk of dissolved organic matter (DOM) in river water apparently exists as brown acidic polymers known as humic substances (Lamar, 1968; Beck et al., 1974). Humic polymers are not found in living organisms; rather, they are thought to be formed by spontaneous extracellular condensation reactions of organic substances released by the microbial degradation of plant and animal remains (Flaig et al., 1975). Consequently, natural humic substances have extremely complex chemical compositions in which only a fraction of the total structure can be traced to known biochemical precursors (Schnitzer and Khan, 1972).

Compounding the problems involved with chemical characterizations of humic substances dissolved in river water are their low average concentrations (2-10 ppm) (Duce and Duursma, 1977) and the resulting difficulty in isolating sufficient material for many analyses. At present the isolation methods of choice are freeze-drying (Beck et al., 1974) and adsorption of protonated polymers onto hydrophobic resins (Perdue, 1979). The latter method has the advantage of also being applicable to seawater samples (Stuermer and Harvey, 1977).

Most chemical characterizations of river water DOM have involved measurements of bulk chemical properties such as molecular weight, functional group distribution, elemental composition, solution thermochemistry, and IR as well as NMR spectral properties (Beck et al., 1974; Perdue, 1979). These determinations demonstrate a chemical similarity between river DOM and soil fulvic acids, their apparent source. Although isotopically distinct, seawater DOM resembles soil fulvic acids and river DOM in many of its bulk chemical properties (Gagosian and Stuermer, 1977), making sensitive detection of river-derived DOM at sea difficult by means of bulk chemical measurements alone.

The presence of an unambiguous land-derived molecular "tag" within the structure of river water DOM would be convenient for sensitive detection at sea. Findings of lignin-derived compounds among the degradation products of soil humic substances (Schnitzer and Khan, 1972), coastal marine humic acids (Hedges and Parker, 1976; Ertel, 1980), and river water DOM (Christman and Ghassemi, 1966) suggest that such a tracer may actually be available, although untested. The high chemical stability of riverine DOM (Dham et al., in press) and recent reports of its near-conservative behavior during estuarine mixing (Sholkovitz, 1976; Moore et al., 1979) suggest that special effort should be made toward developing reliable molecular methods for detecting the pathways of this important component of the total flux of organic carbon from land to sea.

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DEPOSITION OF RIVERBORNE ORGANIC CARBON IN FLOODPLAIN WETLANDS AND DELTAS

Patrick J. Mulholland

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Recent estimates of river flux to the oceans range from 0.2×10^{15} to $>1.0 \times 10^{15}$ gC yr^{-1} (Kempe, 1979; Richey et al., 1980; Schlesinger and Melack, in press). However, river systems are not merely conduits, transporting their entire organic input to the oceans. Because some of the organic material entering rivers and streams is oxidized, the total organic flux to the sea is reduced. Richey et al. (1980) estimated that about 30% of the organic input to a 2,000-km section of the Amazon River during the period of rising water was oxidized within the reach. Smaller rivers and streams appear to be even more efficient in retaining and oxidizing organic inputs, especially particulate matter (Fisher and Likens, 1973; Fisher, 1977; Comiskey, 1978; Mulholland, 1979).

Deposition of riverborne organic carbon in channels and floodplain areas also reduces river loads. Trimble (1975a) has estimated that only about 5% of the total material eroded from the southern U.S. Piedmont since European settlement has been exported to coastal regions. He suggests that much of the remainder has been deposited as floodplain and channel alluvium. If depositional environments are well oxygenated, oxidation will occur. However, deposition in oxygen-limited environments or rapid burial in sediments will inhibit oxidation. Deposition in these areas constitutes a long-term sink for carbon transported in rivers.

Floodplain wetlands and deltas at the mouths of large rivers are environments with large accumulations of organic carbon in their sediments. Floodplain wetlands, although not limited to lowlands, reach their most extensive development in the coastal plains of continents. These stagnant wetlands receive large inputs of riverborne organic material during periods of flooding. Some of this input is deposited as water velocities decrease, and a portion of the deposited material remains unoxidized because of lack of oxygen. Although deposition of organic carbon occurs throughout the floodplains of most rivers, long-term organic carbon accumulation is much greater in floodplain wetlands, where oxidation is reduced. Significant carbon accumulation also occurs in river-mouth deltas where the deposition rate is great enough to rapidly bury sediments and prevent their complete oxidation.

In this paper I present an assessment of the deposition of riverborne organic carbon in floodplain wetlands and river deltas. Few studies have addressed carbon deposition in these types of systems, although they appear to possess high rates of sediment and organic carbon accumulation. These systems may be important globally as sinks for carbon fixed during photosynthesis by upland vegetation.

BACKGROUND

Floodplain Wetlands

Interactions between rivers and floodplain wetlands are dependent on river hydrologic regime (Figure 1). Inputs of water and sediment to floodplain wetlands from rivers are

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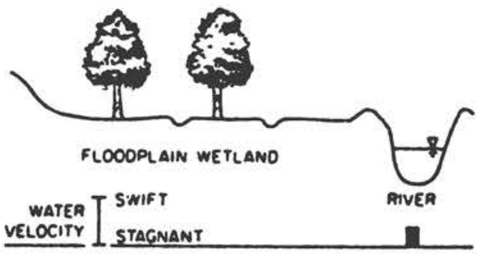
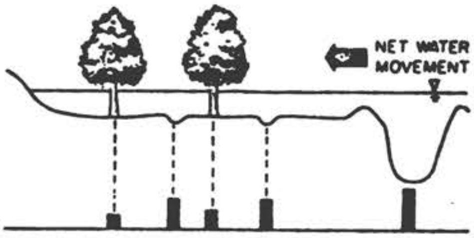
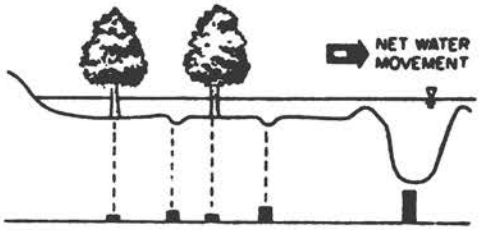


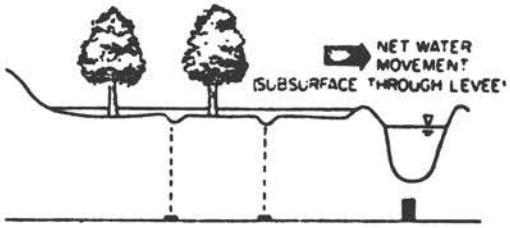
(a) DRY SEASON



(b) FLOOD PERIOD-RISING WATER



(c) FLOOD PERIOD-DECLINING WATER



(d) STAGNANT PERIOD

FIGURE 1

Annual hydrological patterns in floodplain wetland ecosystems. Interactions between the river and floodplain wetland during various periods are presented.

episodic, limited to periods of river flooding (a few weeks to a few months per year). During most periods, natural levees isolate rivers from bordering floodplain wetlands (Figure 1a). However, during floods, as river water level increases, eventually exceeding levee height, water flows into adjacent lowlands (Figure 1b). Velocities begin to decline as waters escape the confines of the main river channel and expand into broad floodplain areas. Particulate materials, eroded from areas upriver and transported in the swift river currents, begin to settle out in the floodplain under reduced water velocities. When river water level begins to decline, floodplain water velocities are reduced still further (Figure 1c). Eventually the water level falls below levee height and floodplain waters become isolated and stagnant (Figure 1d).

This somewhat simplistic presentation of hydrologic and sediment interaction between rivers and bordering floodplain wetlands is complicated by the large standing stocks of litter and organic debris in most wetlands (Conner and Day, 1976; Mitsch et al., 1977; Mulholland, 1979; Brinson et al., in press). In some wetland areas, particularly in shallow floodplain channels, surface organic matter is scoured during floods. However, material scoured from areas where water velocities are relatively high is generally deposited in other wetland areas, such as behind debris dams and in areas where velocities are lower. The physical matrix of living and down trees and herbaceous vegetation in swamps imparts a tortuous path to flowing waters and acts as a filter for large particulate material.

Despite the accumulation of easily eroded litter and organic debris, most floodplain wetlands appear to act as filters for riverborne particulate matter and have an annual net sediment input from bordering rivers (Kitchens _et_ _al_., 1975; Gagliano and van Beek, 1975; Mitsch _et_ _al_., 1977, 1979). Kitchens _et_ _al_. (1975) reported that turbidity decreased by about one-half as water flowed through a large South Carolina floodplain swamp during flood periods. Mitsch _et_ _al_. (1977), working in southern Illinois, reported that about 3% of the suspended sediment delivered to a 30-ha floodplain swamp by river floodwaters was deposited there. Floodplain swamps in tropical regions may act somewhat differently, however. Bonetto (1975) and Richey _et_ _al_. (1980) reported that large mats of floating vegetation are exported from floodplain wetlands along the Amazon and Parana rivers as floodwaters recede. Floodplain wetlands with large accumulations of floating vegetation may export more particulate material than they import, thus increasing river particulate organic carbon loads.

In many cases, accumulation of organic carbon in floodplain wetlands may be the result of inputs from autochthonous sources in addition to allochthonous inputs from rivers. Total annual litterfall in floodplain wetlands is high, ranging from 350 g dry wt m^{-2} yr^{-1} for an Illinois swamp

(Mitsch et al., 1977) to $>$700 g dry wt m^{-2} yr^{-1} for a North Carolina swamp (Mulholland, 1979). Incomplete oxidation of litter inputs as a result of long periods of flooding may result in an additional accumulation of carbon in floodplain wetland soils.

The extent of organic carbon accumulation in floodplain wetlands depends primarily on the hydrologic regime of the wetland; specifically, it depends on the length of time the wetland is flooded and stagnant or its soils waterlogged. In some North Carolina floodplain swamps bordering small streams, I have observed that, in most areas, floodwaters maintain velocities of at least 2 or 3 cm s^{-1} and dissolved oxygen concentrations > 3 mg l^{-1}. As water levels decline in streams bordering these wetlands, drainage is good, leaving the litter and surface soil layers unsaturated and allowing high rates of decomposition. On the other hand, there are a few locations in these swamps where drainage is partly blocked by road embankments. In these areas water is nearly stagnant for long periods each year, and deep muck soils have developed, with large accumulations of organic carbon. In swamps bordering larger rivers with greater sediment loads, natural levees block the complete return of floodwaters to the river channel, and stagnant conditions develop (Figure 1d). Dissolved oxygen is quickly depleted and decomposition is reduced. Significant accumulations of organic carbon can develop if the stagnant period is long enough.

During flood periods floodplain wetlands also export significant amounts of dissolved organic carbon most of which is derived from autochthonous sources (Day _et_ _al_., 1977; Mulholland, in press). Computing annual input-output budgets for a small North Carolina floodplain swamp, I found annual net exports of dissolved organic carbon of 20-25 gC m^{-2} yr^{-1}, primarily from canopy and litter leaching and litter decomposition (Mulholland, in press). Day _et_ _al_. (1977) reported outputs of about 10 gC m^{-2} yr^{-1} from a Louisiana floodplain swamp, mostly as dissolved organic carbon.

Figure 2 summarizes the principal organic carbon flows between rivers and most floodplain wetlands. Floodplain wetlands are (1) sinks for riverborne particulate organic carbon eroded from upland environments, and (2) sources (to rivers) of dissolved organic carbon and perhaps some particulate organic carbon produced by vegetation within the swamp. The net effect is to transfer organic carbon from upland terrestrial soils, where decomposition rates are usually high, to lowland environments where oxygen may be limiting and decomposition rates reduced. Accumulation of carbon in floodplain wetlands due to autochthonous production is also, in part, the result of river processes--flooding and delivery of nutrients. In the remainder of this paper, however, I will address only the deposition of particulate organic carbon transported in rivers.

Global deposition of riverborne particulate organic carbon in floodplain wetlands may be declining as a result

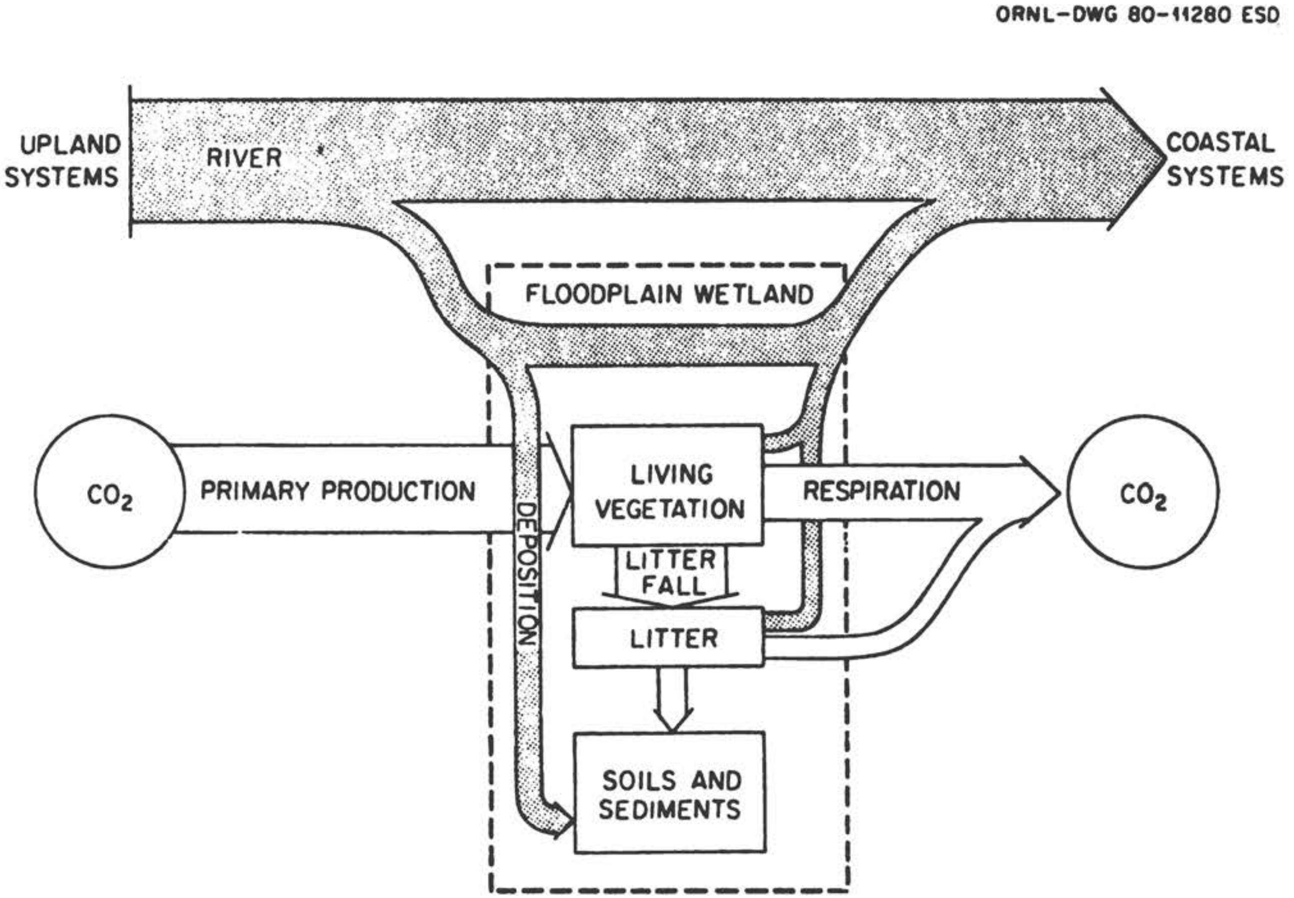


FIGURE 2

Interactions between a floodplain wetland and its bordering river with regard to organic carbon flow.

of some of man's activities. Interactions between rivers and floodplain wetlands have been altered or eliminated in many regions of the world by river channelization, construction of higher river levees, and wetland drainage and clearing. Winkley (1977) asserts that prior to the eighteenth century, when man first attempted to modify the Mississippi River, the entire floodplain valley of its lower 2,000 km was essentially a delta, accumulating sediment as a result of frequent river flooding. Much of the Mississippi River floodplain could be characterized as wetland with reduced rates of organic matter oxidation. However, man's activities over the past 200 years have resulted in reduced flooding and greater particulate transport potential in the partly straightened and confined Mississippi River channel (B. R. Winkley, U.S. Army Corps of Engineers, Vicksburg, Mississippi, personal communication, 1980). Much less organic carbon is currently being deposited and sequestered in floodplain wetlands along the Mississippi (B. R. Winkley, personal communication, 1980). This is likely true for other rivers in the United States and throughout the world. Organic carbon, which formerly was deposited in inland floodplain systems, may now be transported by rivers to the coast.

Conversely, increased river impoundment from dam construction has increased deposition of riverborne organic carbon in floodplains in recent decades. As a result of rapid sedimentation rates and low dissolved oxygen concentration, characteristics of many river impoundments, rates of oxidation of the organic carbon deposited in reservoir sediments are likely lower than those of organic carbon in transport or deposited in occasionally flooded floodplain areas. Thus, man's activities are also increasing the amount of riverborne organic carbon which is annually deposited and preserved in floodplain sediments. Increasing organic carbon preservation in floodplain sediments constitutes an increased sink for atmospheric CO_2 whereas a decrease in floodplain organic carbon preservation from previous decades constitutes an "apparent" source of atmospheric CO_2. The net effect of man's activities is unknown, but could be large.

River Deltas

Deltas at the mouths of large rivers are another potentially large sink for riverborne particulate organic carbon. High rates of sediment deposition in underwater or low-lying deltaic areas limit oxygen availability and reduce rates of oxidation of the organic fraction. Organic sediments are rapidly buried and isolated from free oxygen. Delta soils in temperate regions are typically 10-12% organic matter and can be as high as 30% organic in the tropics (J. M. Coleman, Louisiana State University, Baton Rouge, Louisiana, personal communication, 1980). Since organic contents of some river suspended sediment loads are reported to be similar (Malcolm and Durum, 1976), these high organic contents may indicate that little oxidation occurs as river sediments are deposited in deltas.

Deltaic deposits are found where a stream discharges to a receiving basin, whether the receiving basin is an ocean, inland sea, bay, estuary, or lake (Colemen, 1976). However, the world's major deltaic deposits are limited to the mouths of major river systems carrying substantial quantities of clastic sediments (Figure 3). These are large systems with mean river drainage areas of about 10^6 km^2. In addition to topographic features and climate, their distribution is dependent on global tectonics. About 57% of the major delta-forming river systems emerge along trailing continental coasts and 35% along marginal seacoasts.

Deltas may be important loci for the deposition of dissolved organic carbon (DOC) transported in rivers and flocculated in estuaries. Flocculation of riverborne DOC has been shown to be primarily an estuarine process (Gardner and Menzel, 1974; Sholkovitz, 1976). Sholkovitz (1976) reported that up to 11% of river DOC quickly flocculated upon mixing with seawater. In 1979, I found that about 20% of the DOC of a small, southeastern United States stream flocculated when mixed with seawater (Mulholland, in press). Since DOC constitutes a considerable portion of the total organic carbon transported in rivers, deposition and accumulation of flocculated DOC in deltas would add significantly to the total accumulation of organic carbon in these systems.

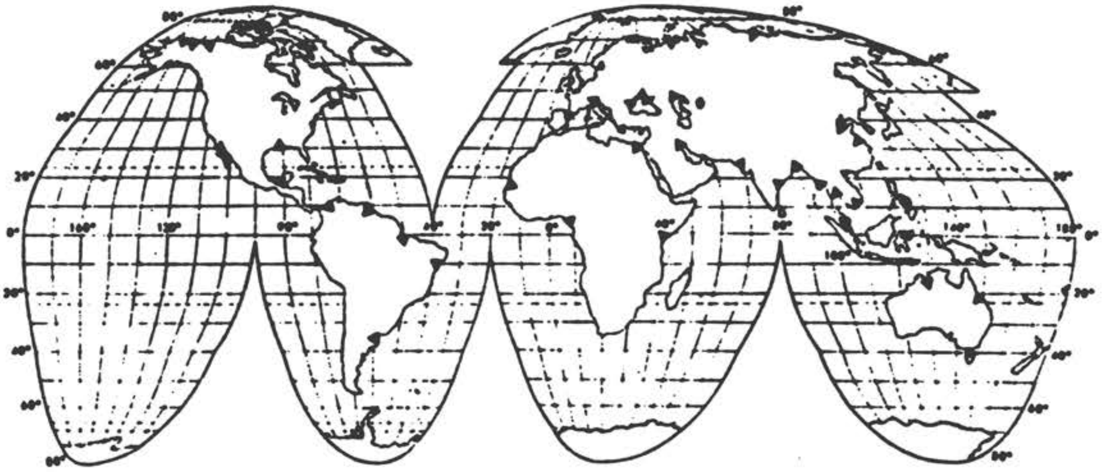


FIGURE 3

Location of major modern Deltas. From Coleman and Wright (1975).

METHODS AND DATA

Rates of riverborne sediments and organic carbon deposition in floodplain wetlands, taken from the literature, are presented in Table 1. Deposition rates are quite variable because of differences in river sediment loads. The Atchafalaya basin receives heavy sediment loads from the Red and Mississippi rivers, which discharge to it. Rivers and streams originating in the Coastal Plain (e.g., Creeping Swamp) carry very low sediment loads (Beck _et_ _al_., 1974).

Deposition rates are also quite variable within the same floodplain wetland as a result of spatial differences in water velocity and natural sediment retention structures. Mitsch _et_ _al_. (1979) reported flood sediment deposition varied by almost two orders of magnitude within the Kankakee River wetland. It should be noted that the rates presented in Table 1 are annual deposition rates and do not necessarily approximate annual accumulation rates of riverborne organic matter in floodplain wetlands. Rates of oxidation of deposited organic carbon increase when wetlands dry out during the drier months of the year.

The most direct method of estimating global accumulation of riverborne organic carbon in floodplain wetlands is to compute mean annual rates of accumulation, corrected for oxidation loss, and multiply them by the global area of floodplain wetlands. Although there are a few measurements

TABLE 1 Riverborne Particulate Organic Carbon Deposition in Floodplain Swamps

		Total Sediment Deposition (g m^{-2} yr^{-1})	Percent Organic Carbon	Organic Carbon Deposition (gC m^{-2} yr^{-1})[a]	References
Kankakee River	Northern Illinois	580	10	58	Mitsch *et al.*, 1979
Cache River	Southern Illinois	447	12	55	Mitsch *et al.*, 1977
Atchafalaya River	Louisiana	4,900	2.3[b]	113	Gagliano and van Beek,1975
Creeping Swamp	North Carolina	135	13	17	Yarbro, 1979

[a] Assuming carbon is 50% of organic matter dry weight.

[b] Approximate value for the Mississippi River (from which the Atchafalaya River receives much of its flow) given by Malcolm and Durum (1976).

or organic carbon deposition, there appears to be no inventory of total floodplain wetland area, even for the United States.

A second approach to a global floodplain deposition estimate is to make a carbon balance on a few river systems, and extrapolate this information to the entire earth. For example, annual organic carbon deposition rates in various floodplain wetlands bordering selected river systems can be measured and applied to the total wetland area along those systems. Total annual deposition could be computed and divided by total annual flux at the mouth of each river. This would yield a factor relating upstream wetland deposition to organic carbon flux at the river mouth, which could be multiplied by global river flux to estimate global wetland deposition.

I attempted this second approach, using some preliminary data for the the Apalachicola River in northwest Florida. John F. Elder (U.S. Geological Survey, Tallahassee, Florida) and co-workers are involved in a study of interactions between the Apalachicola River and its floodplain wetland. Preliminary results indicate that although annual flood deposition of riverborne organic carbon in floodplain areas is spatially quite variable, ranging up to about 140 gC m^{-2} yr^{-1}, a rough mean would be about 25 gC m^{-2} yr^{-1} (John F. Elder, personal communication, 1980). The floodplain wetland along the Apalachicola River comprises about 510 km^2 and is completely inundated by floods with recurrence intervals of 2 years or greater (John F. Elder, personal communication, 1980). Using these values for mean annual deposition rate and wetland area, one finds that about 12.8×10^9 gC yr^{-1} are deposited in the Apalachicola River floodplain wetland. Mean total organic carbon (TOC) concentration in the Apalachicola River near its mouth was 7.9 mg $liter^{-1}$ in 1979, and the long-term average annual discharge at this station is 22.1×10^9 m^3 (U.S. Geological Survey, 1979). Using these figures, one finds that the annual TOC flux is about 175×10^9 gC. Thus, deposition of riverborne organic carbon is about 6% of the river TOC export.

If data from the Apalachicola River are used to represent the world's rivers, global deposition of riverborne organic carbon is found to be about 6% of the 0.4×10^{15} gC yr^{-1} of river flux estimated by Schlesinger and Melack (in press). However, the large rivers of the world, such as the Amazon, have much larger floodplain wetlands bordering them than does the Apalachicola, and global wetland deposition is likely higher than 6% of river flux.

A third, less direct, approach to estimating global floodplain deposition is to estimate land denudation and assume that the material eroded, and not measured in river transport studies, is deposited in floodplain areas upstream.

Trimble (1975a, 1975b) suggested that sediment yield, as measured by river sediment load, may account for only a small part of the total erosion in the southern Piedmont of the southeastern United States. He estimates that only about 5% of the material eroded from the southern Piedmont since European settlement was actually transported out of the region by rivers. Trimble (1975a) suggests that the bulk of the material eroded from Piedmont uplands was deposited in the channels and floodplains of streams and small rivers. Holeman (1968) has also reported that only about 5% of the material eroded in the Potomac River drainage basin is exported annually. If this pattern is true for the entire earth, if mean global river transport is 18.1×10^{15} g sediment yr^{-1} (Holeman, 1968), and if mean organic carbon content of eroded sediments is 3% (Malcolm and Durum, 1976), then global alluvial deposition amounts to about 11×10^{15} gC yr^{-1}. This implies that river and stream floodplains are not in steady state but are aggrading at the expense of upland slopes. The implication is plausible if viewed over a time frame of decades or perhaps even centuries, rather than longer periods. Floodplain aggradation is a relatively slow process, whereas floodplain degradation is a more catastrophic or episodic process on a geologic time frame (Leopold <u>et</u> <u>al</u>., 1964).

Certainly a large fraction of the organic matter in alluvial deposits in the stream valleys and floodplains of the smaller, lower-order drainages is oxidized because these areas are generally well drained. In addition, Trimble (1974) states that most of the erosion and deposition in the southern Piedmont occurred during settlement and expansion of agriculture, prior to the establishment of soil conservation measures in the 1920's. At present, as a result of declining agriculture and better soil conservation practices, erosion rates in this region are low, streams have regained their transport ability, and the alluvial deposits of earlier periods are being dissected (Trimble, 1975a). Nonetheless, with increasing expansion of agriculture in many of the less-developed regions of the world, significant amounts of upland erosion and subsequent accumulation of organic carbon in alluvial deposits may occur in the channels and floodplains of streams and small rivers. Increasing construction of river impoundments throughout the world will also increase deposition and preservation of organic carbon in inland sediments.

Data compiled by J. M. Coleman (1976; personal communication, 1980) in his survey of the world's major deltas have been used in estimating organic carbon deposition in river deltas (Table 2). The rate of delta aggradation was assumed to be uniform during the period since the last great lowering of world sea levels (about 12,000 years). Making some further assumptions about average delta thickness and organic carbon content (see footnotes to Table 2), I have estimated global deltaic organic carbon accumulation to be about 0.55×10^{15} gC yr^{-1} (Table 2).

TABLE 2 Organic Carbon Accumulation in Major Deltas of the World during the Past 12,000 Years (data from Coleman, 1976; personal communication, 1980)

Delta	Location	Drainage basin climate	Deltaic plain climate	Delta area (km^2)	Organic carbon content (%) [a]	accumulation rate ($\times 10^{12}$ gC yr^{-1}) [b]
Amazon	Brazil	Humid tropical	Humid tropical	467,078	10	304
Burdekin	Australia	Dry tropical	Dry tropical	2,112	0.5	0.1
Chao Phraya	Thailand	Humid tropical	Humid tropical	11,329	10	7.4
Colville	Alaska	Arctic	Arctic	1,687	5	0.5
Danube	Romania	Cool temperate	Humid subtropical	2,740	5	0.5
Dneiper	USSR	Cool temperate	Dry steppe	-	5	-
Ebro	Spain	Dry tropical	Dry tropical	624	0.5	0.2
Ganges-Brahmaputra	Bangladesh	Warm temperate	Humid tropical	105,641	10	68.7
Godavari	India	Dry tropical	Dry tropical	6,322	5	2.1
Grijalva	Mexico	Dry subtropical	Humid tropical	17,028	8	8.9
Hwang Ho	China	Dry subtropical	Dry subtropical	36,272	0.5	1.2

TABLE 2 (continued)

Indus	West Pakistan	Dry subtropical	Dry subtropical	29,524	0.5	1.0
Irrawaddy	Burma	Humid subtropical	Humid tropical	20,571	10	13.4
Klang	Malaysia	Humid tropical	Humid tropical	1,817	10	1.2
Lena	USSR	Humid arctic	Arctic	43,563	5	14.2
Mackenzie	Canada	Humid subarctic	Arctic	8,506	5	2.8
Magdalena	Colombia	Humid tropical	Humid tropical	1,689	10	1.1
Mekong	Vietnam	Humid tropical	Humid tropical	93,781	10	61.0
Mississippi	USA	Temperate	Humid subtropical	28,568	5	9.3
Niger	Nigeria	Humid tropical	Humid tropical	19,135	10	12.4
Nile	Egypt	Dry subtropical	Desert	12,512	0.5	0.4
Ord	Australia	Desert	Dry subtropical	3,896	0.5	0.1
Orinoco	Venezuela	Humid tropical	Humid tropical	20,642	10	13.4
Parana	Brazil	Humid subtropical	Humid subtropical	5,440	10	3.5

TABLE 2 (continued)

Pechora	USSR	Subarctic	Subarctic	-	5	-
Po	Italy	Temperate	Temperate	13,398	5	4.4
Red	Vietnam	Humid subtropical	Humid subtropical	11,908	10	7.7
Sagavanirktok	Alaska	Arctic	Arctic	1,907	5	0.6
Sao Francisco	Brazil	Humid tropical	Dry tropical	1,178	5	0.4
Senegal	Senegal	Dry subtropical	Desert	4,254	0.5	0.1
Shatt-al-Arab	Iraq	Dry subtropical	Dry tropical	18,497	0.5	0.6
Tana	Kenya	Subtropical	Dry subtropical	3,659	0.5	0.1
Volga	USSR	Dry subtropical	Dry subtropical	27,224	0.5	0.9
Yangtze-Kiang	China	Dry subtropical	Humid subtropical	66,669	2	8.7
TOTAL						551.3

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[a] Rough estimates based on deltaic plain climate (J. M. Coleman, personal communication, 1980).

[b] Based on delta area, an average delta thickness of 60 m (J. M. Coleman, personal communication, 1980), delta bulk density of 1.3 g cm^{-3} (typical entisol value, Soil Conservation Service, 1975), delta organic carbon content, and a uniform accumulation rate over the last 12,000 years.

Most of the global deltaic organic carbon accumulation takes place in a few large systems. About 79% of it is in the three largest systems--the Amazon, Ganges-Brahmaputra, and Mekong deltas. These deltas are in the humid tropics and should possess high organic carbon contents as a result of large river loads of organic debris and rapid rates of delta formation (J. M. Coleman, personal communication, 1980). From these results it would appear that reasonably accurate estimates of global deltaic organic carbon accumulation can best be made by concentrating efforts on these three deltas, and perhaps the Lena, Orinoco, and Yangtze-Kiang deltas as well.

CONCLUSIONS

1. Interaction between rivers and floodplain wetlands generally results in a net annual deposition of riverborne sediment and particulate organic carbon of up to 100 gC m^{-2} over large wetland areas. Some of this material is certainly oxidized, however, a large part of it likely escapes complete oxidation because of the lack of available oxygen. There is generally a net annual dissolved organic carbon export of up to 25 gC m^{-2} from wetlands to rivers due to litter and canopy leaching and litter decomposition. Tropical floodplain wetlands, with large accumulations of floating vegetation, may export significant amounts of particulate organic carbon from autochthonous sources.

2. The net effect of river-floodplain wetland interactions

is to transfer detrital organic carbon from upland terrestrial systems, where decomposition rates are generally higher, to lowland environments, where oxidation is often reduced and organic carbon can accumulate at a greater rate.

3. Global deposition of riverborne organic carbon in floodplain wetlands is at least 6% of total river flux, and probably higher.

4. Some of man's activities, such as channelization and wetland drainage, are reducing the total area of floodplain wetland receiving river inputs, particularly in the developed regions of the world. However, this reduction may be offset by increased erosion and subsequent floodplain deposition of organic carbon in the less-developed regions. Also, increased construction of river and stream impoundments throughout the world is increasing, to an unknown extent, deposition and preservation of organic carbon in inland sediments.

5. Land disturbance and agriculture increase soil erosion and result in large amounts of sediment deposition in the channels and floodplains of smaller streams and rivers. If present global land-use patterns and agricultural practices are similar to those in the United States in the last century, then organic carbon deposition in these systems could amount to as much as 11×10^{15} gC yr^{-1}.

Actual organic carbon accumulation would be much lower, however, because of oxidation after deposition.

6. If we are correct in assuming that the rates of formation of the world's major river deltas have been uniform over the last 12,000 years, organic carbon accumulation in these systems has been about 0.6×10^{15} gC yr^{-1}.

7. More measurements of organic carbon deposition and accumulation, as well as inventories of total wetland area in the floodplains of the world's major rivers, are needed. Better understanding of river-floodplain interactions during floods is also necessary. Since many of the remaining large tracts of floodplain wetland are located in the tropical and subtropical regions that have received little study, efforts should be focused on making organic carbon budgets on these systems. More measurements of reservoir organic carbon accumulation and good world reservoir inventories are also needed. Organic carbon accumulation in sediments or river impoundments may be quite large.

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THE FLUX OF ORGANIC CARBON TO THE OCEANS: SOME HYDROLOGIC CONSIDERATIONS

Carl F. Nordin, Jr. and Robert H. Meade

Not much is known about the flux of organic carbon to the oceans from the rivers of the world. Programs to collect and analyze samples for organic carbon in rivers systematically have been undertaken on only a few rivers and data have been collected for only a few years. For many of the large rivers of the world, no data exist.

Estimates of the flux of organic carbon to the oceans have been made by several scientists; these are discussed later in this paper. For now, we note that these estimates vary by at least an order of magnitude, and that to some extent they are based on assumptions that either are difficult to verify or are contradicted by existing data. For example, it is sometimes assumed that the ratio of dissolved to particulate organic carbon is constant or that the concentration of particulate organic carbon bears a constant ratio to suspended sediment concentration.

The usual approach for estimating the contribution to the ocean from rivers is to measure or otherwise estimate the flux from the largest rivers, the 40 or 50 that contribute about half the total flow and drain about 60% of the land area, and then to extrapolate the rest. Holeman (1968) did this for sediment and Meybeck (1976) for dissolved inorganic constituents. The same approach can be used to estimate flux of organic carbon. In making estimates from such an approach, however, one must consider certain hydrologic processes. It is extremely important that the samples be representative, and that they are collected in such a way as to define seasonal variations and the relation of concentration to water discharge, if one exists. In addition, it is desirable to collect the kinds of data that will allow one to evaluate the impact of extreme events on the average values of annual flows or fluxes, and that are required to arrive at reasonable figures for determining standard errors of estimates. In the following sections, we consider each of these data needs.

GLOBAL EXTRAPOLATION, SMALL RIVERS, AND EXTREME EVENTS

A summary of annual streamflow and flux to the oceans of sediment, dissolved inorganic constituents, inorganic carbon, and organic carbon is presented in Table 1. The entries were derived from several sources, indicated in the table. The total flow is $1.19 \times 10^6 m^3/s$, and the discharge-weighted concentrations of sediments and dissolved solids are about 530 and 85 mg/l, or a ratio of 6.24:1. The estimates of carbon and organic carbon reflect about an order of magnitude variation, as pointed out by Richey *et al*. (1980) and by Reiners (1973).

The usual strategy for estimating global flux is to measure or sample the 40 or 50 largest rivers in the world and then to extrapolate the rest on the basis of area, usually with some kind of stratified sampling or categorizing into climatic, geologic, or topographic regimes. (See for example, Fournier, 1960, for sediment and Baumgartner and Reichel, 1975, for the world water balance.) The importance of concentrating on large rivers is shown clearly in Figure 1, where the accumulative sum of flows, drainage areas, and sediment loads as percents of totals are plotted against the number of ranked quantities included in the sums. These data are mostly from Holeman (1968). The largest 50 quantities account for about 40% of the sediment, 50% of the flow, and 55% of the drainage area. However the slopes of the curves are so flat that adding the next 100 or 200 largest quantities adds only a few percentage points to the totals.

A simple way to extrapolate flows is demonstrated in Figure 2, where average annual discharge, Q, is plotted along the abcissa against the number, n, of streams with flows equal to or greater than the indicated discharge plotted along the ordinate, both to logarithmic scales. The equation for the straight line drawn by eye to best fit the values of n from 10 to 200 is

$$Q \approx 300,000\ n^{-1.27} \qquad (1)$$

Integrating the curve $n = 10$ to $n = \infty$ and adding flows from the 10

TABLE 1. Summary of Streamflow and Flux to the Oceans of Sediment, Dissolved Constituents, and Carbon

	Discharge (10^{12} kg/yr)	Concentration (mq/l)
Sediment [a]	20	533
Dissolved solids[b]	3.2	85.3
Carbon[c]	0.2 to 1	5.4 to 27
Organic carbon[d]	0.1 to 1	2.7 to 27
Land area [e]	101×10^6 km^2	
Streamflow[e]	1.19×10^6 m^3/s	

[a] Estimated mostly from Holeman's data (1968).

[b] Meybeck (1976).

[c] Reiners (1973).

[d] Richey *et al*. (1980).

[e] Baumgartner and Reichel (1975).

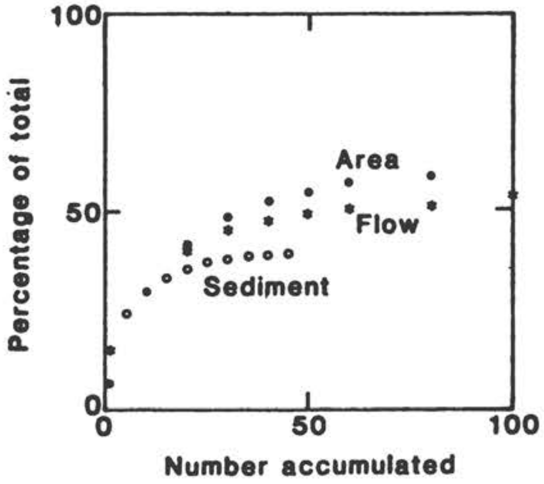

FIGURE 1 The accumulated sums of flows, drainage areas, and sediment loads as percentages of totals plotted against the number of ranked quantities included in the sums.

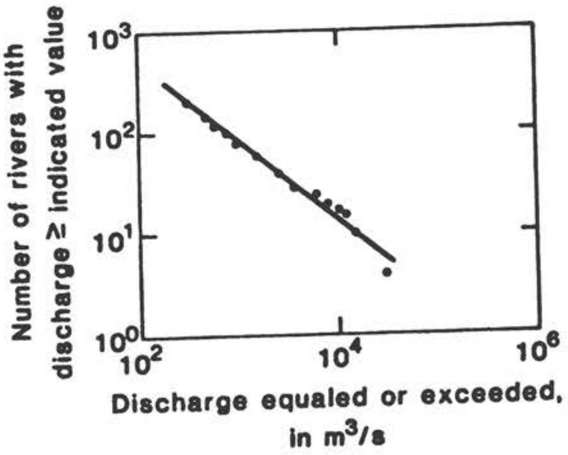

FIGURE 2 Graph showing the number of streams with flows equal to or greater than indicated value.

largest rivers gives the total flow to the ocean of about 10^6 m^3/s, while integrating from n = 1 to n = ∞ yields 1.11 x 10^6 m^3/s. The fair agreement with the value in Table 1 may be fortuitous, but as a first approximation, this sort of extrapolation might be useful.

However, attempts to apply this same type of extrapolation for sediment were not successful, first, because firm values for sediment loads are available only for about 40 large rivers, whereas flow records are available for several hundred large rivers, and second, because values of sediment discharges plotted as in Figure 2 do not fall along a straight line, so simple extrapolation was not possible. It was also found that although water discharges correlate fairly well with drainage areas, no such correlations exist for sediment loads. This finding is reflected in Figure 3 and Table 2. Figure 3 shows monthly hydrographs for four rivers: the Congo, Orinoco, Yukon, and Cho-Shui. Table 2 shows drainage areas, mean flows, and sediment loads to the oceans for these four rivers. The striking feature of thse data is the close correspondence of sediment loads despite the great disparities of flows and drainage areas. These four rivers account for about 1.5% of the sediment load to the oceans and 6.2% of the flow. The flow contribution from the Cho-Shui is almost negligible, but its sediment contribution is not. The Cho-Shui is typical of the rivers of Taiwan. According to the 1977 Hydrologic Yearbook of Taiwan, the streamflow to the ocean from the island was about 1,160 m^3/s, 0.1% of the world total, and the sediment discharge was 236 x 10^9 kg, about 1.2% of the world total. The drainage area is about 24,000 km^2, or 0.025% of the total land area. The sediment discharge to the ocean from the island of Taiwan is about the same as that from the Mississippi River, which drains 3% of the total land area and contributes 1.5% of the total flow to the ocean.

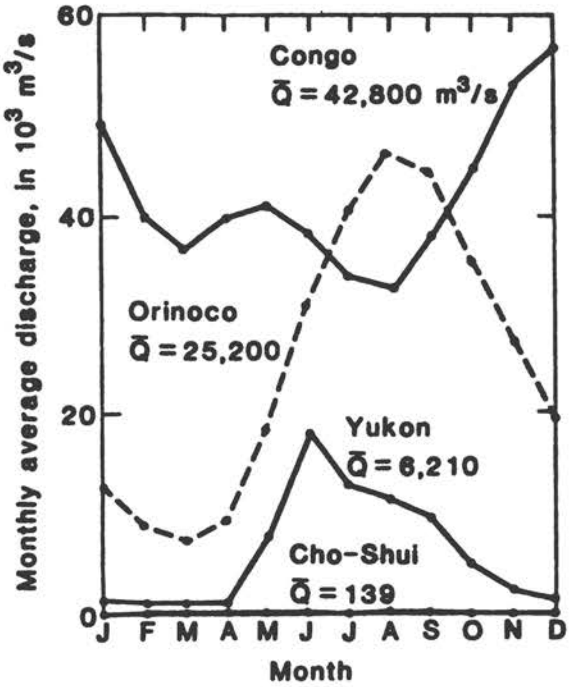

FIGURE 3 Monthly flow hydrographs for four rivers.

TABLE 2. Flows and Sediment Loads for Four Rivers

River	Drainage Area (km^2)	Mean Flow (m^3/s)	Annual Sediment Discharge (10^3 kg)
Congo	3,700,000	42,800	65,000,000
Orinoco	881,000	25,200	100,000,000
Yukon	932,000	6,210	60,000,000
Cho-Shui	2,310	139	65,000,000

The point to be drawn from these examples is that small rivers contribute small quantities to the total streamflow, but it does not follow that their contributions to the flux of sediment are also small. Quite possibly, small streams may also contribute substantial amounts of organic carbon to the oceans, so it would be prudent to design a global sampling program to collect representative data from small to large streams.

Finally, it should be emphasized that the variability in flow and transport, relative to their mean values, is likely to be much greater for small streams than for large streams. The relation of transport, Q_s, to flow, Q, for many rivers can be approximated by the equation:

$$Q_s = aQ^b \tag{2}$$

or

$$C = aQ^{b-1} \tag{3}$$

The exponent b describes the relation of concentration to flow; if b=1, the concentration is constant, if $b > 1$, concentration increases with discharge, and if $b < 1$, concentration decreases with increasing discharge. Generally, for sediment transport in large rivers, b is slightly greater than unity; that is, concentration increases with increasing flows, but not very much, while for small rivers, especially flashy type streams in semiarid and arid regions, b is on the order of 2 or 3 and sometimes greater.

Notice that the average transport, $\bar{Q}_s$, does not equal $a\bar{Q}^b$, so if transport records are collected for a single year of average flow, the results are not representative of the average transport. Furthermore, the greater the value of the exponent, b, the greater the disparity between the single years record and the average is likely to be. The result of this difference in variability between large and small streams is that to obtain the same relative accuracy, longer records are required on small rivers than on large rivers. We return to this point in a later section; for now we simply reinforce this idea by the following data for the Rio Chira in Peru, given by Burz (1977):

Year	Annual Flow (m^3/s)	Annual Suspended Sediment Load (10^9 kg)
1965	278	74.7
1966	51.6	4.0

Notice that the sediment load of 1965 is larger than the annual sediment load of the Congo River. The five-fold difference in flow for the two years is accompanied by an almost 20-fold difference in sediment load. This sort of year-to-year variability, common to small streams in arid regions, is not so likely to occur in large rivers, especially those of humid regions.

Another characteristic of streams with large flow variability is that much of the transport occurs during the few days of highest flows. This is illustrated very well by data from the Eel River at Scotia, California. Figure 4 shows annual flows for 1958 through 1978, together with the quantities discharged during the highest 1% and 10% of the time. A similar graph for sediment discharge is shown in Figure 5. The catastrophic flood during the 1965 water year resulted in an annual sediment load of over 150 million tons, 70% of which was discharged in 4 days, an amount greater than the combined total for the previous 7 years and equal to 24% of the total sediment discharged in the 21-year period of record. Notice also that including the 1965 sediment data in the 21-year average sediment load yields 21.8 x 10^6 tons against 15.3 x 10^6 tons for 20 years excluding 1965. Properly included in the average, this event should be weighted according to its frequency of occurrence, which involves some judgment and extrapolation, because of the short record. Probably, it has a return period of about 200 years. The 1977 water year had

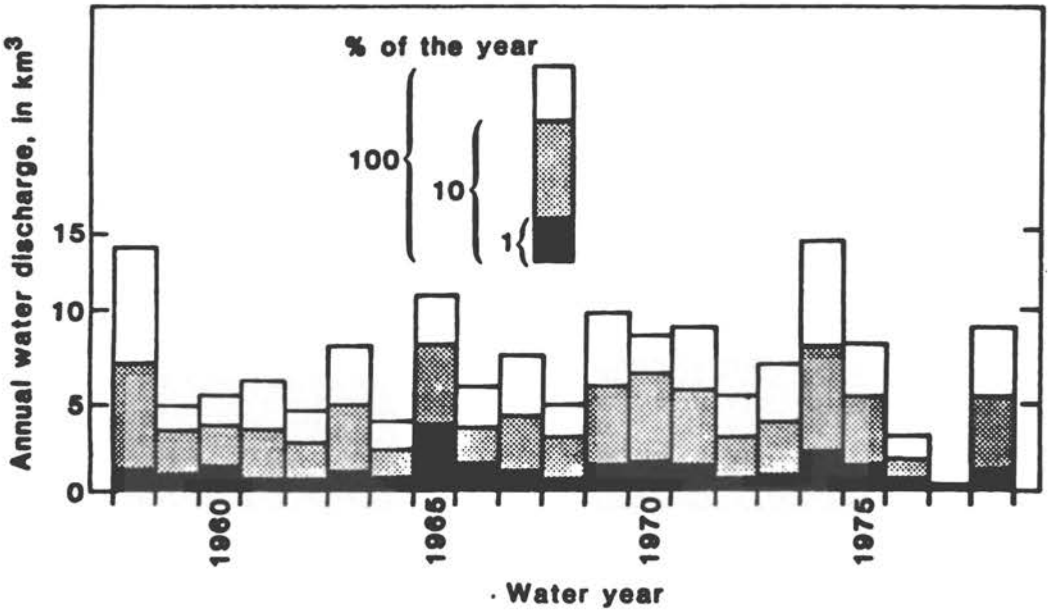

FIGURE 4 Annual flows for the Eel River at Scotia, California 1958 through 1978 water years.

exceptionally low flow, and the sediment load, less than 20,000 tons is too small to be shown on Figure 5. For the 21 years, flows ranged from 14.2 km^3 in 1974 to 0.5 km^3 in 1977, a factor of about 30, and sediment load ranged from 20,000 tons in 1977 to 152,000,000 in 1965, a factor of about 7,000. For most years, a one third of the sediment is discharged in 1% of the time and 90% is discharged in 10% of the time.

The data for the Eel River show two things very clearly. First, there may be great variability in short records, so estimates of mean values may be substantially in error unless extreme events are somehow weighted according to their frequency of occurrence. Second, sampling such streams using a simple time series is not sufficient; rather extensive sampling should be undertaken to cover the high flows, with less frequent samples during low flows.

The impact on sediment discharge of extreme flood events in large rivers is not so great as in small rivers. For example, the 1973 flood of the Mississippi River had a recurrence interval of about 100 years, but the annual sediment load of 210 x 10^6 tons for the station at Tarbert Landing (near Baton Rouge) was only 150% of the average annual load, 140 x 10^6 tons per year, for the period 1963 to 1978.

RIVER MIXING AND REPRESENTATIVE SAMPLES

Many samples of river water are collected by simply dipping a sample bottle into the flow at or near the water surface at a single point in the cross section. Generally, this kind of sampling should be avoided; it cannot be assumed that rivers are well mixed either vertically or laterally. For example, Figure 6 shows lines of equal concentration of suspended sediments for the Amazon River at Manacapuru (Meade _et al_., 1979) and Table 3 gives concentrations of

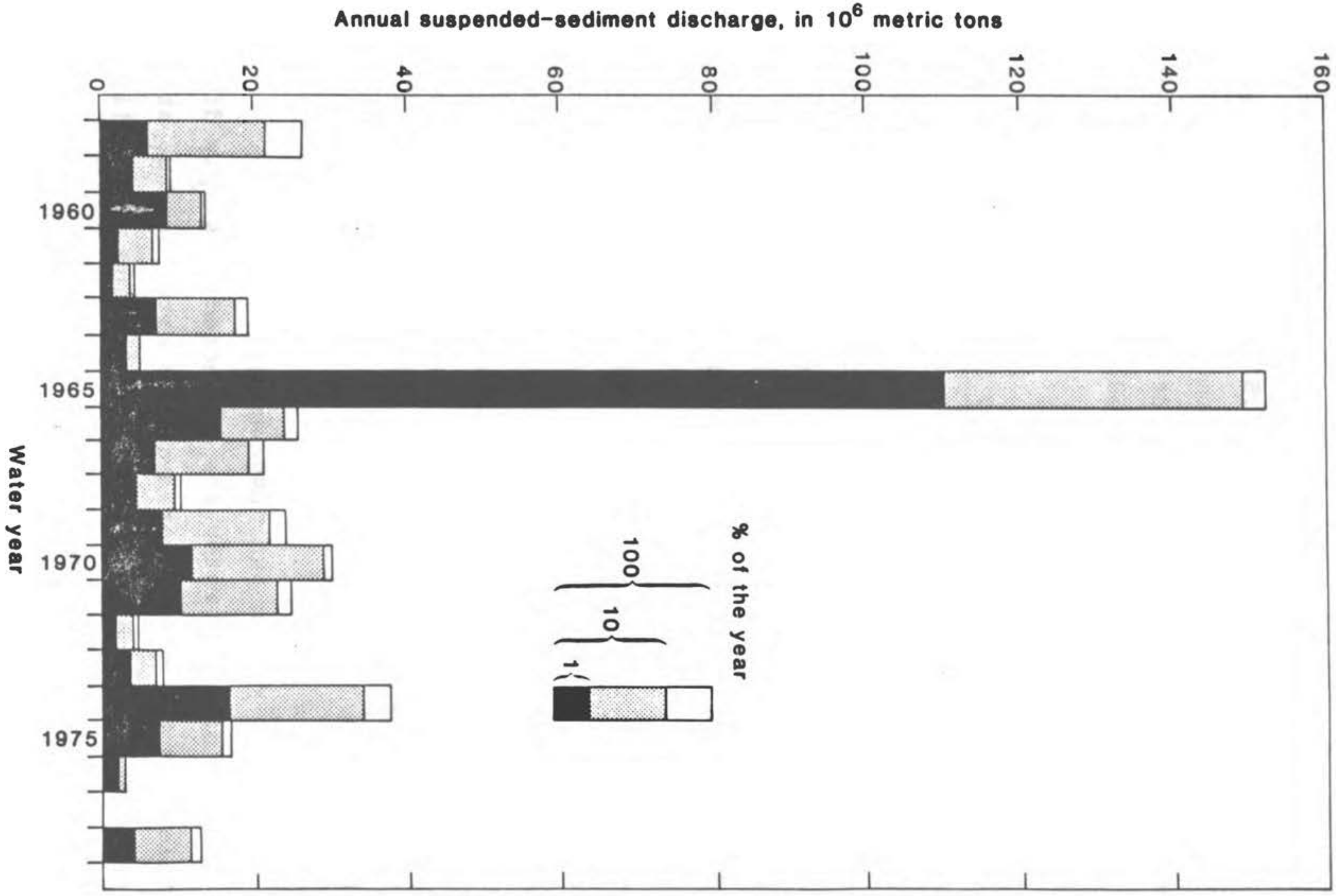

FIGURE 5 Annual sediment loads for the EEl River at Scotia, California, 1958 through 1978 water years.

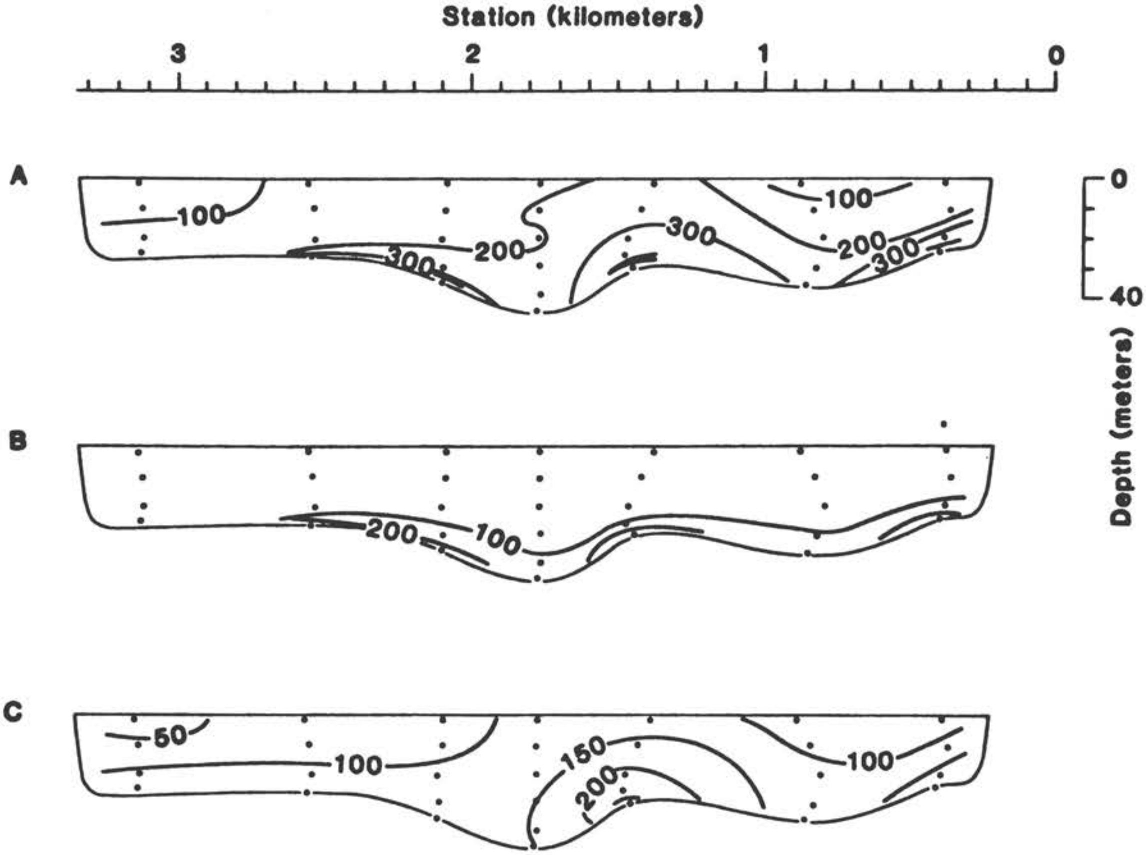

FIGURE 6 Spatial distribution of concentration, in mg per liter, of different-size fractions of suspended sediment, based on data from point samples collected in Manacapuru measuring section, May 27, 1977. A, Total suspended-sediment concentration. B, Concentration of sand (material coarser than 0.063 mm) in suspension. C, Concentration of silt and clay (material finer than 0.053 mm) in suspension.

TABLE 3 Titration Alkalinities for Several Cross Sections of the Amazon River [a]

Station	Sample Locations in a Vertical[b]	Alkalinity[c]		
		Left	Middle	Right
Iquitos	T	1,079	1,213	1,280
	M	1,114		
	B	1,236	1,265	1,285
Santo Antonio	T	443	913	992
	B	457	914	982
Obidos	T	338	387	390
	M	343	388	387
	B	342	385	389

[a] Data from Stallard, 1980.

[b] T is near the water surface; B is near the bed; M is about midway through the depth.

[c] Left, middle, and right refer to cross channel locations of each vertical.

dissolved inorganic constituents in terms of total alkalinity, for several cross sections. Obviously, the flow is not well mixed at these cross sections with regard to either dissolved constituents or sediment particles. Curtis et al. (1979) found the concentrations of surface samples to be about half the concentrations of depth-integrated samples of suspended fine sediments from the Amazon River (Figure 7), and suggest that appreciable errors may result in using surface samples to compute the flux of either dissolved or particulate materials.

The discharge Q_s of any dissolved or suspended solid material transported by a river is defined by the equation:

$$Q_s = \int_0^B \int_0^D C_s \; V_s \; dy \; dz \qquad (4)$$

where B is the river width, z is the cross channel position, y is distance from the bed, positive upward, D is the local depth at position z, and C_s and V_s are concentration and velocity of the material under consideration. Both C and V are functions of y and z. The assumption usually is made that V_s is the same as the local flow velocity, but this is not necessarily so for solid particles.

The distribution of velocity and concentration usually cannot be derived theoretically or described analytically, but if velocities are measured and samples are collected at a number of points in a cross section, it is possible to integrate Equation 4 graphically or numerically, as shown in Figure 8. This method is widely used in sampling large rivers. Figure 9 shows the point sampling device we used on the Amazon River; it can operate to depths of 100 m in velocities up to 3 m per second, and it provides simultaneous measures of V, C, and y. Standard point sampling equipment used in

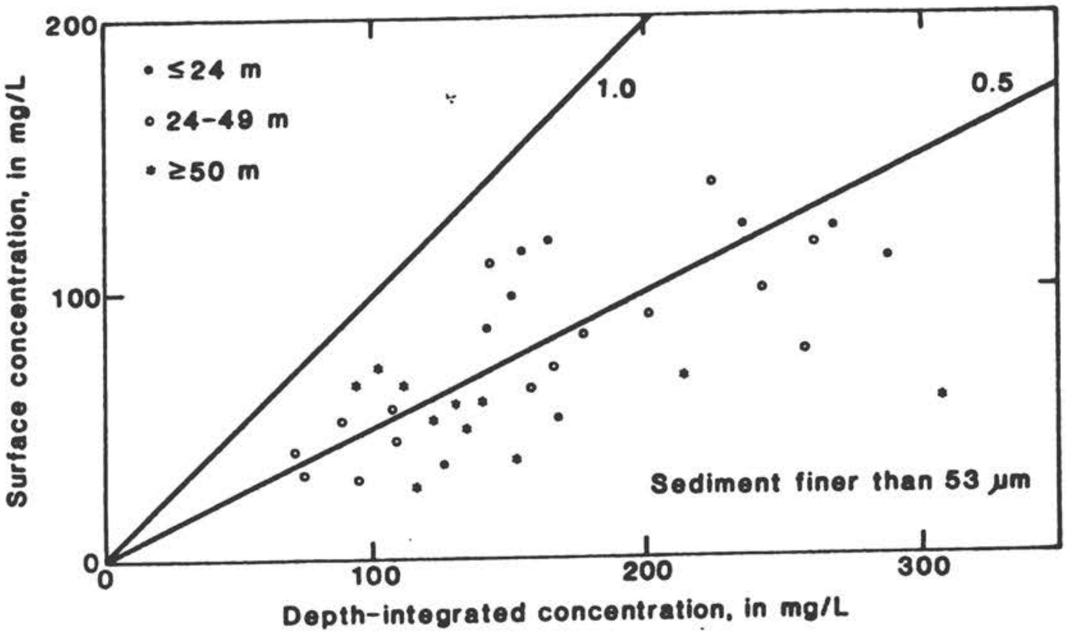

FIGURE 7 Relations between concentrations of fine-grained suspended sediment at the river surface and in depth-integrated samples in the Amazon River mainstem near Iquitos, at São Paulo de Olivença, at Santo Antônio do Içá, at Itapeúa (near Coari), near Manacapuru, and at Óbidos. Points are coded by river depth: ●, depths < 24 m; 0, 24-49 m; Δ , > 50 m. Lines through the graph are not regression lines but are reference lines to show ratios of surface to depth-integrated concentrations.

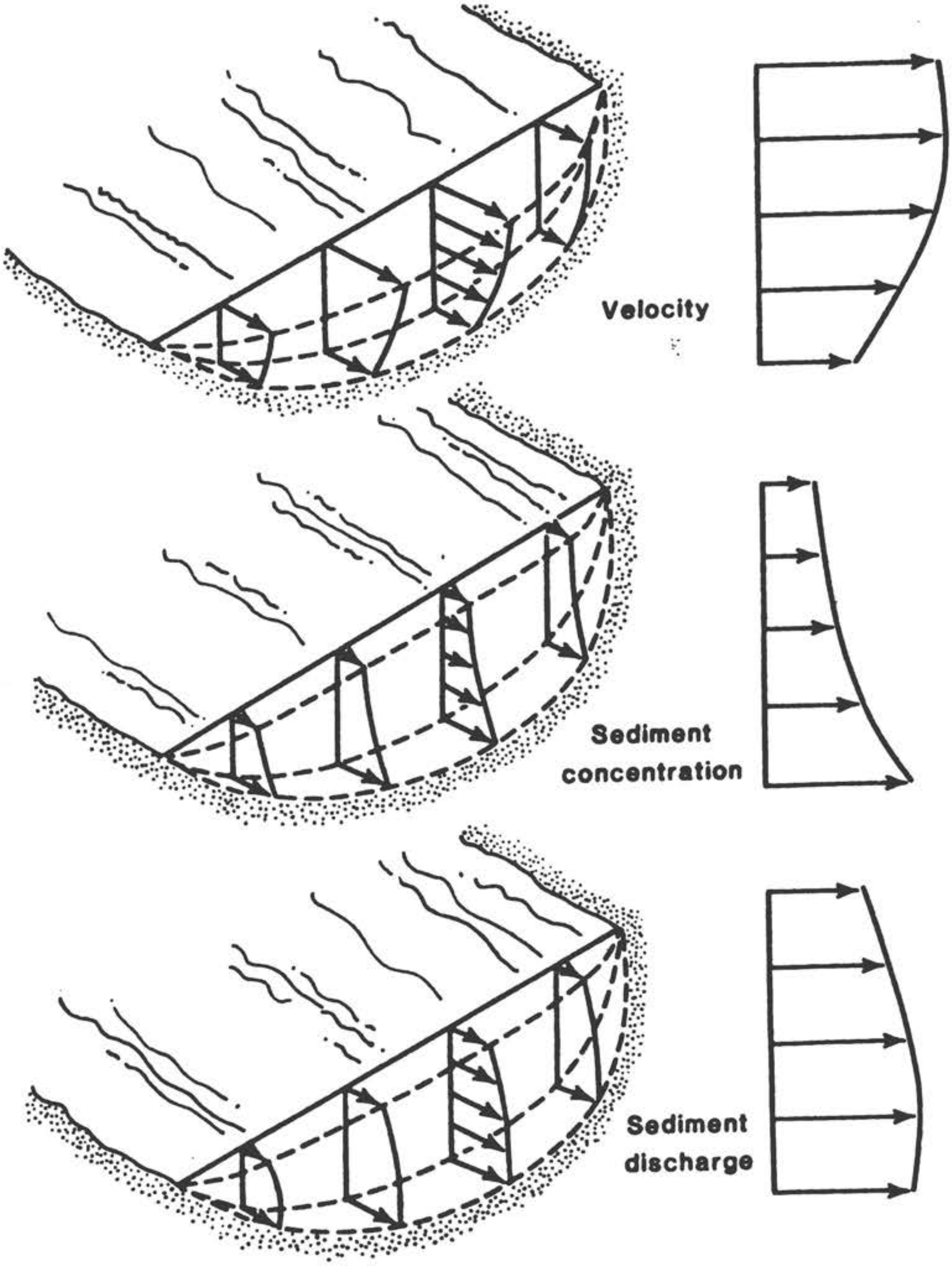

FIGURE 8 A schematic diagram showing the method for integrating Equation 1 by means of point-velocity measurements (top figure) and concentrations from point-integrated sediment samples (middle figure). The sediment discharge shown in the bottom figure is the product of velocity and concentration.

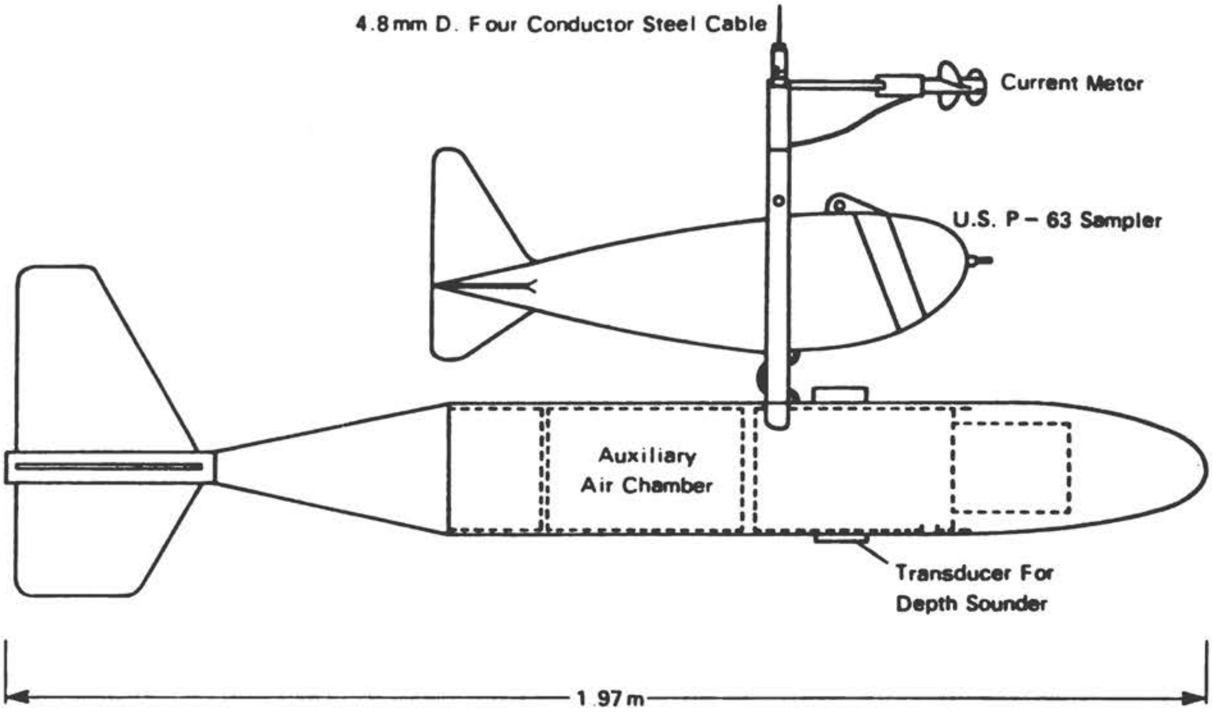

FIGURE 9 Point-sampling equipment used in Rio Amazonas and its tributaries in 1976 and 1977. Upper part shows a modified US P-63 point-integrating sampler. Lower part shows equipment for providing extra air capacity and weight.

the United States are described in Determination of Fluvial Sediment Discharge (U.S. Interagency Committee on Water Resources, 1963).

A much quicker and simpler method of integrating Equation 4 is to do so mechanically by means of depth-integrating samplers. These samplers are designed with a hydraulic efficiency of one, so that the intake velocity of the sampler is equal to the stream velocity at every point in the flow field. If the sampler traverses from the water surface to the bed and back to the water surface at a constant transit rate at each of a number of equally spaced verticals in the cross section, the resulting composite sample is a representative sample of both Q_s, the flux of dissolved or solid particles, and Q, the streamflow. By definition, the mean concentration in the cross section, $\bar{C}$, is equal to the concentration of the composite sample

$$\bar{C} = Q_s/Q \qquad (5)$$

For shallow streams, a number of depth-integrating samplers are available, and all these can be adapted to sampling for organic carbons. Those commonly used in the United States are described, along with the proper sampling procedures, in the interagency report referred to above. For large rivers, the bag sampler developed for use on the Columbia River by Stevens <u>et</u> <u>al</u>. (1980) and modified for the Amazon River (Meade <u>et</u> <u>al</u>., 1979) (Figure 10) can be used to sample for suspended sediments. However, the plastic bag used here for the sample container may not be suitable for DOC (dissolved organic carbons), although it might be suitable for POC (particulate organic carbons). Perhaps there is need for additional developments on depth-integrating samplers for deep rivers.

RELATIONS BETWEEN CONCENTRATION AND DISCHARGE

In many rivers, the concentration of suspended sediment increases and the concentration of dissolved inorganic material decreases with

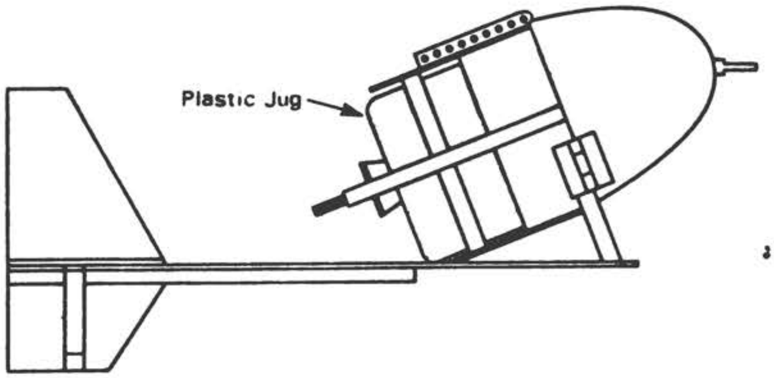

FIGURE 10 Depth-integrating sampler used in Rio Amazonas and its tributaries in 1977. Overall length, not including nozzle, is 0.9 m. For our operations, the sampler was mounted in the sampling array (shown in Figure 4) in the position that was occupied by the P-63 sampler during point sampling. However, the depth-integrating sampler can be mounted on top of any suitable sounding weight.

increasing water discharge. In addition, there is often a hysteresis in the relation between the concentration of sediment and water discharge, with higher concentrations on rising stages and lower concentrations on falling stages. Whether any consistent relations exist between concentrations of organic carbon and streamflow remains to be established for most rivers. The concentrations of POC probably will increase with flows and will correlate with concentrations of suspended sediment for many rivers, and it can be expected that the flux of CPOC (course particulate organic carbon) would be especially high during major floods as course debris that accumulates during normal years is flushed from the watershed during these extreme events. The concentrations of DOC are not as likely to correlate with flows or to show trends similar to concentrations of dissolved inorganic constituents because they are controlled by different and complex processes.

Tables 4, 5, and 6 show current data for the Yukon, Columbia, and St. Lawrence rivers. Notice that the earlier data show only concentrations for TOC (total organic carbon); the separate analysis of DOC and SOC (suspended organic carbon) are available only for the last two years. (For this discussion, POC and SOC may be considered synonomous.) A few generalities can be drawn from these data: (1) the concentrations of organic carbon are low, ranging from 3 to 21 mg/l on the Yukon, 1.2 to 11 mg/l on the Columbia, and 2.2 to 24 on the St. Lawrence, (2) the ratio DOC/SOC ranges from about 2 to about 18, with no apparent relation to flow or season, (3) no seasonal patterns or correlations with flows or suspended sediment concentrations are apparent.

TABLE 4 Concentrations of Suspended Sediment and Organic Carbon in St. Lawrence River at Cornwall, Ontario (Near Massena, New York), 1977 through 1979 Water Years

Date	Flow (m^3/s)	Concentration (mg/l) Sediment	TOC	DOC	SOC
26 Oct 1976	8,468	2	3.8	--	--
26 Jan 1977	6,457	--	13	--	--
27 June	7,080	17	5.6	--	--
29 Aug	7,533	2	5.8	--	--
27 Oct	8,496	1	4.2	--	--
28 Nov	8,468	4	--	7.0	--
27 Dec	6,599	5	9.7	--	--
26 Jan 1978	7,222	13	1.6	--	--
23 Feb	8,355	4	--	3.5	0.8
24 Mar	9,091	7	6.1	--	--
26 Apr	8,723	3	9.7	--	--
25 May	9,063	6	8.3	--	--
26 July	7,958	8	3.2	--	--
28 Aug	7,873	4	2.9	--	--
25 Sept	7,760	2	2.0	--	--
25 Oct	7,363	1	--	6.2	0.7
27 Nov	6,655	1	3.7	--	--
21 Dec	5,664	14	2.5	--	--
25 Jan 1979	6,231	2	3.1	--	--
26 Feb	7,080	1	--	24	--
29 Mar	7,816	6	3.9	--	--
25 Apr	8,270	2	2.2	--	--
29 May	8,496	3	2.4	--	--
26 June	8,213	2	--	15	0.6
26 July	7,788	2	4.0	--	--
27 Aug	7,760	3	2.2	--	--
25 Sept	8,241	2	--	3.4	0.2

TABLE 5 Concentrations of Suspended Sediment and Organic Carbon in Columbia River at Warrendale, Oregon, 1975 through 1978 Water Years

Date	Flow (m^3/s)	Concentration (mg/l) Sediment	TOC	DOC	SOC
11 Oct 1974	3,820	1	2.8	--	--
30 Oct	4,480	1	1.8	--	--
12 Nov	2,910	1	2.1	--	--
25 Nov	3,230	1	11	--	--
11 Dec	4,430	2	3.6	--	--
30 Dec	4,710	35	2.3	--	--
7 Jan 1975	5,070	31	1.7	--	--
21 Jan	5,180	30	2.5	--	--
11 Feb	5,880	--	6.8	--	--
19 Feb	5,840	43	1.7	--	--
4 Mar	6,870	41	2.3	--	--
20 Mar	7,040	--	2.2	--	--
1 Apr	7,370	48	2.4	--	--
15 Apr	7,050	40	1.6	--	--
29 Apr	7,370	28	3.9	--	--
15 May	8,940	21	2.2	--	--
28 May	9,240	26	3.2	--	--
10 June	9,910	26	5.8	--	--
24 June	8,740	20	3.4	--	--
14 July	6,330	13	5.3	--	--
6 Nov	4,760	9	2.8	--	--
3 May 1976	8,100	18	5.8	--	--
5 Aug	7,310	16	3.9	--	--
4 Oct 1976	4,580	6	1.4	--	--
22 Oct	4,390	4	1.2	--	--
24 Jan 1977	5,110	9	1.3	--	--
28 Apr	3,590	10	2.2	--	--
25 July	2,740	9	1.8	--	--
6 Oct	3,740	8	1.3	--	--

8 Nov	3,540	8	1.7	--	--
28 Nov	3,740	22	1.5	--	--
25 Jan 1978	5,130	16	1.7	--	--
13 Feb	4,590	19	2.0	--	--
20 Mar	5,070	10	1.5	--	--
21 Apr	7,030	21	--	1.8	0.6
19 May	8,670	30	3.5	--	--
9 June	8,130	26	3.0	--	--
11 July	6,320	27	--	1.7	0.8
25 Aug	3,450	11	2.1	--	--

TABLE 6 Concentrations of Suspended Sediment and Organic Carbon in Yukon River at Pilot Station, 1977 and 1978 Water Years

Date	Flow (m^3/s)	Concentration (mg/l)			
		Sediment	TOC	DOC	SOC
20 Mar 1977	1,354	--	2.6	--	--
8 June	17,900	512	21	17	2.8
19 July	11,640	203	9.6	7.5	.5
29 Sept	7,930	--	--	16	1.5
1 Feb 1978	1,512	4	3.0	2.9	--
28 June	13,680	308	--	6.4	1.1
22 Aug	8,893	676	9.6	4.2	--
27 Sept	5,324	140	--	5.1	2.0

It should be pointed out that both the Columbia and St. Lawrence are highly regulated and have very low concentrations of suspended sediments; they are not typical rivers. Also, the data for the Yukon are not extensive enough to permit any conclusions about seasonal trends. More extensive data are available in the report by Malcolm and Durum (1976) for four other rivers draining to the Atlantic and to the Gulf of Mexico; the Mississippi, Neuse, Brazos, and Sopchoppy. For the Mississippi River, there is a fair correlation between concentrations of SOC and suspended sediment (Figure 11), and both SOC and sediment concentrations correlate roughly with water discharge (Figures 12 and 13). The DOC concentrations for these data range from 2.2 to 4.5 mg/l, averaging 3.4 mg/l, and were found to be independent of discharge and without seasonal trend (Malcolm and Durum, 1976, p. F20). The ratio of DOC to SOC ranges from 0.48 to 2.55.

For the Brazos River near Richmond, Texas, the SOC concentrations do not correlate with either suspended sediment concentrations (Figure 14) or water discharge (Figure 15), but the suspended sediment concentration shows a fair correlation with flow (Figure 16). DOC concentrations range from 0.5 to 7.7 mg/l, averaging 3.7 mg/l, with an apparent seasonal trend, higher concentrations occurring during December through March. The ratio DOC/SOC ranges from 0.41 to 3.32.

Annual flows and organic carbon loads for the four rivers are summarized in Table 7. Notice in particular the range of the DOC:SOC ratios and the high average concentration, 30 mg/l, for the Sopchoppy River.

Finally, it is of some interest to compare the above figures with a few values found in the literature. Wetzel and Rich (1973)

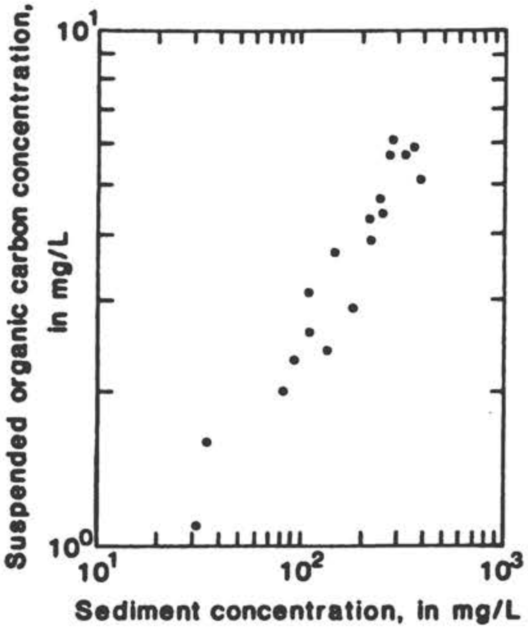

FIGURE 11 Relation between SOC and sediment concentrations, Mississippi River, Louisiana.

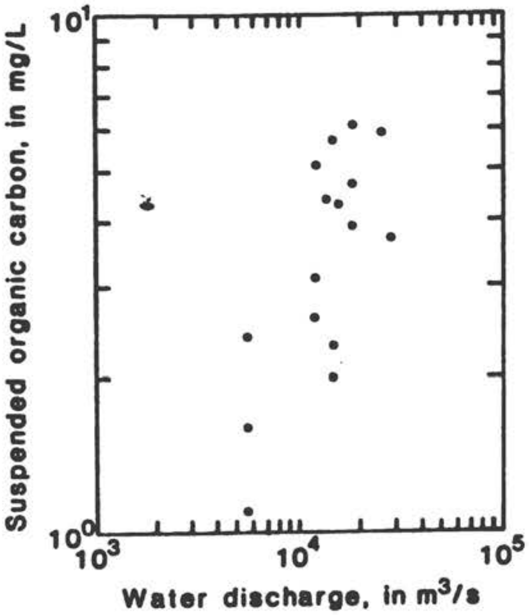

FIGURE 12 Relation between SOC concentration and water discharge, Mississippi River, Louisiana.

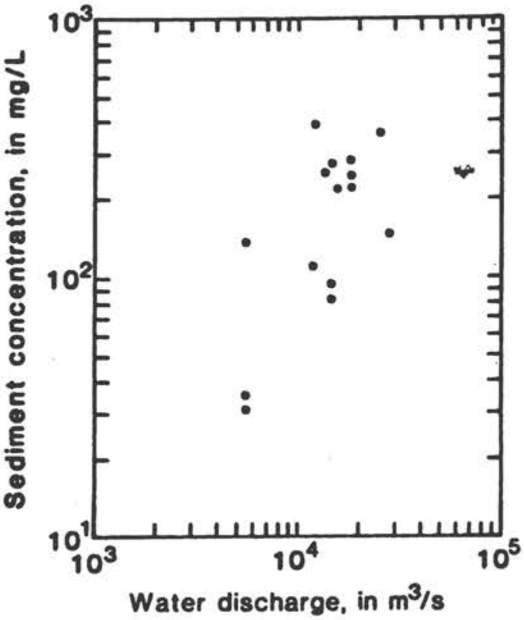

FIGURE 13 Relation between sediment concentration and water discharge, Mississippi River, Louisiana.

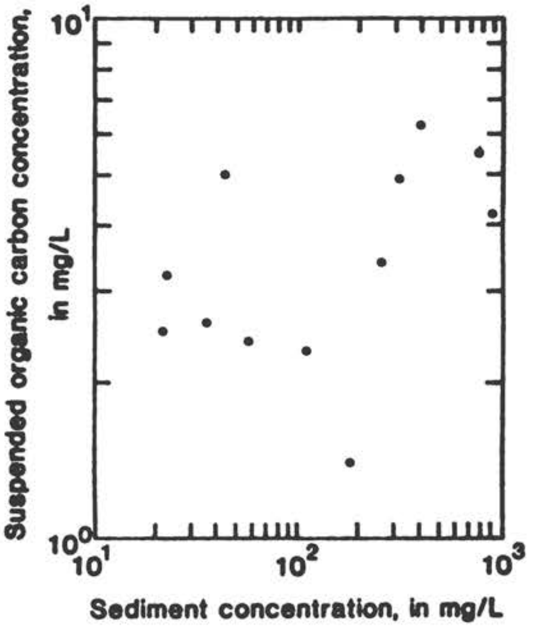

FIGURE 14 Relation between SOC and sediment concentrations, Brazos River near Richmond, Texas.

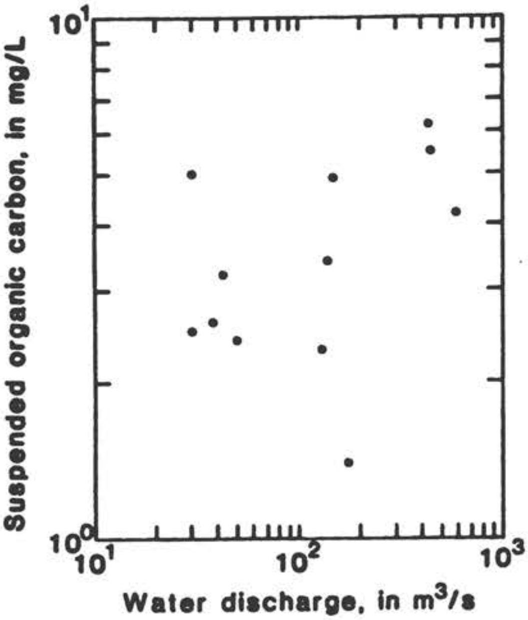

FIGURE 15 Relation between SOC concentrations and water discharge, Brazos River near Richmond, Texas.

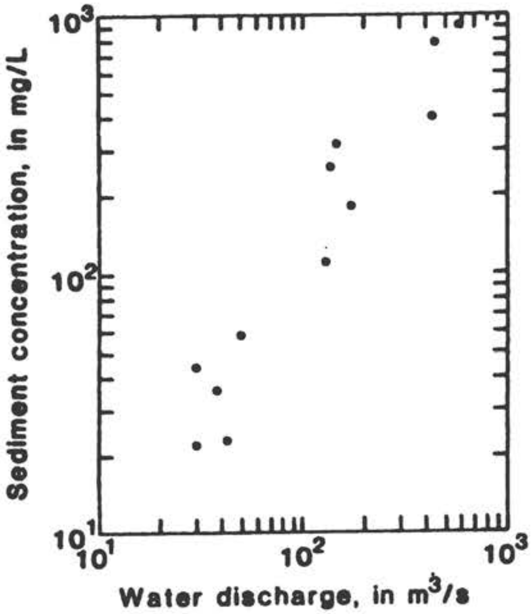

FIGURE 16 Relation between sediment concentration and water discharge, Brazos River near Richmond, Texas.

TABLE 7 Summary of Annual Carbon Load Data for Four Rivers[a]

River	Average Flow (m^3/s)	Annual Load $(10^3$ kg/yr$)$		Average Concentration (mg/l)		Ratio DOC/SOC
		DOC	SOC	DOC	SOC	
Sopchoppy	6.13	6,410	272	32	1.4	23
Neuse	57.7	14,060	4,750	7.5	2.5	3
Brazos	179	21,800	25,100	3.7	4.3	0.86
Mississippi	12,600	1,560,000	1,810,000	3.8	4.4	0.86

[a] Abstracted from Malcolm and Durum (1976, p. F16).

state that "almost universally, the ratio of DOC to POC approximates 10:1 in both lacustrine and stream systems." Kempe (1979) gives figures extracted from Garrels <u>et al</u>. (1975) for average concentrations of rivers of DOC = 3.28, POC = 1.76, for a ratio of 1.86:1. Garrels and Mackenzie (1971) show the concentration of DOC = 9.6, and the figures cited by Richey and others (1980) for the total organic carbon flux of 10^{14} to 10^{15} grams per year yield concentrations from about 2.7 to 27 mg/l. It seems fairly clear that firm figures either for the ratio DOC:POC or for the average concentration of organic carbon in the rivers of the world remain to be established. Global extrapolation based on the limited data now available seems at best a little risky.

In concluding this section, it appears that substantial additional data should be collected on organic carbon in the rivers of the world, and the most effective sampling procedures would be such that the frequency of sampling will define any seasonal trends and correlations with flow or with suspended sediment concentrations for both DOC and POC.

STANDARD ERRORS OF ESTIMATES

Consider a time series of independent values, x_i, with mean, μ and variance, δ^2 A dimensionless measure of dispersion is the coefficient of variation, $C_v = \delta/\mu$ If an estimate of μ is determined from a sample of size n, the unbiased estimate of the mean is $\bar{x}$,

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{6}$$

and the standard error of the mean, SE, is

$$SE = \frac{\delta}{n^{1/2}} \tag{7}$$

In practice, of course, the variance is not known; it has to be estimated from the sample:

$$\delta^2 \approx \frac{1}{n-1} \sum_{i=1}^{n} (x - \bar{x})^2 \tag{8}$$

Assuming the annual flows of the rivers in the world are uncorrelated, the standard error for the total mean annual flow to the oceans is

$$\text{S.E.} = \sqrt{\frac{\delta_1^2}{n_1} + \frac{\delta_2^2}{n_2} + \cdots} \tag{9}$$

Thus, the accuracy of our estimates of global flux of water, sediment, dissolved constituents, and so on, depends on the variabilities of the time series and the lengths of their records.

Flow records generally are longer than transport records, and they exhibit less variability. Table 8 summarizes our investigation of 24 U.S. rivers with daily sediment records of 15 years or longer. Values of C_v average about 0.45 for the flows and 0.70 for the sediment discharges. The standard error as a percentage of the mean value is $100C_v/(n)^{1/2}$, about 7% for the flow and 15 % for the sediment, thus the relative error in sediment records is about twice that in the flow records. Notice also that the sediment records are more highly skewed than the flow records.

Many of the rivers included in Table 8 were small rivers in arid and semi-arid regions of the United States, so the values of C_v are much higher than the values for large rivers. Kalinin (1968) has compiled data for 137 rivers of the world, and Table 9 shows values for 11 large rivers. The C_v values average about 0.15; the large rivers are much less variable than

TABLE 8. Average Coefficients of Variation and Skewness for Annual Flow and Sediment Records of 24 U.S. Rivers

	n	C_v	C_s
Annual flows			
Range	23 to 113	0.245 to 0.782	-0.785 to 1.251
Average	47	0.451	0.536
Annual sediment discharges			
Range	15 to 39	0.374 to 1.070	0.006 to 2.063
Average	22	0.695	1.222

TABLE 9. Statistical Properties of Flows for 11 Large Rivers[a]

River	Mean flow m^3/s	n	C_v	$C_{v/n}$	S.E. m^3/s
Yangtze	23,700	90	0.14	0.0148	350
Ob	12,460	20	0.16	0.0358	446
Yenesi	18,100	20	0.054	0.0121	219
Lena	15,900	20	0.12	0.0269	427
Pearl	7,580	56	0.21	0.0281	213
Amur	7,300	40	0.09	0.0142	104
Volga	7,480	75	0.18	0.0207	155
Danube	5,300	118	0.18	0.0166	88
Columbia	5,420	73	0.20	0.0234	127
St. Lawrence	6,740	98	0.08	0.0080	54
Mississippi	4,900	96	0.29	0.0290	142

[a] From Kalinin, 1968.

small rivers. The dimensionless standard errors of the means for these 11 rivers range from 0.8% to 3.6%. The sum of the flows is about 115,000 m^3/s and the standard error of the sum from equation 9 is 824 m^3/s, or slightly less than one %. As more values are included in the sum the absolute value of the standard error increases, but the percentage of error relative to the sum of flows decreases.

The above values are based on the assumption that the series are independent. In reality, hydrologic time series possess autocorrelation and are cross-correlated, so the standard errors of estimates will always be greater than for independent series. Methods for estimating standard errors of the mean for autocorrelated and cross-correlated time series were developed by Matalas and Langbein (1962) and applications of their theory to flow and sediment records were described by Nordin and Sabol (1973). The details are rather complicated and we will not go into them here except to note that estimates for mean values of sediment loads can almost always be improved by using the relation between water and sediment discharge, Equation 4, to extend the sediment record through the period of flow provided that 10 or more years of concurrent flow and sediment records are available, the correlation coefficient between water and sediment series is 0.5 or greater, and the first order serial correlation for the sediment series is less than 0.6. These conditions usually are met. Because of the high autocorrelation in annual sediment series, the standard errors of estimates are about three times as great as for a random independent series with the same variance.

Standard errors for time series of dissolved constituents have not been estimated, so far as we know, but it might be of interest to do this for a few representative rivers to get some idea of relative errors. No long time series for organic carbon exists, so again, it would be prudent to design a global sampling program to collect such data for at least a few representative rivers. Perhaps such a program could be coordinated with the current efforts of UNESCO to monitor pollution to the ocean from 230 large rivers of the world.

ESTUARIES AND THE COASTAL ZONE

Most gauging stations on rivers discharging to the oceans are located well upstream of major tidal influence, where the flow and transport of solid or dissolved material always are seaward. Records from these stations constitute the basis for many estimates of the total streamflow and flux of transported materials to the oceans. Clearly, the amount of material passing these stations represents a seaward flux, but it does not follow that all of the solid or dissolved materials reaches the deep oceans. Chemical reactions, biological activities, and depositional processes in estuaries and in the near-coast environments probably control the chemical composition and the amount of dissolved and solid material that ultimately reaches the deep oceans.

Estuarine processes are especially important in consideration of organic carbon, because many organic carbon compounds are highly unstable, being subject to mineralization to inorganic carbon, anerobic reduction to gaseous hydrocarbons, assimilation into biomass, and precipitation, adsorbtion, and flocculation interactions.

These complex estuarine and coastal processes and their effects on the flux of organic carbon to the oceans are beyond the scope of this discussion; they are treated elsewhere in this volume and we will not consider them further. However, we emphasize that the quantities of dissolved and solid materials moving past river gauging stations are delivered to estuaries and coastal zones, and these are not necessarily the same as the quantities of materials that eventually find their way to the deep oceans.

CONCLUSIONS

In the previous sections, we considered representative sampling, time series, and the effects of extreme events. In summary, our conclusions are as follows:

1. Generally, rivers cannot be considered well mixed, so point samples or width-depth integrated samples should be collected.

2. For most large rivers, relations between concentrations and flows and seasonal trends in concentration can be defined by sampling as a times series -- for example, monthly or bimonthly samples. For small and "flashy" streams, much of the transport occurs during the few days of high flows, so sampling should be designed to cover the flood events, rather than as a fixed-interval time series.

3. Many small rivers transport large quantities of sediment to the oceans; and they may do the same for organic carbons. Global extrapolation of the flux to the ocean of river-transported materials should include representative sampling of small as well as large rivers.

4. Standard errors of estimates of mean values and the sums of mean values are determined from the statistics of the time series. The shorter the record and the greater the variance of the time

series, the larger the standard error. In order to define the standard errors in flux to the ocean, we need some long-term series of transported quantities from representative rivers of the world.

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RIVER TRANSPORT OF ORGANIC CARBON TO THE OCEAN

M. Meybeck

Rivers are a major form of material transport from land to ocean (Garrels and Mackenzie, 1971; Turekian, 1971). A satisfactory body of knowledge about river inputs of dissolved major ions (Livingstone, 1963; Meybeck, 1979) and of particulate material (Alekin, 1978; Gordeev and Lisitzin, 1978; Martin and Meybeck, 1979) now exists. Despite several specialized conferences on the global carbon cycle (Reiners, 1973; Duce and Duursma, 1977; Bolin et al., 1979) and on river inputs (Duursma, in press), estimates of organic carbon carried by rivers are still based on very few studies and range between 100 10^{12}g.year^{-1} (Duursma, in press) to at least 1,000 10^{12}g.year^{-1} (Richey et al., 1980). The purpose of this paper is to review the existing data on dissolved, particulate, and total carbon (DOC, POC, and TOC) in rivers, to study their variation with time and space, and to extrapolate these data to the global input of organic carbon from rivers to oceans.

Organic carbon has been generally analyzed in four types of studies:

1. Regular monitoring of water quality in rivers in which organic carbon is considered a good indicator of water pollution. These surveys are rare, being limited chiefly to a few national (Canada, Switzerland) or international (Rhine Commission, Leman Commission) programs. A related survey has been running in USSR for two decades; the permanganate value (PV) is regularly measured. TOC is now considered a key parameter

in international surveys coordinated by United Nations (UNEP, UNESCO, WHO, WMO) such as the Regional Seas Programme of the World Register of Rivers (WORRI). However, a few countries have begun to monitor this parameter.

2. Specific surveys to study the origin, distribution, and fate of organic carbon in rivers. More data are found in this category than in any of the others, but they mainly concern very small watersheds (Fisher and Likens, 1973; Beck *et al.*, 1974; Lewis and Tyburczy, 1974; Brinson, 1976; Lewis and Canfield, 1977; Lock *et al.*, 1977; Naiman and Sibert, 1978; Sedell *et al.*, 1978; Mulholland and Kuenzler, 1979; Naiman and Sedell, 1979; Wallis, 1979). Major rivers are seldom studied except the Amazon (Williams, 1968; Richey *et al.*, 1980), the Danube (Tittizer, 1978), U.S. rivers (Malcolm and Durum, 1976), and some of the rivers in the Soviet Union (Tarasov *et al.*, 1977).

3. Carbon budgets of lakes (Wetzel and Otsuki, 1974; de March, 1975; Jordan and Likens, 1975; Odum and Prentki, 1978).

4. General studies of river geochemistry (Brunskill *et al.*, 1973; Wagemann *et al.*, 1977; Zobrist *et al.*, 1977; Capblanc and Decamps, 1978; Eisma *et al.*, 1978) or estuarine geochemistry (Cauwet *et al.*, 1980) where organic carbon is used to describe the geochemical environment. The study of the composition of river organic matter started recently (Beck *et al.*, 1974; Wetzel and Otsuki, 1974; Wallis, 1979), but this question will not be considered here. Selected data are presented in Table 1.

TABLE 1 Selected Data on Organic Carbon in Rivers (concentrations of DOC, POC, and TOC in mg.l^{-1}; specific transport rate (DOC_{exp}, POC_{exp}, and TOC_{exp}) in $t.km^{-2}.year^{-1}$; specific discharge q in $l.s^{-1}.km^{-2}$ [a]

	DOC	POC	TOC	DOC/TOC	DOC_{exp}	POC_{exp}	TOC_{exp}	q	References
TUNDRA									
Char	(1.4)	(0.08)	(1.5)	0.95	0.31	0.017	0.33	(7)	de March, 1975; Environment Canada, 1978
Thelon			5.4				0.72	4.2	Environment Canada, 1978
Kazan			5.0				1.3	8.0	Environment Canada, 1978
Quoich			3.7				0.13	1.1	Environment Canada, 1978
Back			4.0				0.63	5.0	Environment Canada, 1978
TAIGA									
Ob			10.9				1.7	4.9	Tarasov *et al*., 1977
Yenissei			9.2				2.0	6.8	Tarasov *et al*., 1977
Lena			10.5				2.2	6.7	Tarasov *et al*., 1977
Olenek			13.5				1.9	4.45	Tarasov *et al*., 1977
Yana			11.3				1.5	4.25	Tarasov *et al*., 1977
Indigirka			8.9				1.36	4.85	Tarasov *et al*., 1977
Kolyma			6.7				0.73	3.45	Tarasov *et al*., 1977
Qu'appelle			15.9						Environment Canada, 1978
Saskatchewan	8.9		10.9	0.82					Environment Canada, 1978
Red Deer	14.9		23.8	0.63					Environment Canada, 1978
Assiniboine			12						Environment Canada, 1978
Winnipeg			11.7						Environment Canada, 1978
Mannigotagan	13.3		16.1	0.82					Environment Canada, 1978
Pigeon	10.7		12.6	0.85					Environment Canada, 1978
Poplar	12.7		14.8	0.86					Environment Canada, 1978
Brokenhead	15.8		22	0.72					Environment Canada, 1978
Osier	25.1		24.1	1.0					Environment Canada, 1978
Fisher	18.5		20	0.93					Environment Canada, 1978
Nelson	8.2		9.0	0.9	(0.55)		(0.62)	2.2	Environment Canada, 1978
Hay			31.6				(2.0)	2.0	Environment Canada, 1978
Buffalo			20.9				(2.1)	3.2	Environment Canada, 1978
Liard			22				(6.2)	9.0	Environment Canada, 1978
Willow Lake			16.7				(1.55)	2.9	Environment Canada, 1978
Redstone			12.2				(3.45)	9.0	Environment Canada, 1978

	DOC	POC	TOC	DOC/TOC	DOC$_{exp}$	POC$_{exp}$	TOC$_{exp}$	q	References
Great Bear			3.7				(0.45)	3.84	Environment Canada, 1978
MacKenzie			11.5				(1.95)	5.3	Environment Canada, 1978
Arctic Red			12.9				(4.1)	10.1	Environment Canada, 1978
Yukon			12.5				(2.95)	7.2	(b)
TEMPERATE									
Mississippi	3.4	3.8	7.2	0.47	(0.58)	(0.65)	(1.23)	5.45	Malcolm and Durum, 1976
Missouri	4.6	20	24.6	0.19	(0.2)	(0.93)	(1.14)	1.5	Malcolm and Durum, 1976
Neuse	7.1	2.8	9.9	0.72	(2.62)	(1.03)	(3.65)	11.7	Malcolm and Durum, 1976
Ohio	3.1	1.8	4.9	0.63	(1.36)	(0.79)	(2.15)	13.9	Malcolm and Durum, 1976
Alpine Rhone	0.9		2.1	0.43	(1.0)		(2.3)	34.6	Leman Commission, 1978
N. Dvina			16.8				(5.0)	9.5	Tarasov *et al.*, 1977
Mezen			17.5				(6.4)	11.6	Tarasov *et al.*, 1977
Pechora			13.5				(5.75)	13.5	Tarasov *et al.*, 1977
Onega			22.6				(6.15)	8.6	Tarasov *et al.*, 1977
Kem			18.0				(4.8)	8.5	Tarasov *et al.*, 1977
Swedish rivers							2.3	15	Ahl and Oden, 1972
Finnish rivers							4		Wartiovaara, 1978
Apalachicola			4.6				(2.2)	15	(b)
Columbia			2.9				(0.9)	8.95	(b)
Delaware			9.0				(5.3)	18.6	(b)
Hudson			4.6				(2.55)	17.6	(b)
Alabama			4.5				(2.3)	16	(b)
Sacramento			2.6				(0.8)	9.6	(b)
San Joaquin			5.2				(0.6)	3.6	(b)
Savannah			4.2				(1.75)	13.2	(b)
Susquehanna			4.2				(2.0)	15.1	(b)
Fraser			4.4				(2.25)	16.1	(c)
Saint Lawrence			2.7				(0.8)	9.55	(c)
South Carolina rivers	8.5 5.3 5.8								Lewis and Tyburczy, 1974
New Zealand rivers	0.68 to 4.57								Lock *et al.*, 1977
Ontario rivers	4.9 to 24.6								Lock *et al.*, 1977

	DOC	POC	TOC	DOC/TOC	DOC_{exp}	POC_{exp}	TOC_{exp}	q	References
TEMPERATE (cont.)									
Nanaimo	8.7	3.14	11.8	0.74	14.2	5.3	19.5	53	Naiman and Sibert, 1978
Cascade Mountains	(1.75)	0.48	(2.25)	(0.78)					Naiman and Sedell, 1979
	(1.6)	0.29	(1.9)	(0.85)					Naiman and Sedell, 1979
	(1.2)	0.29	(1.5)	(0.80)					Naiman and Sedell, 1979
	(0.6)	0.37	(1.0)	(0.63)					Naiman and Sedell, 1979
Rocky Mountain rivers		1.95							Pennack, 1977
Marmot Creek	2.2						1.2	16.8	Wallis, 1979
Lot	(4.5)	(2.7)	(7.2)	(0.62)	(2.5)			17.3	Capblanc and Decamps, 1978
Garonne	2.2						0.8	11.3	Cauwet *et al.*, 1980
Dordogne	2.7						1.8	20.9	Cauwet *et al.*, 1980
Glen Bwin	13.5								Sholkovitz, 1976
Water of Luce	6.7								Sholkovitz, 1976
Stinchar	7.6								Sholkovitz, 1976
Finchley				(0.83)	6.0			142	Odum and Prentki, 1978[d]
Marion				(0.91)	7.35			63	Odum and Prentki, 1978[d]
Mirror				(0.60)	1.5			21	Odum and Prentki, 1978[d]
Wingra				(0.40)	1.9			116	Odum and Prentki, 1978[d]
Lawrence				(0.84)	3.1			38	Odum and Prentki, 1978[d]
Cree	4.1								Sholkovitz, 1976
Aare	3.5	1.2	4.7	(0.75)	(2.9)	(1.0)	(3.9)	26	Zobrist *et al.*, 1977
Reuss	2.1	1.0	3.0	(0.67)	(2.6)	(1.3)	(3.9)	41	Zobrist *et al.*, 1977
Rhein	2.5	1.0	3.4	(0.72)	(2.3)	(0.9)	(3.2)	29	Zobrist *et al.*, 1977
Rhone	1.4	0.9	2.3	(0.61)	(1.5)	(1.0)	(2.5)	34	Zobrist *et al.*, 1977
Alpine Rivers (France)			0.65				1.05	50	Serra-Bertral, 1976
TEMPERATE SWAMPS									
Sopchoppy	27	1.6	28.6	0.94	(12.8)	(0.75)	(13.5)	(15)	Malcolm and Durum, 1976
Satilla	23				(7.25)			(10)	Beck *et al.*, 1974
North Carolina	(14)	(1.0)	(15.0)	(0.93)			(4)		Mulholland and Kuenzler, 1979
TEMPERATE POLLUTED (?)									
Rhine			13.0				(6.5)	15.8	Rhine Commission, 1975
Ems			15.0				(5.6)	11.8	Kempe in Bolin *et al.*, 1979
Danube	(16)	(6)	(22)	0.73					Tittizer, 1978

	DOC	POC	TOC	DOC/TOC	DOC_{exp}	POC_{exp}	TOC_{exp}	q	References
ARID REGIONS									
Murray			13				(0.28)	0.3	(e)
Brazos	3.3	3.6	6.9	0.48	(0.19)	(0.21)	(0.4)	1.85	Malcolm and Durum, 1976
TROPICAL WET									
Amazon	3.5	1.12	4.42	0.76					Williams, 1968 (dry season)
	4.2	8.2	12.4	0.34					Richey *et al.*, 1980 (rising stage)
	6.5	1.5	8.0	0.81					Richey et al., 1980 (high water)
	(5)	(5)	(10)	(0.5)	(4.4)	(4.4)	(8.7)	27.8 10.4	average J.E. Richey, this volumn
Negro	6.3	2.06	8.36	0.75	(11.7)	(3.8)	(15.5)	59	Williams, 1968
Branco	3.4	1.88	5.28	0.64	(6.4)	(3.55)	(10)	(60)	Williams, 1968
Polochic	(5)		(12)				4.8	61	Brinson, 1976
Sauce	(8)		(10)				3.2	27.2	Brinson, 1976
San Marcos	(3)		(8)				2.2	26.9	Brinson, 1976
Oscuro	(15)		(20)						Brinson, 1976
Caroni	5								Lewis and Canfield, 1977
Carrao	11.4								Lewis and Canfield, 1977
Zaire		(10)							Eisma *et al.*, 1978

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[a] Values in parentheses are estimated from authors' data.

[b] From U.S. Geological Survey, Denver; quoted in UNESCO, in press.

[c] From Inland Waters Directorate, Ottawa; quoted in UNESCO, in press.

[d] Also Wetzel and Otsuki (1974) and Jordan and Likens (1975).

[e] From Australian Water Research Council; quoted in UNESCO, in press.

The most quoted studies in occidental literature are those on the Hubbard Brook Experimental Forest in New Hampshire (Fisher and Likens, 1973; Jordan and Likens, 1979) and on Lawrence Lake in Michigan (Wetzel, 1979) where the carbon cycle has been intensively studied. However, it is difficult to extrapolate these results obtained on a very small area to greater watersheds where regular seasonal monitoring is generally lacking. Another major gap in the present organic carbon studies concerns the tropical environment. Except for some cruises on the Amazon (William, 1968; Richey et al., 1980) and small catchments in Guatemala (Brinson, 1976) and Venezuela (Lewis and Canfield, 1977), this environment has not been much studied.

The heterogeneity of the data must be noticed. Most authors now use carbon analyzers, but in several cases TOC has been obtained from PV as in the Soviet Union, Sweden (Ahl and Oden, 1972) and Finland (Wartiovaara, 1978). Authors differ considerably in their findings on conversion from PV to TOC. In other cases the organic carbon is estimated by measurements of organic matter obtained by ignition (Naiman and Sibert, 1978); the proportion is generally assumed to be 50% (Jordan and Likens, 1975; Richey et al., 1980) but may be less (40% for Brinson, 1976). The proportion of 50% has been taken here unless a different value has been specified.

As for other chemicals (Fe, Al), the distinction between dissolved and particulate carbon is not clear-cut. Most authors have operationally used glass-fiber filters of assumed porosity around 0.5- μm to separate these two forms; some used 1 μm (in the Soviet Union) or 0.2 μm (Tittizer, 1978). Actually an important part of colloidal carbon remains below the 0.45- μm limit — as much as 52.7% (Lock _et_ _al_., 1977). It would be better to speak of "nonparticulate organic carbon" or of "filtered organic carbon." The latter can be separated by ultracentrifugation between colloidal carbon corresponding to a sedimentation coefficient > 100 Svedberg units, and dissolved organic carbon below this limit (Lock _et_ _al_., 1977). Above the o.45- μm limit, other distinctions have been made (Fisher and Likens, 1973; Sedell _et_ _al_., 1978): very fine organic carbon between 53 μm and 1 mm; and, coarse organic carbon greater than 1 mm. Since these distinctions are seldom considered by authors, the usual terms — dissolved organic carbon (DOC < 0.45 μm) and particulate organic carbon (POC > 0.45 μm) — will be used here.

DISSOLVED ORGANIC CARBON VARIATIONS DURING SEASONAL CYCLE

The DOC variation in a river is usually less than one order of magnitude as is commonly observed for the other major dissolved components. Seasonal variations have been described. Wetzel and Otsuki (1974) stated that "the DOC was correlated with the period of active terrestrial growing season: inputs were reducing during the active growing period and increased markedly in the terminal stages of September which coincided with increased precipitation." Here lies the ambiguity of DOC variations in running waters: during the growing season the retention of organic carbon by terrestrial systems should lower DOC in river waters, and during high-water stages the DOC contained in soils and swamps, where higher values are observed (Wallis, 1979; Beck *et al*., 1974; Mulholland and Kuenzler, 1979), is flushed out to the rivers. In most studies the flushing effect has been described. In the Hubbard Brook (Fisher and Likens, 1973), DOC was increasing slightly with specific discharge q according to a relation log DOC = 0.2 log q - b. In Guatemala, Brinson (1976) found an "initial flushing effect of organic matter promoted by early wet season rains and rising stage height." A similar increase of DOC (from 3 to 14 mg/l^{-1}) has been observed in the Nanaimo River (British Columbia) because of autumn freshets (Naiman and Sibert, 1978). In the Amazon River the average DOC was 4.2 mg/l^{-1} at the rising stage and 6.5 mg/l^{-1} at the high-water stage in 1977 (Richey *et al*., 1980), whereas it was only 3.5 mg/l^{-1} during the low-water stage in 1967 (Williams, 1968).

This effect of discharge has been looked for in data that Malcolm and Durum (1976) collected on U.S. rivers (Figure 1). To permit comparison between the Mississippi and Sopchoppy rivers, the specific discharge $q(l.s^{-1}.km^{-2})$ has been used. In these rivers DOC generally presents a fivefold variation. For the Sopchoppy and Neuse rivers, a slight but easily perceptible increase of DOC with q is noted with a rate similar to the one observed in Hubbard Brook. For the Ohio and Mississippi this trend cannot be ascertained, and the Missouri data are dispersed irregularly. This increase of concentration with discharge is generally observed for other elements originating in the

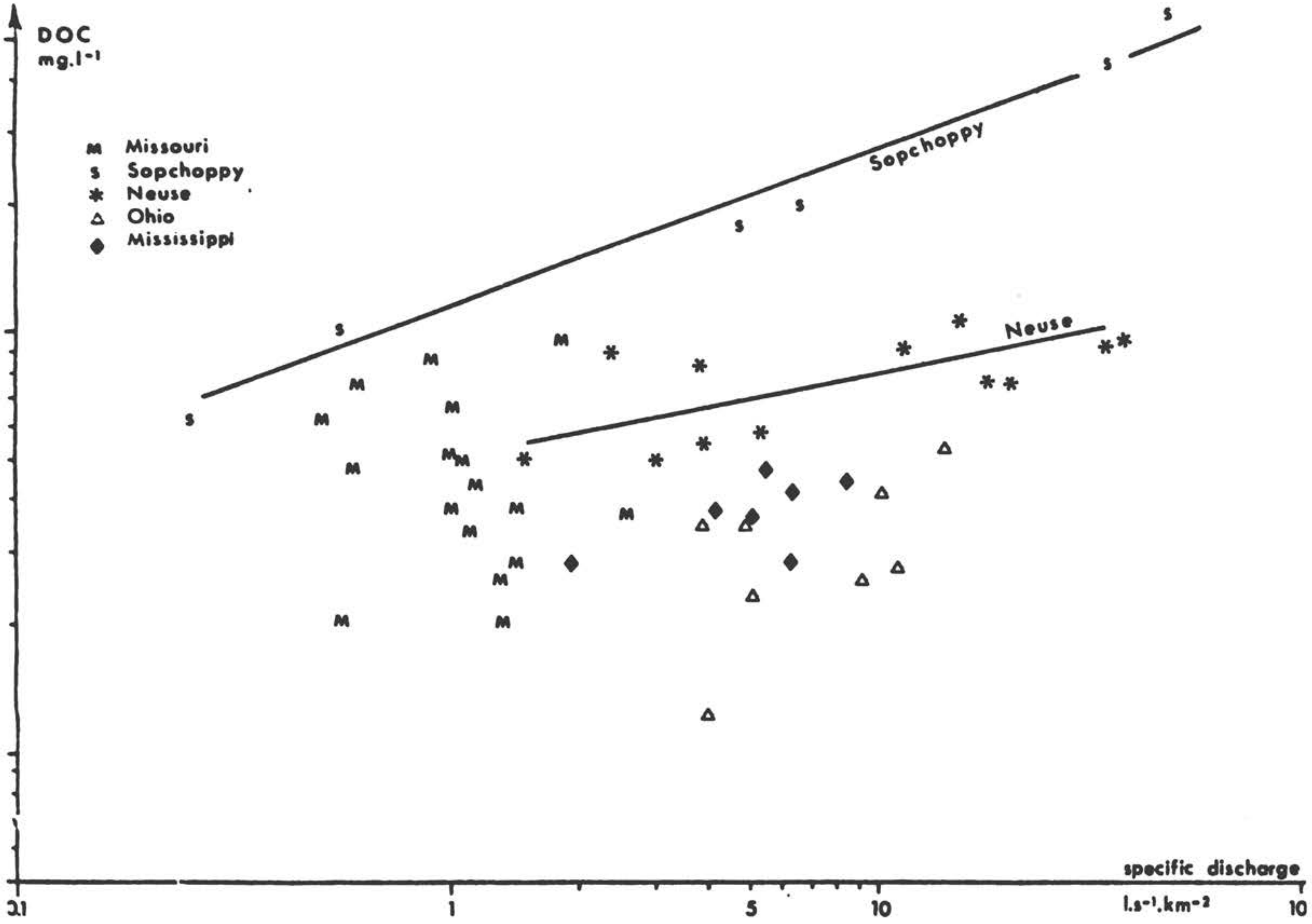

FIGURE 1 DOC variation with specific water discharge q in five U.S. rivers. Data from Malcolm and Durum, 1976.

surface layer (litter, soil), such as N and P compounds, which are flushed out during floods, unlike the major ions, which are diluted by increased river discharge.

GEOGRAPHIC VARIATIONS OF DISSOLVED ORGANIC CARBON

When considering all the data collected for individual rivers (most of them annual averages but sometimes individual values), one finds that the 70-river sample can be divided into 10 tropical rivers, 1 arid river, 43 temperate rivers, and 16 subarctic rivers. Although this sample is obviously biased toward the temperate zone, which represents only 27.5% of the water flowing from land to ocean (Meybeck, 1979), some statements can be made (Table 2).

The median DOC value in rivers is around 5 mg/l^{-1}, and 80% of rivers have a DOC content between 1 and 20 mg/l^{-1}.

The subarctic rivers (located mainly in the Taiga) present a higher DOC value (between 8 and 25 mg/l^{-1}, median 10 mg/l^{-1}) than tropical rivers (2 to 15, median 6 mg/l^{-1}) and the temperate rivers (1 to 10, median 3 mg/l^{-1}, if some obviously polluted rivers - Rhine, Ems, Danube - are omitted from consideration).

Maximum DOC (around 25 mg/l^{-1}) is observed in rivers (Sopchoppy, Satilla) in which the influence of swamps and poorly drained soils is important, such as in southeastern United States (Beck et al., 1974; Malcolm and Durum, 1976; Mulholland and Kuenzler, 1979).

Minimum DOC (between 0.7 and 1 mg/l^{-1}) is found in Alpine rivers. Examples are rivers in New Zealand (Lock et al., 1977) and the Rhone upstream from Lake Leman.

TABLE 2 Frequency of Organic Carbon Contents in Rivers[a]

A. Dissolved and Total Organic Carbon

Ranges $(mg.l^{-1})$	0.4-1	1-2	2-5	5-10	10-20	20-40	Total Number of Rivers
Dissolved Organic Carbon							
Taiga	-	-	1	6	7	2	16
Temperate	6	9	12	9	1	1	38
Tropical wet	-	-	3	4	2	1	10
Semiarid	-	-	1	-	-	-	1
Total Organic Carbon							
Tundra	-	-	5	3	-	-	8
Taiga	-	-	-	5	35	17	57
Temperate	-	6	18	9	3	3	39
Tropical wet	-	-	4	5	2	1	12
Semiarid	-	-	-	1	1	-	2

B. Ratio Dissolved/Total Organic Carbon

Ranges	< 0.4	0.4-0.6	0.6-0.8	0.8-0.9	>0.9	
DOC/TOC	1	3	20	7	3	34

C. Specific Transport of Total Organic Carbon (TOC_{exp})

Ranges $(t.km^2.year^{-1})$	< 0.4	0.4-1	1-4	4-10	10-20	
Tundra	1	5	-	-	-	6
Taiga	-	3	18	3	-	24
Temperate	1	7	17	7	2	34
Tropical wet	-	-	3	3	3	9
Semiarid	2	-	-	-	-	2

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[a] From data given in Table 1

RIVER TRANSPORT OF DISSOLVED ORGANIC CARBON

The specific transport rate DOC_{exp} expressed in $t.km^{-2}.year^{-1}$ (equal 10 $kg.ha^{-1}.year^{-1}$) is obtained as $DOC_{exp}=q.DOC$ where q is the specific water discharge. Computation of DOC_{exp} is not always possible since q is not always given. On 26 values, DOC_{exp} ranges between 0.2 and 14 $t.km^{-2}.year^{-1}$. Since DOC seems to be less variable for a given temperature zone than q, its transport rate within a given climatic zone will mostly be determined by the specific discharge. The highest DOC_{exp} values are effectively observed in British Columbia (14.2$t.km^{-2}.year^{-1}$ for the Nanaimo), in Amazonia (11.2 $t.km^{-2}.year^{-1}$ for the Negro River), and in Florida, where both q and DOC are high (12.8 $t.km^{-2}.year^{-1}$ for the Sopchoppy). The lowest transport rates (<0.4 $t.km^{-1}$) are found in the arid and semiarid environments (Missouri, Dnieper, Brazos) and in the tundra (Char River), where both q and DOC are low. See Naiman and Sibert, 1978 (Nanaimo); Williams, 1968 (Negro); Malcolm and Durum, 1976 (Sopchoppy); de March, 1975 (Char).

PARTICULATE ORGANIC CARBON IN RIVERS

The content of particulate organic carbon (POC) in rivers is generally expressed in $mg.l^{-1}$. POC content increases with water discharge as allochtonous particulate organic material is flushed out from the watershed to the river. This variation is clearly observed in the Hubbard Brook study (Fisher and Likens, 1973; Bilby and Likens, 1979) and is obvious in data published by Malcolm and Durum (1976) for U.S. rivers.

The particulate organic carbon can also be expressed as the amount of carbon per unit mass of particulate matter carried by the river, POC_s (expressed as % dry weight) defined as POC_s=POC/C_s where C_s is the suspended matter content. POC_s in rivers ranges between 0.5 and 40%. The minimum value is observed for highly turbid rivers ($C_s > 1,000$ mg/l^{-1}) such as the Redstone in the Canadian Rocky Mountains (Wagemann et al., 1977) or the Brazos and Missouri rivers (Malcolm and Durum, 1976). The maximum corresponds to lowland rivers with very low suspended material ($1 < C_s < 10$ mg/l^{-1}) such as the Sopchoppy river in Florida, in which almost all the particulate matter is organic (Malcolm and Durum, 1976). High values from 22 to 44% are also reported by Eisma et al. (1978) for the Zaire river: these values correspond to C_s from 44 to 25 mg/l^{-1}.

POC_s from individual measurements in U.S. rivers has been plotted against observed suspended matter C_s (Figure 2). For all rivers except the Sopchoppy there is a marked decrease of POC_s with increasing C_s, and the amount of carbon at a given C_s is similar from one river to another. If other data from the Soviet Union or Canada (Wagemann et al., 1977) are added, this trend is confirmed. The lower limit of POC_s for very turbid waters ($C_s > 5000$ mg/l^{-1}) found in California and China is not yet known, but probably it will not be very different from the average organic carbon content in sedimentary continental rocks, 0.5% according to Ronov (1976). If this value is accepted, the maximum POC load in rivers could reach 100 mg/l^{-1}. Since in 99% of river waters the suspended matter ranges between 5 and 5,000 mg/l^{-1}, the corresponding POC variation will be much less, between 1 and 30 mg/l^{-1}. This is about what has been observed from the data of Malcolm and Durum (1976), which show that 80% of measured POC values in various rivers are between 1 and 10 mg/l^{-1} with a median value of 2.5 mg/l^{-1}.

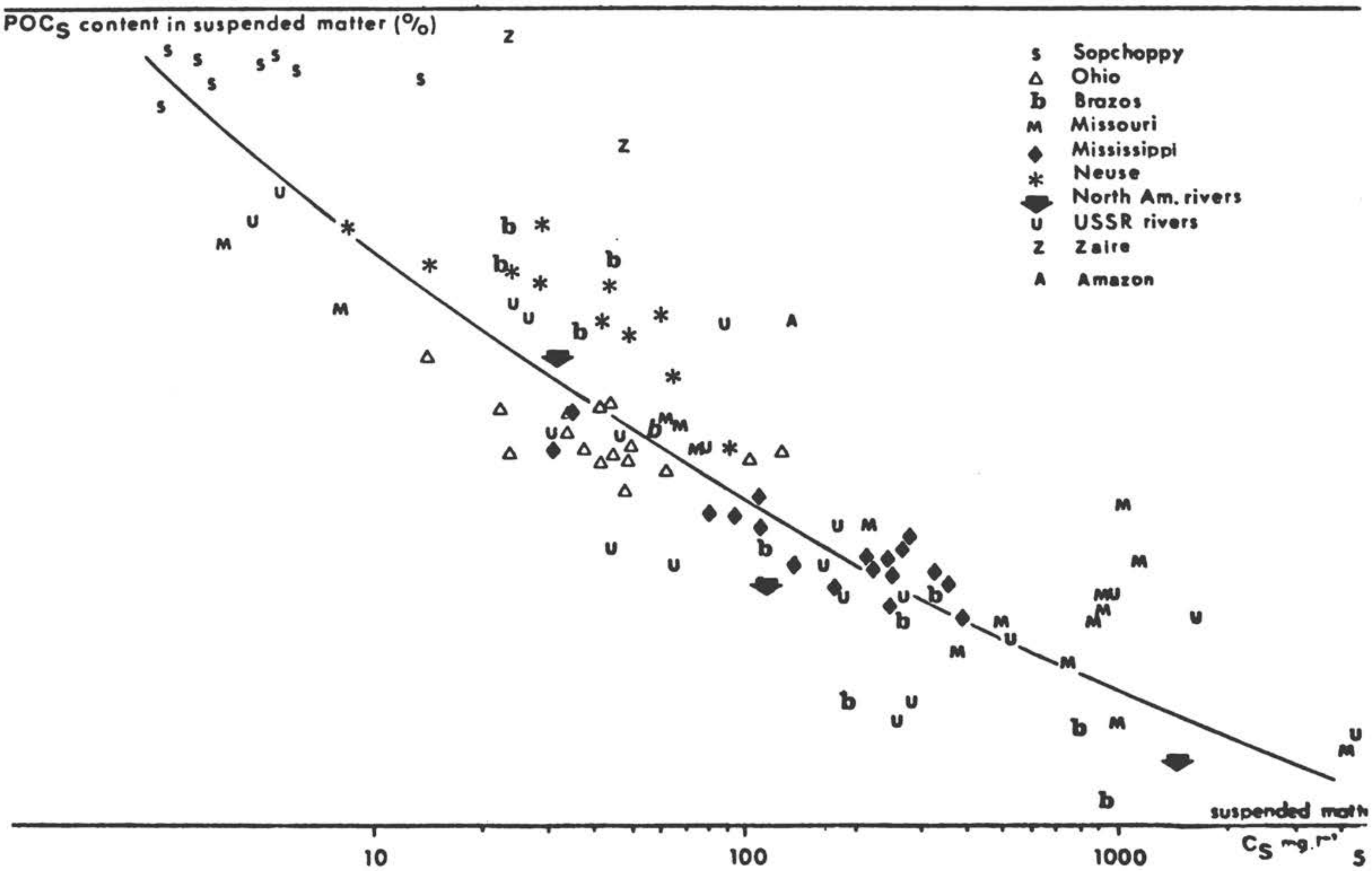

FIGURE 2 Variations for individual samples of organic carbon content in river particulate matter (POC$_s$ in %) with suspended matter C$_s$ (mg.l^{-1}). Data for Sopchoppy, Ohio, Brazos, Missouri, Mississippi, and Neuse from Malcolm and Durum (1976): for USSR rivers from Nesterova (1960) and V.E. Artemeev (V.V. Gordeev, personal communication): for North American rivers from Wagemann et al. (1977) and Pennak (1977): for Amazon from J.E. Richey (this volume): for Zaire from Eisma et al. (1978).

From the first results on the Zaire and Amazon (Figure 2), it seems that lowland tropical rivers may present higher POC_s values, for a given C_s, than other rivers. This effect has not been taken into account here in determining the relationship between POC_s and C_s on which the world budget is based.

Two processes may explain the variation of POC_s with the amount of suspended matter: (1) Land-derived organic material (wood debris, leaves) is diluted by land mineral material (rock debris, soil particles, clays) at higher erosion rates. This would mean that denudation of organic soils is less active than linear erosion (gully erosion, landslide and the like. (2) POC in rivers is mainly autochtonous (periphyton, phytoplankton) and diluted by land mineral material. Probably both sources of POC exist. In some rivers the POC variation is even more complicated: POC is not conservative and can be mineralized during its transport; this behavior has been proposed for the Amazon (Richey, et al., 1980).

RIVER TRANSPORT OF PARTICULATE ORGANIC CARBON

As continuous monitoring of POC in rivers has not yet been achieved, it is necessary to compute average loads from individual measurements. Since POC_s varies with suspended load (C_s) which is often measured, the best procedure would be: (1) To establish the relationship between POC_s and C_s classes of known distribution (e.g., the C_s class from 50 mg/l^{-1} to 150 mg/l^{-1} accounts for 23% of the global sediment discharge), and (3) to multiply each C_s interval by its relative importance in the sediment load and by its corresponding POC_s value. This method, which will be applied later to the world POC budget, has generally not been used because of lack of adequate data: therefore, average POC contents in rivers have been taken as needed from the literature.

According to present data, the specific transport of particulate organic carbon (POC_{exp}, in $t.km^{-2}.year^{-1}$) has a narrow range: between 0.2 $t.km^{-2}$. $year^{-1}$ and 5 $t.km^{-2}$. $year^{-1}$. But it must be kept in mind that higher values could be observed for highly erosive rivers (found in semiarid climates or in the highlands), particularly for those of Southeast Asia, in which levels of both suspended matter and organic matter are probably high. Lowest transports are observed for semiarid rivers (e.g., Brazos) or for low gradient rivers in which erosive power is low (Ohio, Mississippi), sometimes despite very high POC_s (Sopchoppy). Highest transports occur in Amazonia. (See Table 1.)

RELATIVE IMPORTANCE OF DOC AND POC

Most authors follow the statement by Wetzell (1975) that "there is approximately 10 times more organic dissolved matter than particulate organic matter." As stated in the introduction, this is the result of the extrapolation of numerous studies made in temperate lowland regions of North America, where the erosive power of rivers is rather low. Data published since 1975 do not support this assumption.

Again the list of individual measurements published by Malcolm and Durum (1976) for U.S. rivers will be valuable. The frequency of DOC/TOC ratios for these measurements is as follows:

Cumulated frequency	10%	25%	50%	75%	90%
DOC/TOC ratio	0.30	0.40	0.55	0.80	0.90

When these individual DOC/TOC ratios are plotted against the suspended sediment content, it is clear that DOC/TOC decreases with increasing C_s (Figure 3). This trend is obviously due to the relative increase of POC content (in mg/l^{-1}) with increasing C_s. The Brazoa River is a surprising exception.

The same trend is seen in the yearly averages of DOC, POC, and C_s given by Malcolm and Durum and by other sources (Williams, 1968; Environment Canada, 1978; Leman Commission, 1978; Richey _et al._, 1980; V. V. Gordeev, personal communication). See Figure 4.

It is noteworthy that for some major rivers the ratio DOC/TOC is less than 0.5; i.e., the particulate organic transport is dominant (Mississippi, DOC/TOC = 0.47; Missouri, DOC/TOC = 0.19). The swamp-draining rivers are the only ones that present a ratio in keeping with Wetzel's statement. When we consider 33 rivers of various environments, but mostly in the temperate and subarctic lowlands, we find that 50% of them present a DOC/TOC ratio between 0.6 and 0.8. This figure is probably valid for lowland rivers but not for highland rivers, in which DOC/TOC can be less than 0.5.

The question of correct yearly average of POC remains: Are the samples really representative of the sediment load? The most common suspended-matter content, therefore the most commonly sampled, is generally much less than the discharge-weighted average (Fisk Laboratory, 1977). An example can be given for the Mississippi: the average C_s obtained by Malcolm and Durum (1976) is 165 mg/l^{-1}, whereas the weighted average is around 500 mg/l^{-1}. The corresponding POC content should be around 6 mg/l^{-1} instead of 3.8 mg/l^{-1}, and the DOC/TOC ratio should be lowered (0.36 instead of 0.47).

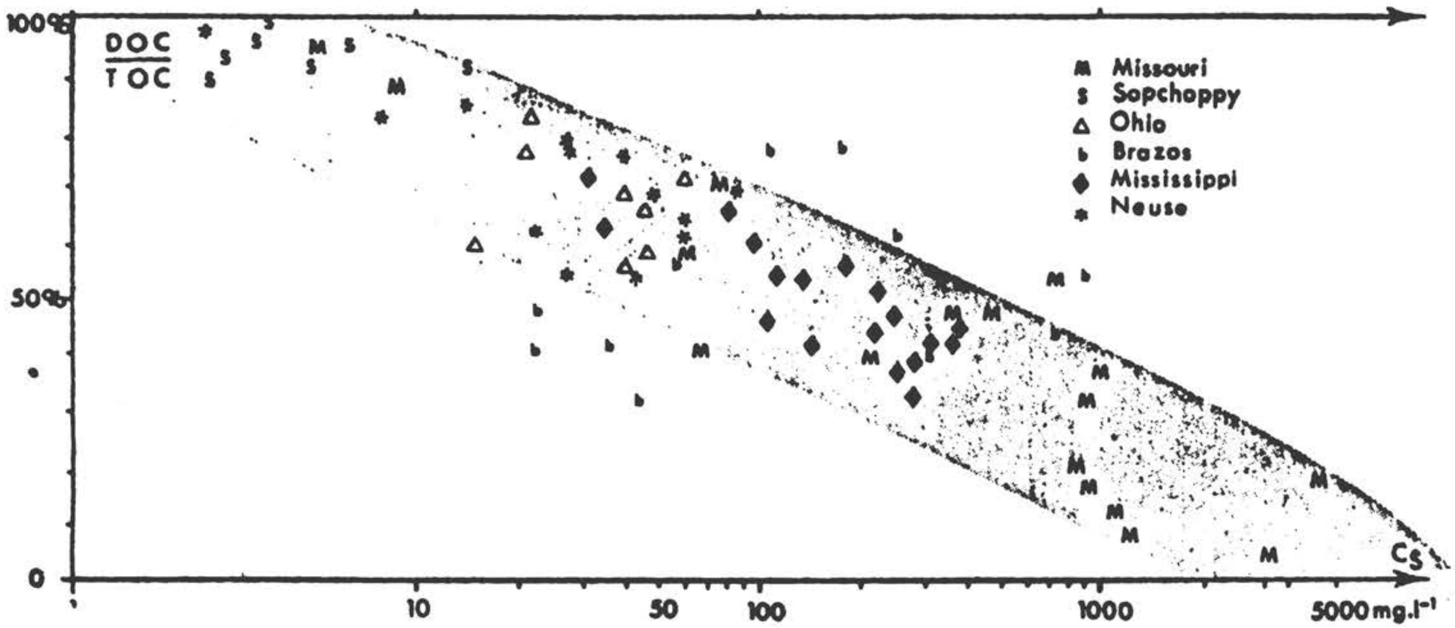

FIGURE 3 Variation of DOC/TOC ratio in individual water samples of U.S. rivers with suspended matter C_s. Shaded area: general range excluding the Brazos river. Data from Malcolm and Durum (1976).

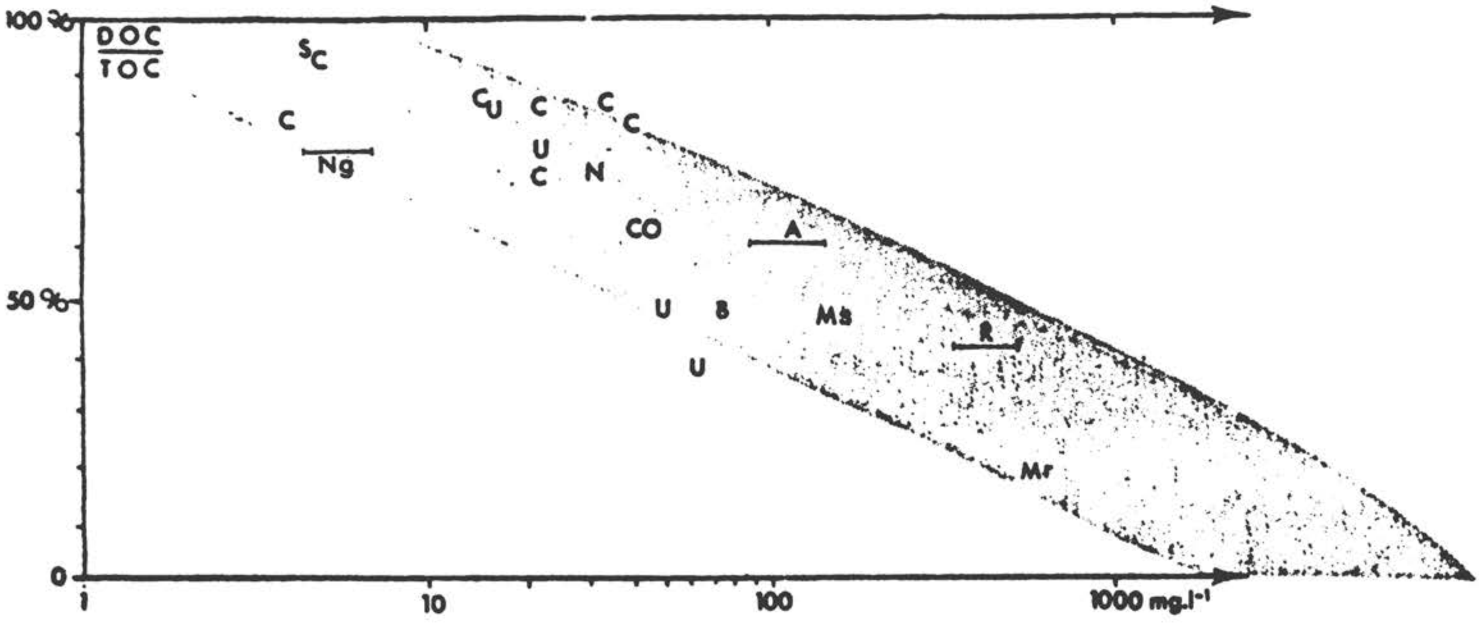

FIGURE 4 Variation of average DOC/TOC ratio in some world rivers with suspended matter C_s. S = Sopchoppy, O = Ohio, N = Neuse, Ms = Mississippi, Mr = Missouri, B = Brazos (data from Malcolm and Durum, 1976). Ng = Negro (data from Williams, 1968). A = Amazon (data from Williams, 1968; J.E. Richey, this volume; Richey <u>et</u> <u>al</u>., 1980). R = Rhone (data from Zobrist <u>et</u> <u>al</u>., 1977). U = USSR rivers (data from V.E. Artemeev [V.V. Gordeev, personal communication]). C = Manitoba rivers (data from Environment Canada, 1978). Shaded area: same range as for Figure 3.

TOTAL ORGANIC CARBON IN RIVERS

For a given river the total organic carbon (TOC) generally increases with water discharge. This is the result of a slight increase of DOC with discharge and a net increase of POC with river suspended matter, itself directly related to water discharge. This trend can be seen for instance in the Hubbard Brook study (Fisher and Likens, 1973; Bilby and Likens, 1979).

There are more data for TOC in rivers than for its components, DOC and POC. Many values can be found for medium-sized and major rivers in the temperate and subarctic climatic zones. (See Malcolm and Durum, 1976; Tarasov et al., 1977; Environment Canada, 1978; UNESCO, in press; and Table 1, this article.) If the Rhine, Danube, and Ems rivers are omitted from consideration, 90% of the remaining 118 rivers have average TOC contents between 2 and 30 mg/l^{-1} with a median around 10 mg/l^{-1} (Table 2). However, this total sample is biased toward the 57 taiga rivers surveyed in Canadian publications. Since DOC abundance is probably linked to climate, and POC abundance to climate and erosion, TOC variations cannot be simply related either to specific discharge q or to suspended matter C_s. When the sample is divided into climatic subsamples, some rough distinctions appear: most of the TOC values are between 2 and 10 mg/l^{-1} (median 5 mg/l^{-1}) for the temperate regions, between 10 and 30 mg/l^{-1} (median 15 mg/l^{-1}) for the taiga rivers, between 2 and 8 mg/l^{-1} (median 4 mg/l^{-1}) for the tundra rivers, and between 2 and 15 mg/l^{-1} (median 8 mg/l^{-1}) for the tropical rivers. These figures must be considered with caution because they are representative of lowlands or mid-altitude areas; about the only mountainous rivers in this sample are some Alpine rivers of low TOC values (Serra-Bertral, 1976; Zobrist *et al*., 1977).

RIVER TRANSPORT OF TOTAL ORGANIC CARBON

The specific transport rate TOC_{exp} = TOC.q (in $t.km^{-2}$ $year^{-1}$, or 10 $kg.ha^{-1}$.year, or $gC.m^{-2}.year^{-1}$) is roughly related to the specific discharge q (Figure 5) since the relative variation of q is much higher (two orders of magnitude). The whole available sample of TOC_{exp} in rivers is now 75 rivers: 90% of TOC_{exp} values are between 0.4 and 10 $t.km^{-2}.year^{-1}$. Higher values are found in Amazonia (Negro River), according to Williams (1968), and in British Columbia (Nanaimo River), according to Naiman and Sibert (1978). See Tables 1 and 2.

The export of TOC by rivers is linked to the climatic environment, and some figures can be proposed (Table 3). Published average values for Siberia (2.25 $t.km^{-2}$. $year^{-1}$), Sweden (2.3 $t.km^{-2}.year^{-1}$), and Finland (4 $t.km^{-2}.year^{-1}$) are consistent with these figures. (See Tarasov _et_ _al_., 1977 (Siberia); Ahl and Oden, 1972 (Sweden); Wartiovaara, 1978 (Finland); Environment Canada, 1978 (rivers in Northwest Territories). The minimum TOC_{exp} occurs in tundra rivers (based on Quoich, Back, Thelon, Kazan, and Hanbury rivers in Northwest Terriories), in which both TOC content (4 mg/l^{-1}) and q(4 $l.s^{-1}.km^{-2}$) are very low. Data from Canada and the Soviet Union for similar rivers (Mackenzie and Siberian rivers) are very close.

When comparing the river transport of organic carbon to the terrestrial net primary production (Table 3), it is striking that the amount of organic matter carried by rivers is always the same percentage, around 1% of the production (Figure 6). If the total amount of carbon carried by rivers (400 10^{12}gC per year to the exoreic part of the continent, i.e.,

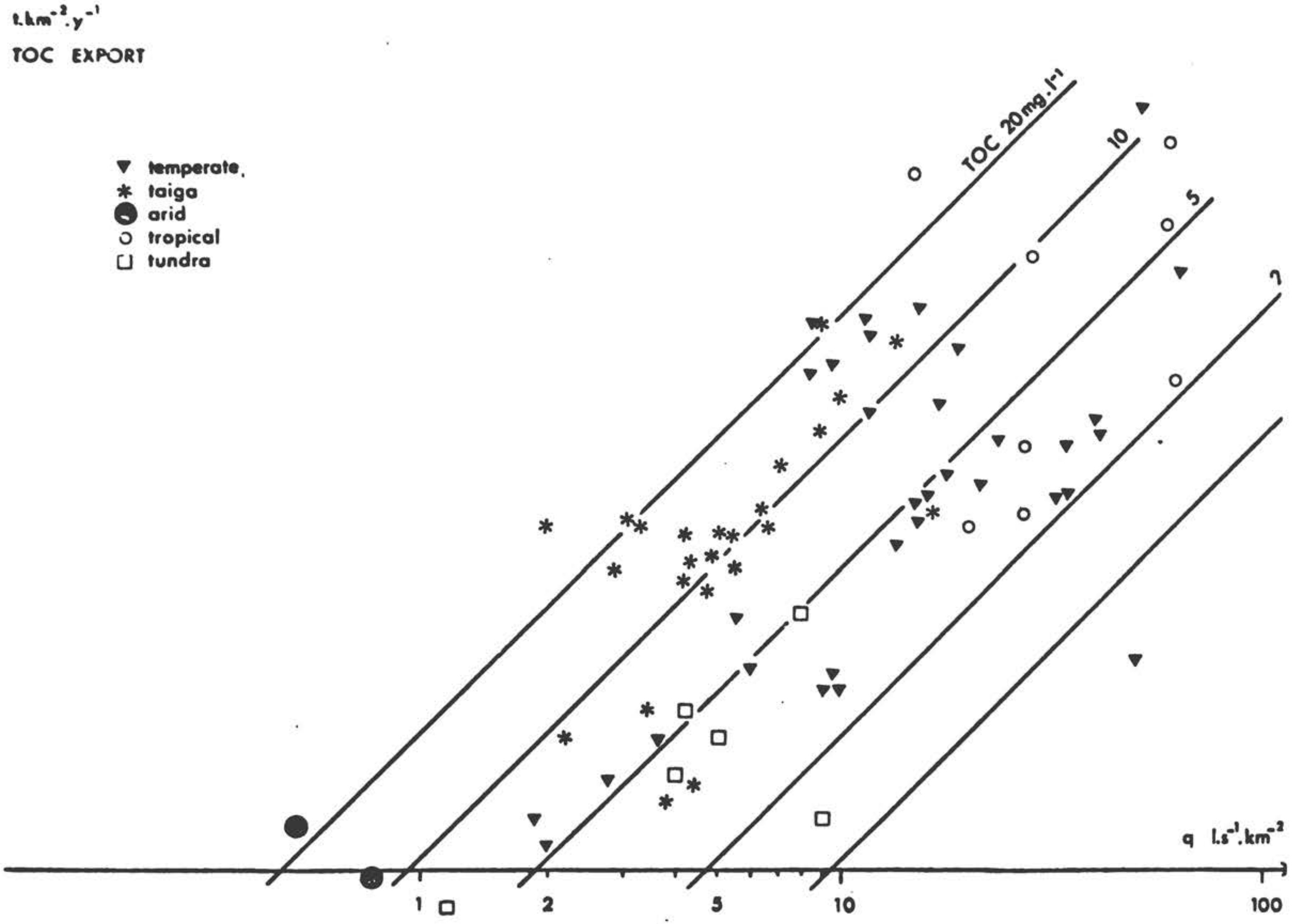

FIGURE 5 Variation of TOC specific transport rate (TOC_{exp}) in $t.km^{-2}.year^{-1}$ (or $gC.m^{-2}.year^{-1}$), with specific water discharge q in $l.s^{-1}.km^{-2}$ for various climatic environments.

TABLE 3 Range of TOC Specific Transport by Rivers in Various Climatic Zones

	TOC_{exp} (t.km^{-2}.year^{-1} or gC.m^{-2}.year^{-1})	Mean Net Primary Production (gC.m^{-2}.year^{-1}) (a)
Tropical wet regions	3 - 15	675 - 900
Temperate regions	1 - 7	225 - 585
Taiga	1 - 4	360
Tundra	0.3 - 1	65
Semiarid regions	<0.4	32
World average	4	480

(a) in the related vegetation zones, from Whittaker and Likens, 1973.

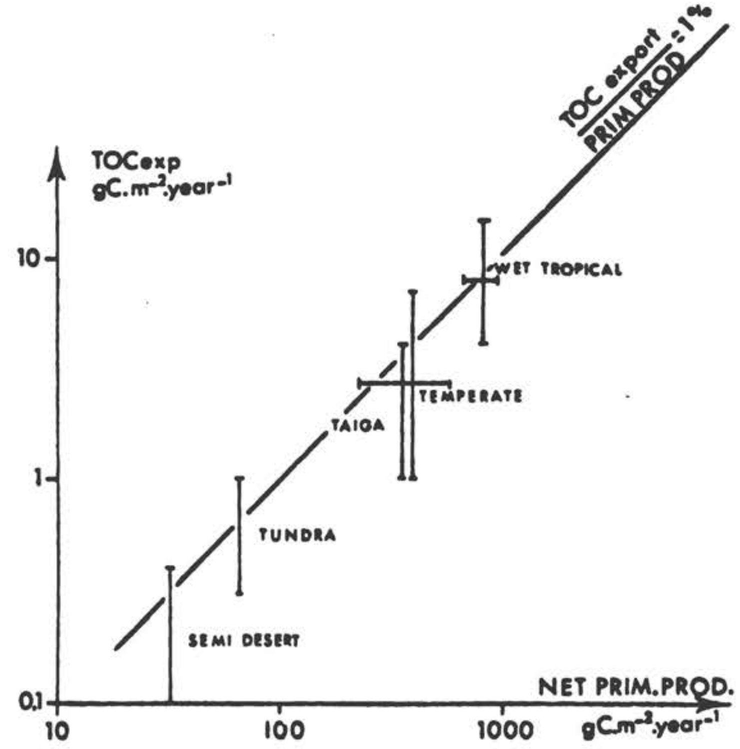

FIGURE 6 Transport rate of TOC by rivers in various climatic environments, compared with net primary production according to Whittaker and Likens (1973).

about 450 10^{12}gc, taking into account the endoreic rivers) is compared with the total world production in terrestrial ecosystems (48,000 10^{12}gc per year) (Whittaker and Likens, 1973), the same proportion is found.

INFLUENCE OF MAN ON ORGANIC CARBON CARRIED BY RIVERS

Three methods can be applied to study the influence of man on river chemistry: (1) comparison of neighboring watersheds, one in a natural state and the other in a state influenced by man's activities (the latter state is exemplified by clear-cutting one of the Hubbard Brook watersheds); (2) study of the change of representative rivers since the beginning of the industrial era and of intensive agriculture; (3) direct measurement of various wastewaters (which can only refer to the effect of direct pollution. These methods applied to dissolved inorganic carbon have not revealed a significant increase of C (< 5%) in world rivers (Meybeck, 1979). Thus, there is no sizable variation of HCO_3^- in rivers affected by man (Mississippi, Saint Lawrence, Rhine) in which Cl^- and SO_4^- have already increased severalfold.

Sufficient data have not been found for organic carbon but we have sign of possible human influence: (1) TOC content in already treated urban wastewaters is between 20 and 50 $mg.l^{-1}$ (Various values, see Alberti <u>et</u> <u>al</u>., 1977). (2) TOC values found in temperate rivers exposed to heavy human pressure are higher than for the others: 13 and 20 $mg.l^{-1}$ for the Rhine Commission, 1975; 15 $mg.l^{-1}$ for the Ems, and 22 $mg.l^{-1}$ for the Danube (Tittizer, 1978). However, TOC values for the Mississippi and Ohio are surprisingly low, perhaps because of degradation of organic wastes within the waterbody by self-purification.

(3) Widespread eutrophication of water bodies in Europe and North America caused by higher N and P contents may result in TOC increase of autochtonous origin, however the corresponding organic matter should be recycled rapidly and this effect on river TOC should remain secondary. According to Zobrist et al. (1977), the natural DOC values in Swiss rivers might have represented only 50% of the present-day level.

INPUT OF RIVER ORGANIC CARBON TO THE OCEAN

Some estimates of river organic carbon transported to the ocean have already been presented (Garrels et al., 1973; Duce and Duursma, 1977). Most of these estimates were based on sparse data obtained on small watersheds. Two other estimates (Alekin, 1978; Richey et al., 1980) have been proposed on the basis of some major rivers (Siberian rivers, the Amazon). The total sample of rivers discharging into the oceans for which any data on total organic carbon is available do not exceed 27% of the total water discharge or drainage area; the rest must therefore be estimated.

It must be noted that the study of more rivers will not greatly increase this proportion since the number of rivers needed varies exponentially: 30% of the water is discharged to the ocean by 10 rivers, 50% by 60 rivers, and 60% by 260 rivers. The corresponding figures for the exoreic drainage area are 10 rivers, 18 rivers, and 80 rivers (UNESCO, in press). The figure for the discharge of suspended matter is slightly different. If we take into account the latest measurements on the Amazon, where the estimate of suspended load had been doubled (Meade et al., 1979), we can estimate the total suspended load at about 16,000 10^{12} $g.year^{-1}$ on the basis of published data on major rivers (Meybeck, 1976) and by extrapolation for the remaining (Meybeck in preparation). This figure is of course an estimate of the natural transport occurring before damming of several major rivers (Colorado, Indus, Nile). If we listed the rivers of the world in the order in which they discharge sediment to the sea (those with the highest discharge at the tope of the list), we would find that the 10 largest rivers (the 10 at the top of the list) discharge to the sea 52% of the sediments and that the 20 largest rivers discharge 60%. It would therefore be "easier" to estimate the composition of particulate matter than to estimate the composition of dissolved matter. This discrepancy is due to the fact that the Huang Ho river is responsible for 0.13% of the water discharge but for 20% of the sediment discharge. Although we are speaking of river input to the ocean, we are not considering at this point the possible flocculation of dissolved organic carbon during river and sea water mixing (Sholkovitz, 1976), nor are we considering the possible primary production in these areas. The global effect of the estuarine zone on the carbon budget is not yet fully understood.

There are several ways to estimate the budget of an element carried by rivers to the ocean (Meybeck, 1979):

1. Data on as many rivers as possible are collected and this sample is considered as representative of the total river load. A simple extrapolation is then made through the hypotheses of either constant concentration (for the remaining water discharges) or constant specific transport (for the remaining area). The representativeness of the sample must be checked, taking into account among other things, the distribution of climatic zones, of specific water discharge, and of highlands and lowlands.

2. The sample of collected data is not considered as representative (for example: all data from North America). The extrapolation should be based on a typology of concentration or specific transports according to various criteria, such as climate, vegetation, lithology, and hydrology. The total water discharge (or drainage area) to the ocean is distributed among the classes of rivers defined in the typology. The amount of water discharge (or drainage area) found in the sample of collected data must be divided into the various classes. The extrapolation is then made inside each class. An example will be given for the temperate zone: the studied rivers in this zone represent only $4.3\ 10^6 km^2$, discharging $4.83\ 10^{12} gC.year^{-1}$, as compared with $22.10^6 km^2$ for the total drainage area of the temperate zone. An average transport rate $TOC_{exp} = 5t.km^{-2}.year^{-1}$ corresponding to a discharge of $88.5\ 10^{12} gC.year^{-1}$ will be assigned to the remaining area, $17.7\ 10^6 km^2$. The total temperate zone would therefore account for $93\ 10^{12}$ $gC.year^{-1}$ discharged to oceans.

3. If the sample of studied rivers is definitely too small (< 20%), a complete extrapolation is needed. There are two ways: (a) A relationship between the unknown parameters and a well-studied parameter (g, C_s, temperature) is looked for and used to support the extrapolation. (b) If no relationship is found, the estimate is based entirely on a typology defined from the study of smaller watersheds. It must be understood that a typology may be concerned either with distribution or concentration found in waters or with distribution of specific transport rates.

Three types of budgets have been used for organic carbon. One is the type described in paragraph 2 above and used for TOC. It is used for TOC known in about 27% of rivers. The second is the type designated as "(a)" in paragraph 3 above. It is used for POC on the basis of the relationship between POC_s and C_s. The third is the type designated as "(b)" in paragraph 3 above. It is used for DOC.

RIVER INPUT OF DISSOLVED ORGANIC CARBON TO THE OCEANS

The budget is estimated from the average DOC contents found in various climatic zones (Table 4). The average DOC value of the subarctic zone may be slightly lowered since the values in tundra rivers are probably much less than 4 $mg.l^{-1}$ (average TOC is 4 $mg.l^{-1}$), but direct measurements are needed to confirm this minor correction. Since the published values for three major rivers (Mississippi, 3.4 $mg.l^{-1}$; Amazon 5.0 $mg.l^{-1}$, and Nelson, 8.2 $mg.l^{-1}$) are close to the average contents chosen for their climatic zone, they can be considered as included in this budget.

The budget depends mainly on the tropical zone, which is so far the least studied. As for other dissolved elements, such as silica (Meybeck, 1979), this zone is the main source of DOC going to the ocean. The total budget is slightly greater than the previous estimate (130 10^{12}gC.year $^{-1}$) of Garrels _et al_. (1973), which has often been quoted although no details have been given concerning this figure.

RIVER INPUT OF SUSPENDED MATTER AND PARTICULATE CARBON TO THE OCEAN

The POC content of major rivers is known only for the Mississippi and Amazon, which represent only 7.5% of the total sediment discharge to the ocean. It is therefore necessary to make a complete extrapolation based on the relationship between POC_{exp} (in % of suspended matter) and C_s (amount of suspended matter). The particulate matter in rivers is not evenly

TABLE 4 River Input of Dissolved Organic Carbon to the Ocean

	Average DOC[a] (mg.l^{-1})	Water Discharge to the Oceans[b] ($km^3.year^{-1}$)	DOC Input (10^{12}gC.$year^{-1}$)	% Total Input
Subarctic zone	10	5,500	55	25
Temperate zone	3	10,300	31	15
Tropical zone	6	21,400	128	60
Arid and semiarid zones	3	200	0.6	0
Total	5.75	37,400	215	100

[a] From Table 2.

[b] From Meybeck (1979).

distributed because it is significantly affected by a few highly turbid rivers, such as the Huang Ho, which should be taken into account.

For this purpose a special sediment budget has been formulated in order to divide the particulate material carried to the oceans into nine classes of suspended matter C_s, from 5 to more than 50,000 mg. l^{-1}. This grouping has been set up on a sample of 46 major rivers (Meybeck, 1976) corresponding to 44% of the world water discharged to oceans and 55% of the drainage area. This sample has been considered representative of the $10^8 km^2$ drained to the ocean.

The 46 rivers have been arranged into classes according to their average C_s. The Amazon (average C_s = 160 $mg.l^{-1}$) Meade et al., 1979), has been divided as follows: one third into the 50– 150 mg. l^{-1} class and two thirds into the 150 — mg. l^{-1} class. Thus, rivers in the 50150 mg.l^{-1} class correspond to 32% of the water discharge of the sample, and to 5.5% of the sediment discharge. These proportions have been extrapolated to the total drainage area (Table 5). Therefore, a total water discharge of 37,400 km^3 x 0.32 = 11 970 km^3 has been assigned to this class for an average C_s of 80 mg.l^{-1}, corresponding to a sediment discharge of 957 10^{12}g. $year^{-1}$. This computation has been made for the eight classes, to which the Huang Ho, a special case, has been added.

The total load to the ocean estimated by this medthod is 17,500 10^{12}g.$year^{-1}$, which is fairly close to another estimate based on sediment transport typology (Meybeck in preparation) and to other values found in recent literature (Alekin, 1978).

TABLE 5 Loads of Suspended Material and of Particulate Organic Carbon from Rivers to Oceans

C_s range ($mg.l^{-1}$)	5-15	15-50	50-150	150-500	500-1,500	1,500-15,000	15,000-50,000	15,000-50,000	50,000 (b)	Total
Water discharge 0/0	3.8	18.2	32	20.2	23.4	1.8	0.07	0.15	0.3	100%
Water discharge $km^3.year^{-1}$	1,420	6,800	11,970	7,550	8,750	670	26	56	48	37,400
Average C_s $mg.l^{-1}$	8	30	80	300	800	3,000	8,000	30,000	65,000	-
Particulate load $10^{12}g.year^{-1}$	11	204	960	2,260	7,000	2,010	208	1,680	3,180	17,500
Particulate load 0/0	0.07	1.2	2.5	12.9	40.0	11.4	1.2	9.6	18.2	100%
POC_p content in 0/0 a	15	6	3	1.6	0.9	0.6	0.5	0.5	0.5	-
POC load $10^{12}g.year^{-1}$	1.65	12.2	28.8	36.2	63	12	1.0	8.4	15.9	179
POC load 0/0	0.9	6.8	16.1	20.2	35.2	6.7	0.5	4.7	8.9	100%

a From Figure 2

b Huang Ho is the only river found in this category

To each class an average POC_s content is assigned according to the POC_s - C_s relationship (Figure 2). In our example (the 50-150 $mg. l^{-1}$ class) the average POC_s is 3%, resulting in a total POC discharge of 28.8 10^{12} $gC. year^{-1}$ for this class of rivers.

Several observations can be made:

The weighted-average suspended load in rivers is probably between 400 and 500 $mg. l^{-1}$ (470 $mg. l^{-1}$ here), but 75% of the world's rivers carry less than 500 $mg. l^{-1}$ and 50% less than 150 $mg. l^{-1}$. This confirms previous statements (Meybeck, 1976) on the relative importance of dissolved and particulate mineral transports: the dissolved transport being dominant in about 35% of the world's rivers.

More than 40% of the world suspended load is carried by highly turbid waters ($C_s > 1,500$ $mg. l^{-1}$) that represent only 2.3% of the water discharge. These rivers are mainly found in the arid and semiarid zones (Indus, Orange, Rio Grande, Colorado, Huang Ho).

The mountain rivers (such as Irrawady, Mekong, YangTse, Ganges, Brahmaputra, Magdalena, Rhone, MacKenzie) carry 40% of the suspended load in the C_s range 500-1,500 $mg. l^{-1}$.

The rest of the suspended load (about 20%) is transported by plain rivers with headwaters flowing from mountainous areas (such as Amazon, Amur, Indigirka, Parana, Danube, Zambezi). These rivers have C_s contents between 50 and 500 $mg. l^{-1}$ and correspond to 52% of the water discharged to oceans.

The POC input from rivers to oceans is around 180 10^{12} g. year^{-1}, and 71% of it would originate in highland rivers and mixed rivers (plain and mountainous watersheds) -- 35% in the former and 36% in the latter. The rivers from the arid zone would account for only 21% of the POC load.

The weighted average POC_s content in suspended matter is about 1.0%. However, because of the distribution of loads, 70% of running waters carry a suspended load with much higher values, between 1.6 and 6%.

Similarly, the weighted POC concentration in waters is about 4.8 mg. l^{-1}, but 70% of rivers have lower contents— between 4.8 and 1.8 mg. l^{-1}.

This budget should be refined by establishing POC_s-C_s relationships for given environemntal conditions. For example, if the higher POC_s values observed in the Amazon and Zaire rivers are confirmed, the total POC input to the sea could be somewhat higher than the estimate given above.

It must be noted that POC carried by bedload is not considered here. However the corresponding transport is probably very low due to the density of organic debris. The large particulate fractions (large wood debris, tree trunks) is also taken into account.

RIVER INPUT OF TOTAL ORGANIC CARBON TO THE OCEAN

This budget has been computed according to the method described in the paragraph number 2 on page 248. TOC is more often measured in major rivers than POC or DOC and, adding the Siberia regional budgets of Tarasov et al. (1977), their drainage area corresponds to 27% of the total exoreic area (Table 6A). However, this sample is not at all representative of the world's rivers; it is greatly biased toward the colder regions. The extrapolation of the remaining 72.2 $10^6 km^2$ has been made on the basis of TOC_{exp} typology defined for six major climatic environments (Table 6B). The total load given for all climatic zones is around 380 10^{12}g.C $year^{-1}$ (Table 6C).

The budget seems to be in agreement with the individual DOC and POC budgets. However, all these figures must be considered with caution. Values higher by 20 or 30% can easily be obtained. For example, the present TOC budget is increased by 25% if a TOC_{exp} value of 9 $t.km^{-2}.year^{-1}$ for the tropical zone is accepted instead of 6 $t.km^{-2}.year^{-1}$. (The latter value, lower than the Amazon tranport, has been chosen to take into account the drier savanna regions of the tropical zone.)

With these restrictions in mind, a few conclusions can be drawn:

The average TOC load from rivers to oceans is of the order of 400 10^{12}gC.$year^{-1}$. About half of it is in the particulate form, but in most of the rivers the particulate organic carbon is about half as abundant as the dissolved carbon.

TABLE 6 Input of Total Organic Carbon from Rivers to Oceans

A. Studied rivers

	Area ($10^6 km^2$)	TOC_{exp} ($t.km^2.year^{-1}$)	Annual Load ($10^{12} gC$)
Siberian rivers[a]	12.6	2.25	28.3
Nelson	1.15	0.62	0.7
MacKenzie	1.8	1.93	3.5
St. Lawrence	1.03	0.81	0.83
Mississippi	3.27	1.23	4.0
Amazon	6.3	8.7	54.8
Murray	1.1	0.28	0.3
Total known sample	27.25	3.4	92.4

B. Extrapolated sample

	Remaining Area[b] ($10^5 km^2$)	Typical TOC_{exp}[c] ($t.km^{-2}.year^{-1}$)	Annual Load ($10^{12} gC$)
Tundra	4.4	0.6	8.6
Taiga	3.45	2.5	2.6
Temperate	17.7	5	88.5
Tropical	31.0	6	186
Semiarid	14.4	0.3	4.3
Desert	1.7	0.0	0
Total extrapolated sample	72.65	4.0	290

C. Total river discharge

	Total Area[b] ($10^6 km^2$)	Total TOC Load ($10^{12} gC.year^{-1}$)	% TOC Load
Tundra	7.55	4.5	1.2
Taiga	15.85	39.6	10.3
Temperate	22.0	93	24.3
Tropical	37.3	241	62.9
Semiarid	15.5	4.6	1.2
Desert	1.7	0	0
Total	99.9	383	

[a] From Tarasov *et al.* (1977); for the other rivers, see Table 1.

[b] From Meybeck (1979).

[c] From Table 2.

The tropical zone is contributing about two-thirds of the organic load and the subarctic zone only about 12%.

The weighted average TOC content is about 10 $mg.l^{-1}$, and the average TOC_{exp} about 4 $t.km^{-2}.year^{-1}$ or 40 $kg.ha^{-1}.year^{-1}$.

The organic load carried by rivers to oceans is about 1% of the total terrestrial primary production (48,000 10^{12}gC.$year^{-1}$) (Whittaker and Likens, 1973). The exchange of organic carbon between land and ocean is almost totally accomplished through transfer of atmospheric CO_2.

This budget is somewhat higher than the estimate by Garrels _et_ _al_. (1973)--200 10^{12}g.C.$year^{-1}$--but lower than the one by Richey _et_ _al_. (1980)--1,000 10^{12}gC.$year^{-1}$. We know from present data that the latter estimate is too high. The estimate by Alekin (1978)--360 10^{12}g.$year^{-1}$--refers to dissolved organic carbon; but since it is obtained by extrapolation of permanganate value in Soviet Union rivers, it might as well refer to TOC concentrations.

OTHER FORMS OF CARBON CARRIED BY RIVERS TO OCEANS

The other forms of carbon carried by rivers are dissolved inorganic carbon (DIC) CO_3^{--} and HCO_3^-, and particulate inorganic carbon (PIC). The total amount of DIC carried by rivers to oceans is estimate at 401 10^{12}g.$year^{-1}$, of which 19 10^{12}gC is derived from man's activities, 217 10^{12}gC from atmospheric CO_2 involved in rock weathering, and 164 10^{12}gC from dissolution of carbonate minerals occuring in sedimentary rocks (Meybeck, 1979). It is noteworthy that the CO_2 involved during rock weathering (igneous rocks as well as of sedimentary rocks), is one of the few sinks of CO_2.

Inorganic carbon in river particulate material is poorly understood. Most probably PIC occurs as residual carbonate material not completely dissolved by chemical erosion. Wagemann _et_ _al_. (1977) measured PIC_s values of 2.4 and 1.5% in suspended material of the Redstone and MacKenzie rivers, which drain extended sedimentary regions. These PIC values are probably not representative of world rivers since the Ca content in particulate matter in the MacKenzie (3.58%) is much higher than the average Ca content in the world's rivers (2.15%) (Martin and Meybeck, 1979). Values found by Malcolm and Durum (1976) in U.S. rivers range between 0.0% (Neuse) and 1.3% (Brazos), with 0.35% for the Missouri and 0.15% for the Mississippi.

An average of 0.9% for the PIC content seems to be reasonable. It would correspond to an input of about 150 10^{12}gC.year^{-1}. The various carbon inputs to the sea are summed up in Table 7. The dissolved transport index, defined as the ratio dissolved load/total load for a given element, would be 50% for organic carbon and 70% for inorganic carbon. For the combined forms, this ratio is 63%, less than for chloride and sulfur but higher than for nitrogen (Martin and Meybeck, 1979). It is striking that the organic and inorganic carbon loads are similar, but when the atmospheric CO_2 carried in river waters as HCO_3^- is added to the organic load, the mass of carbon directly linked to the biogenic cycle represents two-thirds of the carbon river transfer but only one-third for the continental erosion.

TABLE 7 River Inputs of Carbon to Ocean (10^{12}gC.year^{-1})

	Dissolved	Particulate	Total	Dissolved Load/ Total Load
Organic	215	180	395	54%
Inorganic	380	150	530	72%
Total	595	330	925	64%

CONCLUSIONS

Despite the heterogeneity of data and a general lack of measurement of organic carbon in major rivers, some conclusions can be drawn:

1. The variability of the organic carbon content in rivers is relatively high: 90% of waters for which data were found had DOC values between 1 and 20 $mg.l^{-1}$ and TOC values between 2 and 30 $mg\,l^{-1}$.

2. The POC_s content in river particulate (in % dry weight) is inversely related to the amount of suspended material (C_s), but the POC content in river water (in $mg.\,l^{-1}$) increases slightly with C_s.

3. Contrary to statements generally made, river POC is not negligible. It probably represents about 45% of the organic carbon carried to the ocean. However, the POC commonly observed is between 20 and 40% of TOC.

4. 43% of the carbon carried to the sea by rivers is in organic compounds ($400\ 10^{12} gC.year^{-1}$, corresponding to an average TOC of 10.5 $mg.\,l^{-1}$). This organic input represents only 1% of the net primary production of the continents.

5. The POC budget brings to attention the sediment discharged by rivers in the semiarid zone. These rivers could account for 40% of the sediment discharge even though they account for only 2.3% of the water discharge.

6. According to the few data available, tropical rivers do not present very high levels of organic matter, but because of their important runoff they probably represent more than 60% of the organic load to the oceans.

7. One possible use of river budgets is to facilitate consideration of steady state in the geocycle of elements. Evidence of perturbation of the carbon cycle is found in the atmosphere, and is likely to occur in surface waters (organic wastes, eutrophication). It will not be possible to see any trend in the river load of organic material unless the budgets are realized with a much better accuracy (about 30% here).

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FLUXES OF ORGANIC MATTER IN RIVERS RELATIVE TO THE GLOBAL CARBON CYCLE

Jeffrey E. Richey

Rivers transport large quantities of dissolved and particulate matter of mineral and organic composition from terrestrial drainage basins to the oceans. The current megascale estimates of organic export in the range of 10^{14} to 10^{15} g C/yr, suggest that rivers may be significant in the global carbon cycle, particularly with regard to increased atmosphere CO_2. For the rivers to be "significant," it must be determined that river fluxes are of a magnitude comparable with the other fluxes involved in carbon pathways. That is, the problem is to assess the fluxes of human-induced transient carbon of terrestrial organic and riverine origin transported and ultimately buried through river processes.

The purpose of the National Research Council "Workshop on the Flux of Organic Matter to the Oceans" (Woods Hole, September 21-24, 1980) is to examine this role of rivers in the global carbon cycle. The intent of this contribution is to provide a framework for the workshop by reviewing the biogeochemistry of carbon in rivers, and to evaluate carbon fluxes for a specific river, the Amazon. Finally, existing estimates and assumptions on river carbon transport will be reviewed.

THE BIOGEOCHEMISTRY OF CARBON IN RIVERS

Rivers are of interest here not only because they are large, complex, and dynamic ecosystems in their own right, but also because they constitute a pathway between two of the largest carbon reservoirs: the terrestrial biosphere and the oceans. We are concerned not only with how much carbon is exported from rivers to the marine environment, but also with how much carbon is imported from land to the rivers and how much carbon is produced within the rivers. Of these materials, how much is ultimately buried? Further delineation must be made between steady-state, background fluxes, and anthropogenically induced transient fluxes, under both current and potential future CO_2-enhanced conditions.

This is clearly an extremely difficult and complex problem. The only data currently available, which are very rudimentary, are of bulk export and say little of material origin, sensitivity to land disturbance, and so on. The identity of the fluxes that need to be assessed has not yet been made clear, much less their magnitude. This suggests that a brief review of carbon biogeochemistry in rivers is in order.

Ecosystem-level studies of streams and rivers have focused on the relative significance of various carbon fluxes and the factors controlling them, including the strong influence of the physical environment (Baker and Baker, 1979; Cummins, 1974, 1977; Cummins et al., in preparation; Dahm, 1980; Fisher and Likens, 1973; Hynes, 1970; Naiman and Sedell, 1979; Sedell et al., 1974; Whitton, 1975). In streams, energy sources include inputs of leaf litter, woody debris, leachates, and primary production by attached algae and mosses. The relative distribution of these sources is governed by the extent of canopy and stream physiography. Microbial production in lotic systems of forested regions usually involves heterotrophic benthic processes supported by energy derived from terrestrial matter. In contrast, larger rivers usually show a decrease in the importance of benthic processes, while in downstream reaches they can support vascular hydrophytes and plankton.

Thus, the organic content at one site of a river is dependent both on immediate circumstances and on events farther up in the watershed. Qualitative and quantitative changes in the organic load are brought about by specialized biological communities and physical retention processes. The production and processing of organic materials have been documented in the form of budgets. Our concept of rivers has evolved to the point that streams and rivers are no longer viewed as open systems that exist primarily to export terrestrial products, but rather as producers and processors of organic material (Cummins _et_ _al_., in preparation). Carbon and nutrients that are not processed or retained within one stream segment, or reach, are exported to the next reach. This process has been referred to as "spiraling" (Elwood _et_ _al_., in press; O'Neill _et_ _al_., 1975; Webster _et_ _al_., 1975). Rzoska (1980) argues that rivers are not "ecosystems," precisely because material is not recycled at the same point in space. His is a somewhat restricted view of ecosystems, but it does illustrate this special property of rivers.

Not all organic carbon that enters a reach is processed immediately or exported. Some is retained in storage in or on channel sediments or on the floodplain. These materials are then subject to extreme flooding events that can operate on a time scale of decades (which demonstrates the danger of assuming a steady-state situation in streams and the importance of discharge history). Flood events, the import and export of large and small organic debris, and major changes in in-channel storage are the elements of fluvial geomorphology that define the substrate basis for the establishment of biological communities.

This brief description suggests that a biogeochemical framework is appropriate for assessing the river carbon question here. This approach requires first that a river-watershed system be divided into a series of discrete sectors on the basis of relative homogeneity within each sector, and that these sectors be sampled over time. Then, the processes controlling the fluxes must be assessed. An integral part of this approach is the identification of the sources of the different carbon species, and at least a functional characterization of their chemistry. This provides some index for assessing how refractory or labile different carbon species are, and thus what subsequent fates might be. The characteristics of floodplain rivers and of carbon dynamics discussed above can be related schematically into a general river "model" (Figure 1). Papers by Spiker, Hedges, O'Brien and Stout, Turekian and Benoit (Part II) address in detail the utility of tracers and other features of this model. The carbon species and their fluxes identified here are those that must be assessed.

CARBON FLUXES OF THE AMAZON RIVER

The only large river from which even cursory data are available for estimating the fluxes identified in Figure 1 is the Amazon. An assessment of the temporal and spatial patterns in the load and processing of organic carbon in the Amazon is reported in Richey et al. (1980) and Wissmar et al. (in press). They conducted two cruises on the Amazon. The first cruise extended 2,000 km from Manaus to Iquitos, in February - March 1977, near the beginning of the rainy season when water levels were rising at 1 m per week. The second extended 3,400 km from Iquitos to Belem, in May - June 1977, during peak flooding when the entire varzea was inundated. On the basis of these data and other literature results, the following analysis of annual carbon fluxes into, through, and out of the reach extending from Iquitos to Obidos is attempted (Figure 2). Some of the estimates are little better than "back of the envelope" calculations, but they do serve to establish possible ranges.

Production (litterfall) over the area drained by Amazonian waters is 470 × 10^{13} g C/yr. About 1% of the area is covered by flowing waters. Concentrating factors in temperate systems result in a severalfold increase in concentration in headwater regions of POC, and an equivalent amount of DOC. If these relations hold, 14 x 10^{13} g C/yr of POC and 14 x 10^{13} g C/yr DOC should enter the extensive tributary system of the Amazon, as the terra firme flux. Since erosion is not included, these estimates could be conservative.

A source of CPOC (large POC) is trees. The carbon content of the average tree floating in the Amazon is roughly 2 x 10^{6} g/C (C.Jordan, personal communication). If one tree per minute floats by Obidos during the 6-month portion of the ascending hydrograph, then (2 x 10^{6} g C/tree x 1 tree/min x 2.63 x 10^{5} min/6 mo) = 5.3 x 10^{11} g C/6 mo is exported. Depending on the location of the trees, this flux would be from the varzea or from tributaries. These estimates could also be conservative, since only floating materials are included.

Macrophytes are another source of CPOC. Macrophyte production is about 500 g C m^{-2} yr^{-1}, or 5 x 10^{13} g C/yr. Production of trees and grasses is about 2.4 x 10^{13} g C/yr (W. Junk, personal communication). Much of this production is decomposed *in situ*, so roughly 1 to 2 x 10^{13} g C/yr might be exportable.

There are three sources of production in the varzea: phytoplankton, macrophytes, and "terrestrial" (trees and grasses). T. Fisher and J. Melack (personal communication) estimated that about 0.3 x 10^{13} g C/yr could be exported to the main river as DOC and POC (less than 1 mm). Results suggest that considerable plankton carbon is oxidized *in situ*. Most of the exported carbon may be macrophytic, or at least vascular, material with a large amount of lignin. On the basis of Junk's estimates of macrophyte degradation *in situ*, about 1 x 10^{13} g C/yr may be exported. Sediment respiration has been shown to be of considerable potential, perhaps comparable with water column oxidation at times (though shifted temporally).

From the data of Richey *et al.* (1980) and Stallard (1980), Richey (in press) estimated the following fluxes (in 10^{13} g C/yr):

Import from upriver: POC, 1.0: DOC, 0.4; DIC, 1.2
Tributary input: POC, 5.4; DOC, 2.7; DIC, 1.0
Water column respiration: 3.2
Evasion: 2.0
Downriver export: POC, 3.1; DOC, 3.1: DIC, 2.2

No data at all are available for estimating deposition, entrainment, and storage. From floodplain volume, T. Dunne (personal communication) estimated that about 180 km^3 of carbon has been sequestered during the Holocene (the last 10,000 years). This is equivalent to an annual storage flux of about 2 x 10^{13} g C/yr.

These estimates are highly subjective. However, they do indicate that even very large rivers are dynamic systems. These results indicate that export to the marine environment is considerably less than the terrestrial carbon input to the river system, with storage and oxidation reducing export.

MEGASCALE CALCULATIONS OF GLOBAL CARBON FLUX IN RIVERS

Few systematic surveys of the organic carbon flux in rivers are available. Most current estimates are based on some assumed averaged concentration of TOC (as DOC plus FPOC), usually 2-10 mg TOC-C/liter times global discharge (Table 1). The largest documented estimate, 10×10^{14} g C/yr, included adjustments for depth-weighting and oxidation, and attempted to differentiate between tropical and nontropical rivers (Richey *et al.*, 1980). Meybeck (Part II) has done the most complete analysis of organic carbon flux in rivers.

Most of the estimates do not differentiate between large and small rivers, regions, and land forms, and scarcely differentiate between chemical species. Such factors must be considered. In the following, one further manipulation of the data will be attempted to provide some idea of the sensitivity of the various assumptions.

The intent here is to separate carbon discharge into large and small rivers by geographic region, by relating sediment to TOC yield for those systems having data (Table 2). With the resulting ratio, carbon export by region can be calculated under different assumptions (Figure 3).

The results show a wide range, judged by the initial assumptions. Clearly, the uncertainty with the greatest

TABLE 1 Survey of Global River Estimates

Reference	Estimate $gCx10^{14}y$	Method
Skopintsev (1971)	1.4	Average concentration of water soluble organic humus from Soviet references; thus DOC.
Williams (1971)	0.3	Assumed average TOC of 2 mg/liter and discharge of 1.58×10^{16} liter/year.
Garrels and MacKenzie (1971)	3.2	DOC of 9.6 mg/liter (from P. Williams, 1966 personal communication). No DOC.
Reiners (1973)	2-10	No justification
Garrels *et al*. (1975)	2	From Garrels and MacKenzie (1971).
Duce and Duursma (1977)	1-1.5	Average of 3.5 mg/liter DOC and 2 mg/liter POC times 3×10^{16} liter/year.
Handa (1977)	3.1	Rivers, from Garrels and MacKenzie (1971).
	0.8	Groundwater, average DOC of 20 mg/liter.
Stewart *et al*. (1978)	5.2	No justification
Kempe (1979)	1.9	From Garrels *et al*. (1975), DOC = 3.28 mg/liter. POC = 1.76 mg/liter: discharge of 3.77×10^{16} liter/year.
Richey *et al*. (1980)	10.0	For 20 largest rivers, POC = 5% and 2% TSS in tropical and nontropical rivers, respectively. DOC = 4 mg/liter; times processing, depth-weighting, and total discharge.
Schlesinger and Melack (in press)	0.39	Log extrapolation from 12 rivers.
	0.41	Terrestrial denudation estimates.
Meybeck (Part II)	0.4	POC, DOC, TSS and runoff relationships for about 100 rivers.

TABLE 2 Region-specific Discharge for 50 Largest Rivers.

Region	Discharge (m^3/yr)	Drainage Basin Area ($m^2 \times 10^{11}$)	TSS Load ($g/yr \times 10^{12}$)	TSS Yield ($g\ m^{-2}\ yr^{-1}$)	TOC Yield ($g\ C\ m^{-2}\ yr^{-1}$)	TOC/TSS
Asia (Exclusive of USSR)[b]						
Hwang Ho	1.03	6.73	2,083	3,095		
Yangtze	6.86	19.4	552	285		
Pearl West	2.52	3.1	25	80		
Mekong	3.48	8.03	187	233		
Salween	0.47	2.80				
Irrawaddy	4.27	4.30	331	770		
Brahmaputra	6.24	9.35	800	856		
Ganges	5.88	10.6	1,600	1,511		
Godavari	1.13	2.98				
Krishna	0.62	3.08				
Indus	1.75	9.27	616	665		
Shatt-al Arab	0.46	5.41	62	114		
Large river weighted sum (or average)	34.71	85.05	6,983	821		

North America[c]						
Mississipppi	5.45	32.20	303	94.1	1.3*	0.02*
St. Lawrence	4.46	12.90	4.4	3.1	0.34*	0.11
MacKenzie	2.50	18.05	45.9	25.4	1.40*	0.06
Columbia	2.28	6.68	10.3	15.4		
Yukon	1.60	9.32				
Fraser	1.01	2.38				
Nelson	0.71	16.72				
Mobile	0.52	1.09				
Susquehanna	0.34	0.73				
Large river weighted sum (or average).	18.87	94.07	489	52.01	2.32*	0.045
South America[d]						
Amazon	66.9	57.78	800*	138.4	10.38*	0.08
Tocantins	3.21	9.06				
Sao Francisco	0.89	6.73				
Orinoco	5.35	8.81	95.3	100.2		
Parana	4.69	23.05	90.0	39.0		
Uruguay	1.21	2.33	15	644		
Magdalena	2.36	2.41				
Large river weighted sum (or average).	84.61	110.17	1,091	99.0		

USSR (North)[e]						
Ob	3.93	24.84	15.7	6.3	--	--
Yenisei	5.47	25.90	11.6	4.5		
Lena	4.88	24.24				
Kolyma	1.19	6.45				
Amur	3.46	18.44				
Pyasine	0.80	1.92				
Indigirka	0.57	3.60				
Yana	0.31	2.46				
Large river weighted sum (or average).	20.61	107.8	58.2	5.4		
Europe[f]						
Volga	2.52	13.50	20.8	15.4	1.29*	0.08
Danube	1.94	8.16	21.4	26.2	1.04*	0.04
Pechora	1.28	3.26				
Dvina	1.11	3.60				
Rhine	0.70	1.45	0.5	3.4	5.34*	
Dnepr	0.53	5.02	1.2	2.4		
Rhone	0.53	0.96				
Po	0.46	0.70	16.8	240		
Vistula	0.34	1.97	1.7	8.6		
Neva	0.82	2.82				
Large river weighted sum (or average)	10.23	41.44	84	20.26		

Africa[g]						
Zaire	12.50	40.15	43	10.71	2.96*	0.28
Zambezi	2.23	12.95				
Niger	1.92	11.14	5	4.5		
Nile	0.89	29.79	122	41.0		
Large river weighted sum (or average).	17.54	94.03	197	20.97		

[a] Asterisks indicate data from specific sources. Other data are composites from Holeman (1968), van der Leeden (1975), Todd (1970), and Holland (1978).

[b] Total large and small river discharge for this region: 68.1.

[c] Total large and small river discharge for this region: 59.6.

[d] Total large and small river discharge for this region: 103.8.

[e] Total large and small river discharge for this region: 40.0.

[f] Total large and small river discharge for this region: 31.1.

[g] Total large and small river discharge for this region: 42.3.

potential impact is associated with the rivers of Asia. Assuming a TOC/TSS ratio of 0.01 leads to an estimate of a flux comparable to that of South America. Anything larger leads to a dominance by Asian rivers. How likely are these estimates? The erosional sediment load of these rivers is obviously extremely high, which might suggest low organic content. However, these regions are very heavily populated and are subject to heavy monsoon events. G. Saunders (personal communication) has reported POC concentrations in excess of 100 mg/liter in waters draining into the Ganges. Thus, higher organic content than might otherwise be expected is possible. The extrapolation from the large rivers to all rivers is solely on the basis of relative discharge.

CONCLUSIONS

In addition to the details provided above, several salient points should be emphasized:

> Determining the role of rivers in the global carbon cycle and ultimately in the CO_2-increase problem involves more than export to the oceans. Fluxes from land into the rivers and within-river processing and storage must be assessed, along with marine deposition and eutrophication induced by river nutrients.
>
> Estimates of global river export by region are very sensitive to assumptions used in extrapolation. Estimates for South America and especially Asia have the smallest data base and are the most sensitive to assumptions, and could thus have the largest error.

More detailed discussion on the issues raised here are contained in other papers presented in this workshop.

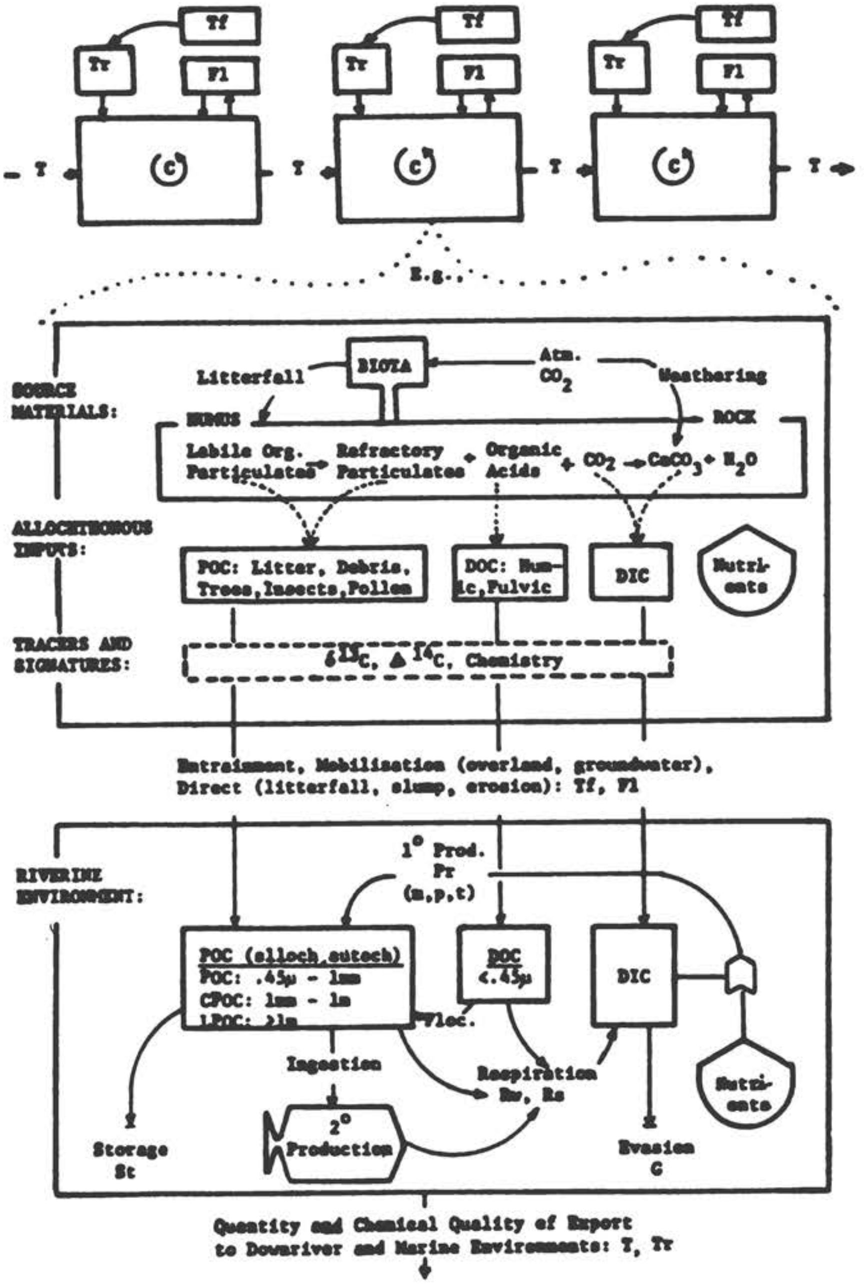

FIGURE 1

General model of the biogeochemistry of carbon in large floodplain rivers. (a) Spatial separation of a river watershed into a series of discrete sectors, or reaches, with separate tributary (Tr), terra firme (Tf), and floodplain pathways into a main channel, with transport excahnge (T) between reaches and carbon transformations (C) within. For example, each reach is divided into (b) the terrestrial source material, originating from the indicated processes, which are available as inputs of POC, DOC, and DIC, with respective tracers, via several pathways to the riverine environment (c), where production (Pr: <u>m</u>acrophytes, <u>p</u>hytoplankton, <u>t</u>errestrial), respiration (in <u>w</u>ater, in <u>s</u>ediments), evasion, storage, and flocculation occur.

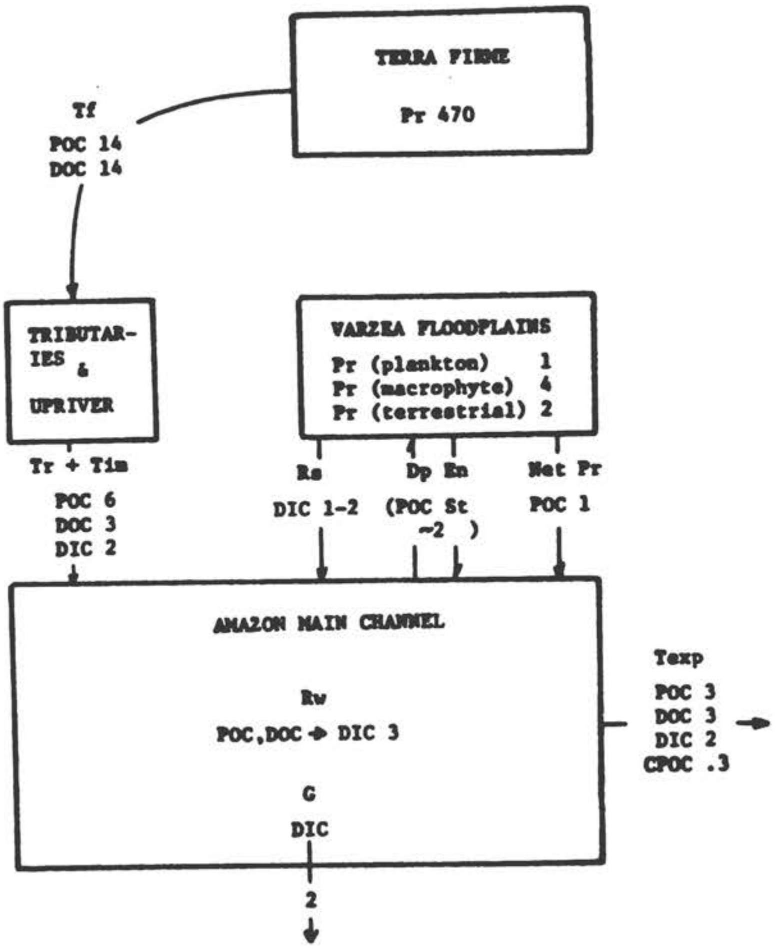

FIGURE 2

Estimates of major carbon fluxes through the Amazon River, g C x 10^{13}/yr. Pr = production, Tf = terra firme inputs, Tr = tributary inputs, Tim = upriver import, Rs = sediment respiration, G = CO_2 evasion, Rw = water column respiration, Texp = downriver export. River reach is from Iquitos, Peru, to Obidos, Brazil (about 3,000 km).

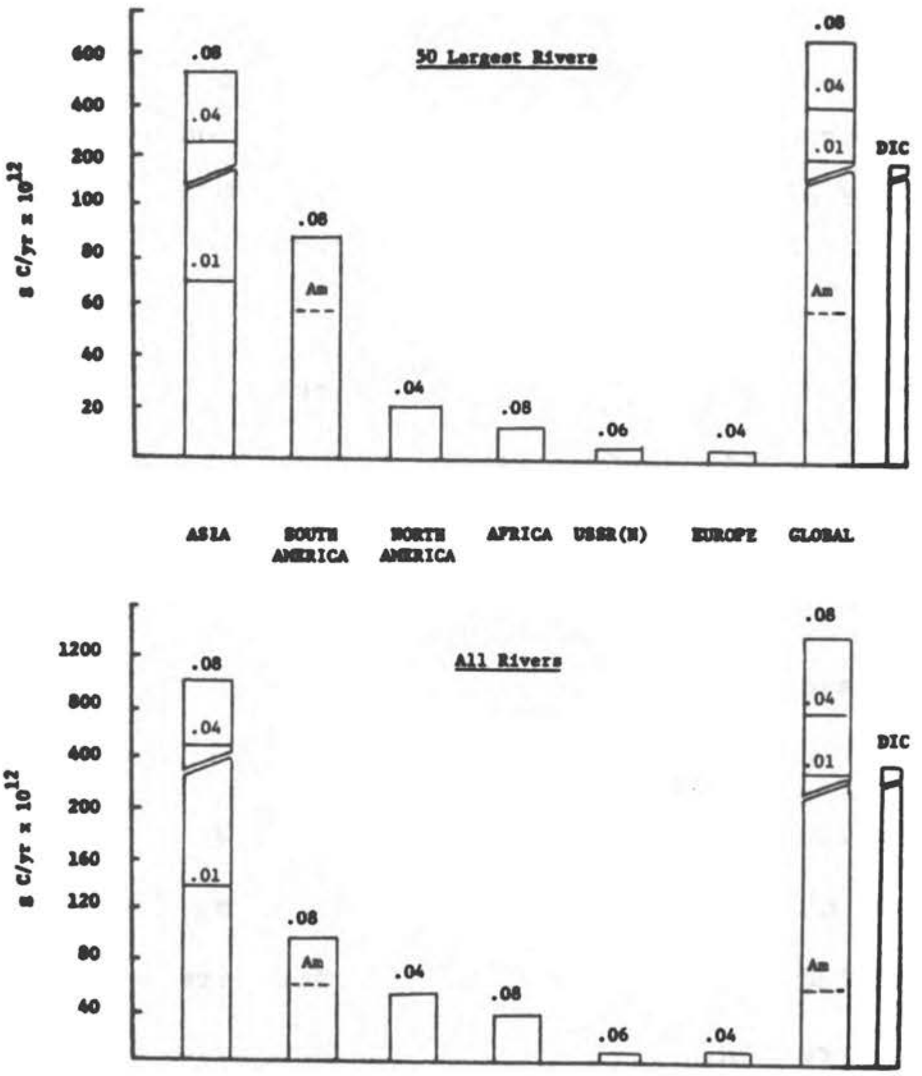

FIGURE 3

Total organic carbon (TOC) export by region, calculated as a function of total suspended solids (TSS). Number over each bar is the ratio of TOC to TSS used for that region (see Table 2).

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THE FATE OF SEDIMENTED ORGANIC CARBON IN ESTUARIES

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I have been asked to discuss the fate of organic matter after sedimentation in the estuaries. For reasons that will become obvious as I proceed, I will not attempt a megacalculation of the amount of organic matter stored in the sediments of estuaries. Rather, I propose to consider the mechanisms involved in storage and remineralization in these sediments and to estimate their probable contribution to the oceanic carbon cycle.

The overriding consideration in any estimate of the fate of sedimentary organic matter must be the input of turbulent energy into the estuary. Resuspension of sediments is the quickest route to recycling of the organic materials. Estimates of the normal or average amount of turbulence in any area of an estuary can be derived from rates of sedimentation. However, much of the resuspension of sediments would appear to be episodic rather than continuous (Burnett, 1971; Hargrave, 1976; Hargrave and Taguchi, 1978), related to local winds, and tidal action, and related to disturbance of the bottom by isolated incidents. We have as yet no way to handle the isolated incidents, save over spans of time long enough for the incidents to be considered statistically: in oceanography we have traditionally studied the climate, ignoring the weather as much as possible. It is only in recent years, with the advent of in situ continuously recording methods of measurement, that we have begun to understand the importance of the isolated incident. The average river and tidal currents in a given area might not be sufficient to move sediments down an estuary; yet the turbulence added to the system by a windstorm or by heavy rains in a river watershed might move the accumulated sediments of several years. Our estimates of sedimentation rates in an area can depend upon the season in which we sample, and our estimates of current speeds, if derived from the record of sediment movements, may be biased upward by movements resulting from isolated incidents.

A further limitation on theoretical approaches to sediment resuspension can result from occurrence after deposition. Frankel and Mead (1973) showed a binding of sand grains in an estuary by a mucilaginous matrix apparently resulting from activities of interstitial microorganisms. Such a matrix would help to preserve sediment structures until bacterial decomposition of the organic matter was advanced.

If our estimates or direct measurements of resuspension are considered untrustworthy, perhaps we can instead consider reactions taking place in "undisturbed" sediment as a limiting case.

While it is not specifically within the frame of reference of this paper to discuss sources of the organic matter in the estuarine sediment, it is necessary to my argument to indicate expected compositions and expected patterns of distribution. Much of the estuarine research over the past few years has indicated that particulate and colloidal organic matter, including the humic acid fraction normally considered as part of the dissolved organic matter, coagulates and sediments as salinity increases. The mechanisms involved have been examined in laboratory studies, often by following the precipitation of trace metals associated with the particulate matter (Bewers and Pearson, 1972; Sakamoto, 1972; Eckert and Sholkovitz, 1976; Sholkovitz, 1976; Boyle, et al., 1977; Brown, 1977; Sholkovitz, 1978; Hunter and Liss, 1979; Kranck and Milligan, 1980). Precipitates of this kind will also carry down organic pollutants such as DDT (Poirrier, et al., 1972; Pierce et al., 1974).

Field work, documenting the removal of river-borne particulates within the estuaries has been carried out in the Amazon (Sholkovitz et al., 1978; Sholkovitz and Price, 1980). The Beaulieu Estuary (Holliday and Liss, 1976), the Connetquot River (Hair and Bassett, 1973), the Conway Estuary (Hydes and Liss, 1977), the Penzé (Martin et al., 1977), the Potomac (Eaton, 1979), the St. Lawrence (Sundby, 1974; Cossa and Poulet, 1978; Kranck, 1979; Tan and Strain, 1979), the Waters of Luce (Sholkovitz et al., 1978), and the Ythan (Leach, 1971).

We would expect, then, a sediment in which the organic material contained an inorganic fraction, consisting of clay-size materials held together by associated organic debris, along with trace metals and various organic pollutants. Some sorting would be expected, certainly for size, with the large particles deposited upstream, but possibly also for composition. Work in our own laboratory has shown that organic materials of different composition, displaying differing surface charges in freshwater, coagulate and precipitate at different salinities. This type of sorting has not yet been sought in natural sediments. The disappearance of terrestrially derived particulate organic carbon (POC) from the water column with distance down the estuary has been documented in Chesapeake Bay (Biggs and Flemer, 1972) and in Southampton Water (de Souza Lima and

and Williams, 1978), and the equivalent disappearance of clearly terrestrial materials from the sediment has been shown in the St. Lawrence (Pocklington and Leonard, 1979).

Once the organic matter has sedimented, the normal processes of microbial degradation can begin. In most estuaries, a preliminary step will involve passage through the gut of some bottom-feeding invertebrates. This step may well result in the breakdown of particles into free organic molecules of low molecular weight (Wangersky, 1978); we have little information on this step, but I would hazard a guess that it is the most probable route for the return of organic carbon to the water column. What estimates we do have stem largely from work in the open ocean, and suggest that greater than 90% of the organic material reaching the sea floor is taken up by bottom organisms, rather than incorporated into the sediment (Eadie and Jeffrey, 1973). Our investigations into the return of organic materials to the water column by this mechanism have been hampered by our inability to sample in and just above the sediment-water interface without disturbing this interface. In addition, our methods for determining dissolved organic carbon (DOC) have been neither precise enough nor rapid enough to make such investigation seem worthwhile. Further, it is quite possible that the large number of bottom organisms that can take up and utilize small organic molecules may well ensure that any release to the water column would be transitory.

Once organic materials have been incorporated into the sediment, the normal processes of decomposition proceed. A fairly extensive literature exists on the changes in particular classes of compounds to be expected during this early diagenesis.

Amino acids, chlorine, fatty acids, hydrocarbons, humic and fulvic acids, isoprenoid alcohols, and phytyl esters have all been followed in the upper layers of the sediment (Brown, et al., 1972; Rosenfeld, 1979; Van Vleet and Quinn, 1979; Jones, et al., 1980). For the purposes of this paper, however, the more general studies of remineralization are more important.

The general features of this remineralization are well-defined; in the upper, aerobic zone there is an exponential decrease in organic carbon. This continues until the oxygen content of the interstitial water is used up. The depth to which aerobic decomposition extends depend on the organic content of the sediment and the rate at which the oxygen of the interstitial water is replenished. Revsbech, et al. (1980) have demonstrated that the resupply of oxygen is more dependent upon macrofaunal activity than upon molecular diffusion in marine sediments; I see no reason to expect the situation to be different in estuaries. Indirect measurement of oxygen uptake by sediments suggests that oxidation of organic matter in newly sedimented material may be essentially complete within a year of deposition (Hargrave, 1978). In this region of relatively rapid diagenesis, it is possible that small, readily soluble organic molecules may be freed into the interstitial water and diffuse or otherwise escape into the water column. Again, we have no measurements of gradients of DOC close to the bottom in estuaries, and we can only speculate about this possibility.

Below the level of aerobic decomposition, a layer can be found in which sulfate reduction is the predominant mechanism for the decomposition of organic materials (Whelan, 1974; Martens and Goldhaber, 1978; Dyrssen and Hallberg, 1979; Kepkay and Novitsky, 1980). Associated with this sulfate reduction may be some production of new organic compounds from available inorganic carbon by chemoautotrophy (Kepkay and Novitsky, 1980). Below this level, anaerobic decomposition, with the production of methane as an end product, is to be expected. This methane, along with some volatile products of greater molecular weight, certainly can return to the water column, at least in areas where unobstructed passages, such as worm tubes and abiogenic bubble tubes, exist (Barnes and Goldberg, 1976; Keen and Piper, 1976; Martens and Klump, 1980; Martens _et_ _al_., 1980). This evasion of methane into the water column is our best evidence of movement of organic carbon from the sediments, it is our best-documented case. Yet even in this case the number of measurements is small.

An indication of the possible escape of small organic molecules to the water column can perhaps be found in the remobilization and escape of trace metals originally sedimented either as parts of organic particle and freed by the decomposition of these particles, or as insoluble oxides and freed on reduction of these oxides in the region of anaerobic decomposition (Dunker _et_ _al_., 1974; Elderfield and Hepworth, 1975; Cranston, 1976; Graham _et_ _al_., 1976; Evans _et_ _al_., 1977; Lu and Chen, 1977; Morris and Bale, 1979; McCaffrey _et_ _al_., 1980; Ullman and Aller, 1980). We can only infer that some organic material could have diffused out with these trace elements; we have no measurements of actual movements of material.

In the absence of direct measurements of the return of organic material to the water column, we are forced to fall back on indirect measurements, examining results instead of reaction rates. Our best source of information on the return of terrestrial or fresh-water aquatic materials to the sea is the composition, – particularly the stable isotope composition – of the organic material in the sediments immediately outside the estuaries. Hopper and Larsson (1978) showed that the uronic acid composition in the water column and sediments of the Baltic and Black seas is characteristic of algae, rather than of terrestrial plants. Milliman, _et al_. (1975) found that more than 95% of the terrigenous sediment in the Amazon settles out before the salinity reaches 3 ^{o}/oo, and practically none of this escapes offshore. Similarly, Barretto and Summerhayes (1975) found that only 1% of the suspended load of the Sao Francisco River in Brazil escapes as far as 10 km from the river mouth. Zsolnay (1979) found much the same for the colloidal organic carbon in coastal North Carolina. In an admittedly special case, Loder and Hood (1972) considered the ocean as a source of DOC to a glacial estuary in Alaska, rather than the reverse. The ratios of carbon to nitrogen and carbon to chlorophyll _a_, along with the stable carbon isototope ratios, convinced Haines and Dunstan (1975) that the detritus in the Georgia Bight came mainly from marine sources. Finally, carbon and hydrogen isotope ratios of near-shore sediments suggested that little organic carbon escapes the estuaries, even in so large a river as the Mississippi or the St. Lawrence (Nissenbaum and Kaplan, 1972; Nissenbaum, 1974; Shultz and Calder, 1976; Tan and Strain, 1979).

I think it is fair to conclude that at this time the evidence strongly favors the retention of almost all of the sedimented organic carbon within the estuary. Certain types of pollution may reinforce this tendency; many of the pesticides and chlorinated hydrocarbons are preferentially adsorbed on organic particulate matter (Oloffs et al., 1973; Saleh et al., 1978; Duinker and Hillebrand, 1979; Pavlou and Dexter, 1979). This accumulation could result in a slowing of the microbial decomposition of the organic material. There would then be less opportunity for diffusion of organics back into the water column.

If we wish to define the term "almost all" with greater precision, we must develop better methods for sampling the interstitial water and the water just above the sediment-water interface; our present in situ samplers (Sayles et al., 1976) take a sample too small for our present analytical methods. We also need to refine our DOC methods in order to achieve sufficient sensitivity and precision to measure reliably the small difference we are likely to find. Even our present methods, however, suggest that any large movement of organics out of the estuarine sediments is improbable.

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RADIOCARBON IN NEW YORK BIGHT SEDIMENTS AND THE USE OF CARBON ISOTOPES IN DELINEATING CARBON SOURCES

Karl K. Turekian and Gaboury J. Benoit

Organic carbon in contemporary nearshore sediments is derived from both natural and artificial (more properly, human-processed) sources. The quest for identifying these various sources has led to the search for diagnostic chemical, physical, or isotopic properties of the different components. One promising property is the carbon isotope imprint. Marine-derived organic carbon and terrestrial (soil-derived) carbon are the most obvious natural sources. The distinction between these two sources in sediements has been discerned on the basis of $\delta^{13}C$ values (Craig, 1953; Sackett, 1964) since marine planktonic carbon formed in most temperate open ocean waters ($\delta^{13}C \cong -21$) is generally heavier than soil and plant carbon ($\delta^{13}C \cong 26$). As high latitudes are approached, however, planktonic carbon becomes lighter (Sackett <u>et al</u>., 1965). It is also known that in lakes and certain estuarine bodies the oxidative recycling of biogenic carbon may lighten the total inorganic carbon pool from which the plankton carbon (Sackett and Moore, 1966; Spiker, 1980) is formed, thus also confounding the oceanic with the terrestrial sources (Sackett and Moore, 1966; Spiker, 1980).

The artificial sources are oil and coal products and sewage sludge. These sources have $\delta^{13}C$ values close to terrestrial carbon although some crude oil may be lighter and some may be heavier, depending on the origin (Craig, 1953; Hartman and Hammond, in press; Monster, 1972; Reed and Kaplan, 1977; Silverman and Epstein, 1958). Thus, by using $\delta^{13}C$ it may be possible, in temperate zones, to distinguish an open-ocean plankton source of sedimentary carbon from all other sources, but a further identification is not possible.

It is possible, however, to refine our knowledge of the sources of carbon in coastal sediments by combining $\delta^{13}C$ data with ^{14}C data. The measured values of $\delta^{13}C$ and the $^{14}C/^{12}C$ ratios of various possible organic carbon contributors to the sediments of the New York Bight and adjacent regions are shown in Figure 1. Coal and oil, of course, are devoid of ^{14}C activity ($A/A_o = 0$) because of their antiquity. We have analyzed contemporary sewage sludge from New Haven for ^{14}C (Table 1), and we assume a $\delta^{13}C$ value between -26 and -27 since sewage sludge is derived mainly from terrestrial materials. A contemporary sediment sample from New York Harbor (Simpson, 1979) strongly resembles sewage sludge so far as the ^{14}C specific activity is concerned and has a $\delta^{13}C$ value of -27. Burnett and Schaeffer (1980) report $\delta^{13}C = -26$ for sewage sludge from some New York City outfalls. The contemporary plankton ^{14}C value is based on a sample from Long Island Sount (Benoit *et al*., 1979). Another plankton sample collected recently in Long Island Sound by J. Westrich was analyzed at Yale for $\delta^{13}C$ by D. Rye and M. Krom and shown to have $\delta^{13}C \cong -27$. However, it is known that total inorganic carbon in some estuarine waters may be light because of supply of total CO_2 by respiration from bottom sediments (Sackett and Moore, 1966; Spiker, 1980). On the other hand, the high salinity (but less than open-ocean salinities) values in coastal waters such as the San Francisco Bay system (Spiker and Schemel, 1979) yield particulate organic matter with $\delta^{13}C = -22$. We think that the $\delta^{13}C$ value of planktonic material supplied to the New York Bight sediments will be controlled by the open-ocean inorganic-carbon system.

We have determined that the preindustrial organic carbon preserved in Long Island Sound sediments is about 2,300 yr old (Benoit *et al*., 1979). The $\delta^{13}C$ of this carbon has been

TABLE 1 Radiocarbon Data and Organic Carbon Concentration of Box Cores from the New York Bight

Core	Location	Depth in Core (cm)	% LOI[a]	% C	^{14}C (A/A_o)[b]	^{14}C "age" (years BP)[b] ± 1σ
BX-6	40°24.15'N,73° 47.30'W 36m	0 - 11	10.0	0.83	0.732	2,580±520
		11 - 39	4.4	1.41	0.516	5,470±230
BX-9	40°19.60'N, 73°48.78'W 38m	0 - 10	3.5	1.01	0.629	3,830±300
		10 - 40	3.9	1.43	0.662	3,410±240
BX-10	40°12.70'N, 73°44.99'W 62m	0 - 10	4.7	1.48	0.759	2,280±220
		10 - 40	3.0	1.70	0.639	3,700±140
Sewage sluge (New Haven CT)				31.6	1.434	-2,980± 70

[a] % LOI = Loss on ignition.

[b] (A/A_o) = ^{14}C specific activity relative to 0.95 times NBS oxalic acid standard. The ^{14}C "age" is calculated by using this standard, assuming $\delta^{13}C \cong -25$ and a half life of 5,730 yr.

determined at Yale by D. Rye and M. Krom to be about - 26. Olsen *et al*. (1978) and Simpson (1979) have analyzed the Hudson River estuarine organic carbon from surface sediments in the area of low-salinity water for $\delta^{13}C$ and ^{14}C. The $\delta^{13}C$ for samples from which the humic fraction had been extracted is -27 and the ^{14}C age is about 4,300 yr BP. Olsen *et al*. (1978) ascribe this carbon isotopic imprint to old soil carbon from the Hudson River system contaminated by coal and petroleum products from the ship and barge traffic on the river. This latter effect is observed in surface sediments of Long Island Sound (Benoit *et al*., 1979). The humic acid component of the Hudson River sediments has ^{14}C ages of about 1,600 yr BP (Olsen *et al*., 1978), but one sample has a $\delta^{13}C$ value of -26 (Simpson, 1979). The age is compatible with the Long Island Sound sediment date but the $\delta^{13}C$ is significantly lower. Indeed, it is lower than that of any material measured in the sediments of Long Island Sound or the New York Bight (Burnett and Schaeffer, 1980).

The New York Bight box cores we analyzed were composed of fine-grained sediments high in organic carbon (∿ 1%C). BX-6 and BX-9 are closest to the Bight Apex and near the site of dredge spoil dumping. BX-10 is farther down the Hudson Shelf Valley. The data are shown in Table 1. (Benoit *et al*. (1979) describe the analytic technique.) There is no clear common pattern of ^{14}C variation with depth in the cores. BX-6 has an older age for the deeper sample (5,470 yr BP) than the surficial sample (2,580 yr BP). BX-9 shows little or no variation with depth, and BX-10 again shows the older value at depth. Because plutonium and excess ^{210}Pb are found at depth in all these cores (Benninger and Krishnaswami, in press), we interpret the differences in the ^{14}C "ages" to be due to mixing of high ^{14}C material and low ^{14}C material.

We do not have $\delta^{13}C$ values for the cores we analyzed for ^{14}C. Burnett and Schaeffer (1980), however, have made a thorough study of the $\delta^{13}C$ of grab samples throughout the inner Bight and along the Hudson Shelf Valley. They show that the $\delta^{13}C$ pattern varies regularly in the area and that the lowest value is centered at the head of the Hudson Shelf Valley, which is also coincidentally the site of major dredge spoil and sewage sludge dumping. From their $\delta^{13}C$ survey we have chosen the closest sample to each of our three box cores and assigned the $\delta^{13}C$ to the topmost portion of each core. We did not extend this to the deeper part of the core because of the large difference in ^{14}C with depth in BX-6 and BX-10. We believe that the grab sample most closely approximates the top 10 cm of the sediment pile. Table 2 shows the properties of the samples analyzed for $\delta^{13}C$ by Burnett and Schaeffer that correspond with regard to location, to our three box cores.

The $\delta^{13}C$ and ^{14}C data of Table 2 are plotted in Figure 1. The relationship between the organic carbon in the sediments at each location and the designated end members as discussed above is thus graphically displayed.

Site C (corresponding to BX-10) can be interpreted as a linear combination of fossil fuel carbon and prebomb open-ocean plankton. Because the $\delta^{13}C$ is virtually indistinguishable from marine carbon, however, it could be planktonic carbon stored in old sediments that has been biologically or physically remobilized from adjacent deposits. Bothner et al. (1980) report ^{14}C values for the mud area south of Martha's Vineyard that at the surface are slightly higher in ^{14}C content than the values observed at Site C. (They do not show $\delta^{13}C$ values

TABLE 2 Summary of Carbon Isotope Data for Selected "Sites" in the New York Bight

Site	Yale Core (0-10 cm)	% C	^{14}C (A/A_0)	Stony Brook Grab Sample [11]	% C (avg)	$\delta^{13}C$ (avg)
A	BX-6 40°24.15'N 73°47.30'W	0.83	0.732	34 40°25'N 73°45'W	2.24	-25.3
B	BX-9 40°19.60'N 73°48.78'W	1.01	0.629	56 40°19'N 73°45'W	1.63	-23.9
C	BX-10 40°12.70'N 73°44.99'W	1.48	0.759	HSV53 40°00'N 73°22'W	0.51	-22.1

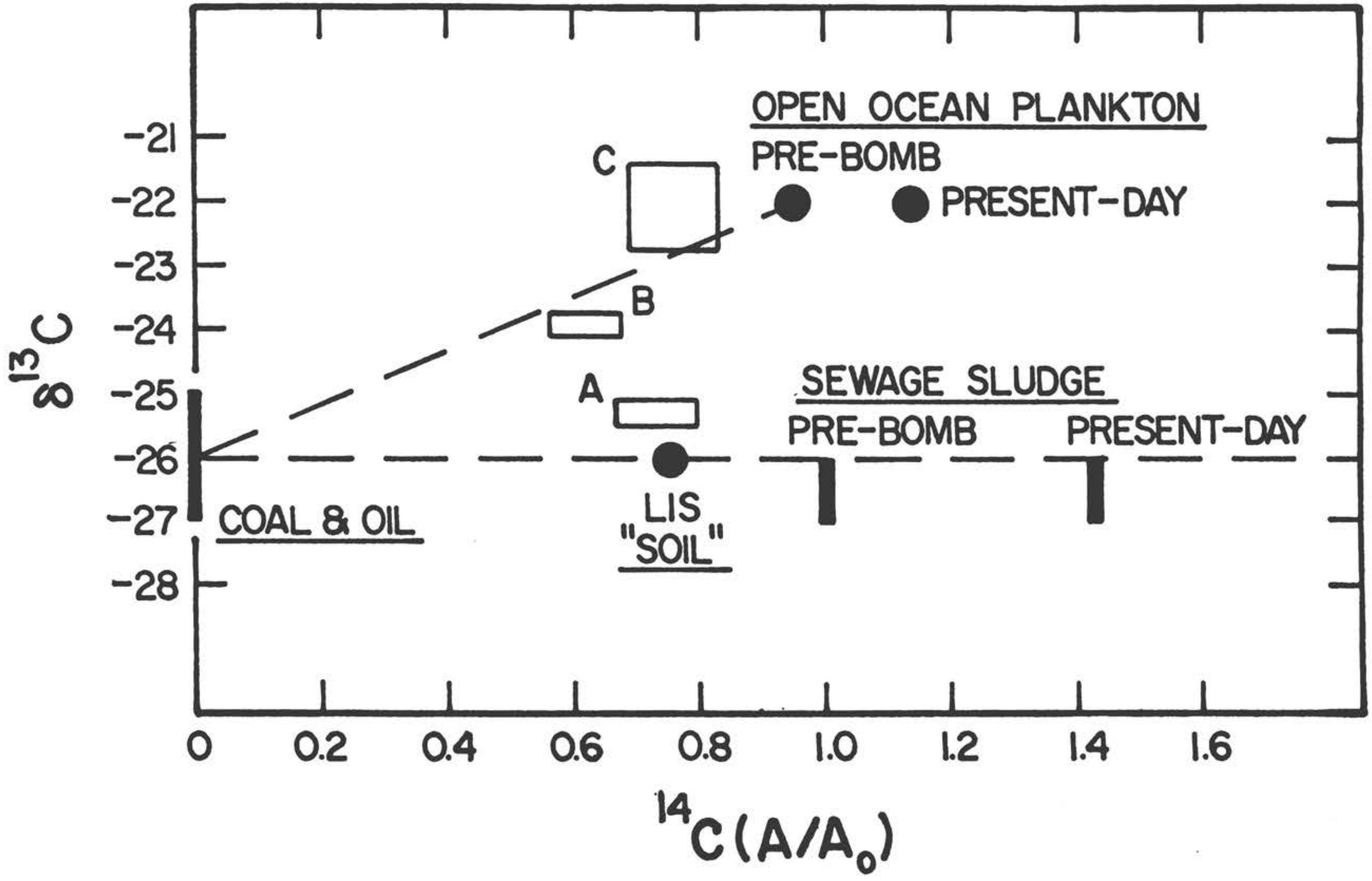

FIGURE 1 ^{13}C versus ^{14}C diagram for potential organic carbon sources to the New York Bight. The ^{14}C axis (A/A_o) is the ratio of the specific activity (A) of the sample to 0.95 times the specific activity of NBS-1 oxalic acid (A_o). The areas marked A, B, and C are the three sites in the New York Bight identified in Table 2.

for this region in their paper, but on the basis of regional data they should be the marine value.)

Site B (corresponding to BX-9) may also be the result of mixing between the prebomb plankton carbon and the fossil fuel carbon and members. Since the point falls below the mixing line we have drawn, this could be accomodated using one of two options. Either the mixing line should be drawn with a weighting toward present-day plankton with a high ^{14}C content; or, if the prebomb plankton end member is retained there must be a small contribution from either the "soil" component or even a smaller contribution from sewage sludge or a combination of "soil" and sludge.

Site A (corresponding to BX-6) is representative of the site of maximum sewage sludge dumping, and the first impression would be that the carbon there whould be dominated by this component. It is clear from the ^{14}C data that a large component of sewage sludge carbon could be present in the cores only if a large amount of fossil carbon were also present. The contemporary bottom sediments at the Battery (in New York harbor) apparently are dominated by ^{14}C-rich material like sewage sludge. If this kind of material has been dumped into the New York Bight Apex, little or none has been preserved in the organic-rich sediments there. Even prebomb sewage sludge would have ^{14}C values much higher than those.

Alternatively, Site A could be predominantly "soil" carbon with a small addition of prebomb plankton and fossil fuel carbon with no sewage sludge component at all required. Thus, there is no unambiguous solution for the Site A sample. All the main possibilities are listed in Table 3, based on mixing of the end members of Figure 1.

TABLE 3 Possible Combinations of Source Materials Compatible with the Carbon Isotope Imprint of Site A Sediment

Mix	% "Aged" Plankton	% Prebomb Plankton	% Soil	% Fossil Fuel	% Prebomb Sewage Sludge	% Present-day Sewage Sludge
1	17	0	83	0	0	0
2	17	0	0	23	60	0
3	17	0	0	41	0	42
4	0	17	80	3	0	0
5	0	17	0	22	61	0
6	0	17	0	41	0	42

End members:

	$\delta^{13}C$	^{14}C (A/A_o)
"aged" plankton	- 22	.76
prebomb plankton	- 22	.95
present-day plankton	- 22	1.14
fossil fuel	- 26	0
soil	- 26	.75
prebomb sewage sludge	- 26	1.00
present-day sewage sludge	- 26	1.43

There is clearly a difference in survival times of terrestrial and refractory fossil fuel carbon delivered to the oceans on the one hand and to marine planktonic and sewage sludge carbon on the other. In Long Island Sound we were able to show that the mean residence time of planktonic carbon in the top 5 cm of the sediment pile is about 2 yr relative to metabolic loss (Benoit et al., 1979; Turekian et al., 1980). Berner (1980) has sown at another site in Long Island Sound, on the basis of sulfate reduction kinetics, that organic carbon of planktonic origin has a residence time of about 20 mo. Thus, we would expect preservation of only the most refractory parts of the carbon supplied by plankton in sediments depositing in oxic waters and subject to macrofaunal bioturbation and bacterial activity. This component obviously becomes associated with the fine mud fraction as indicated in Figure 1 and can persist for a long time.

Sewage sludge seems to be at least as reactive as planktonic carbon (Grunseich and Duedall, 1978). The average rate of destruction of particulate carbon from sewage sludge in the presence of sea water and sediment was investigated under several aerobic and anaerobic conditions at 4°C and 21°C. Grunseich and Duedall found that the average rate of carbon metabolism for all these conditions was 13 mg carbon lost per week per gram of carbon present. This corresponds to a mean residence time of 1.5 yr similar to that for planktonic matter. The more refractory carbon compounds will persist longer and provide a residuum that will imprint the sediment. We believe that only a small fraction of sewage sludge carbon is preserved. This will be the most refractory carbon compound found in the sludge, or produced during marine diagenesis, and may explain the observation made by Hatcher and McGillivary (1979) indicating the presence of coprostanol, a fecal steroid, in the sediments of the New York Bight Apex. Hatcher and McGillivary determined the ratio of this to steroids derived from other sources to show that sewage sludge was a major component of the carbon delivered to the Bight.

The quantity of sewage sludge carbon contributing to the sediments of the New York Bight cannot be determined by using the ratio of a refractory compound to the total in the raw material, as Hatcher and McGillivary (1979) have proposed, since the most labile components of both the sewage sludge and marine components are destroyed on a rapid time scale. This would lead to an overestimation of the sludge contribution to the sediment organic carbon burden.

Likewise, it is clearly not possible to use $\delta^{13}C$ as an index of the sewage sludge component as Burnett and Schaeffer (1980) propose, since the value of about -26 is not diagnostic of sewage sludge alone. It is characteristic of virtually any terrestrial material (except C-4 plants) and most fossil fuels used on the east coast. The addition of the ^{14}C information helps in one important way. Although it does not provide a unique solution to the source material problem, it does put a constraint on the amount of fossil fuel carbon that is allowed in various mixing models. For example, if all the nonplankton carbon in Site A were due to the mixing of fossil fuel carbon and prebomb sewage sludge carbon, then 25% of the carbon would have to be fossil fuel carbon and 75% prebomb sewage sludge carbon (Table 3). Griffin and Goldberg (1979) made an assay of fossil fuel carbon contributions in a Lake Michigan sediment core, using morphology for identification. A similar program in New York Bight sediments combined with carbon isotope data can, in principle, resolve the problem. Comparisons of the amount of sewage sludge carbon preserved in the sediment estimated by this method with the amount of a refractory organic compound, such as coprostanol, will provide the concentration factor of the refractory compound as a result of diagenesis. The useof this concentration factor will then provide a method of estimating the amount of sewage sludge carbon preserved in the sediments of the New York Bight.

Under the best conditions the identification of the dominant sources of carbon accumulating in coastal deposits in contemporary times will be a difficult matter where there is a possiblity of human involvement. We may never be able to determine if there has been a change in the carbon flux to coastal sediments from rivers alone in recent times due to changing land use because of the direct impact in coastal areas of fossil fuels and sewage sludge.

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THE FATE OF TERRESTRIAL ORGANIC CARBON IN THE COASTAL AREA

Roland Wollast and Gilles Billen

In order to elucidate the behavior of dissolved and particulate organic carbon in shallow coastal areas and more precisely to evaluate how much of the carbon transported to coastal areas by major rivers is either oxidized, stored in sediments or exported to the open ocean, we will first discuss the mechanisms of transfer, production, and removal of organic matter in the estuarine zone.

We will then describe the main characteristics of the carbon cycle in the coastal zone and the relative importance of riverborne organic matter in this cycle.

We have tried through out this review to consider realistic figures for the various fluxes involved in the carbon cycle. However, this task is especially complicated in the coastal area because of the high diversity of the situations that one may encounter. We are aware these values are not complete but we have the feeling that they are sufficiently coherent on a global basis to give an idea of the relative importance of the various processes involved in the carbon cycle.

TRANSPORT OF ORGANIC MATTER BY RIVERS TO THE COASTAL AREA

The estuarine system is usually a very active zone where dissolved or particulate organic matter transported by freshwater may be removed by precipitation, flocculation, sedimentation or biological uptake during the mixing with seawater. On the other hand, estuaries are also productive areas, and the organic matter synthesized in the water column, salt marshes, and swamps associated with the estuaries may become the dominant part of the organic material transported to the sea.

In addition the relative importance of the physical, chemical or biological processes affecting the organic matter in the estuaries is furthermore strongly dependent on the hydrodynamic characteristics and on the geomorphologic features of the estuary. It is thus difficult to give a general picture of the transfer of organic matter in such complicated systems. However, it is now generally accepted that the organic matter of terrestrial origin carried by freshwater is at least partly and in some cases almost completely removed in the estuarine zone and does not reach the coastal environment.

When the salinity exceeds a few parts per thousand (3 - 5‰), both the particulate matter and high molecular weight dissolved substances may floculate which increases substantially the chances for this material to be removed by sedimentation (Meade, 1972).

In vertically homogeneous or in partially stratified estuaries, usually with long residence times, this process is coupled with a turbidity maximum where intensive shoaling occurs. In the Scheldt estuary for instance, of the 152 x 10^3 T/y of particulate organic matter carried by freshwater, 115 x 10^3 T/y are deposited in a restricted zone (30 km) corresponding to a well defined range of salinity (5 - 15‰) (Wollast and Peters, 1978). Calculations based on long term deposition in the Gironde estuary (Allen et al., 1976) gave similar results: 75% of the suspended load is definitively trapped in the estuarine zone and does not reach the sea.

In vertically well stratified estuaries, like those of most large rivers, the picture may be different. In the case of the Amazon 95% of the terrigenous sediment settles out within the river mouth before the salinity reaches 3‰ (Milliman et al., 1975). This intensive local sedimentation is mainly due to the existence of an extensive shoal occurring before the Amazon River mouth which gives rise to efficient vertical mixing (Gibbs, 1970).

In the Zaire River, (Eisma et al., 1978) the outflow of river water is concentrated in a narrow surface layer at the center of the stream which prevents rapid sedimentation. However, the heavier and larger mineral particles soon settle in the inner estuary while the smaller and lighter particles, including organic matter, remain more in suspension. As a consequence, particulate organic matter settles and accumulates near the head of the canyon, inducing an oxygen-depleted zone in the bottom waters.

The removal during estuarine mixing of a fraction of dissolved organic matter, particularly the humic material, is also a well established phenomenon (Matson, 1968; Sieburth and Jensen, 1968; Nissembaum and Kaplan, 1972; Gardner and Menzel, 1974; Nissembaum, 1974). Laboratory experiments (Höpner and Orliczek, 1978) show that humic matter present in freshwater coagulates and settles within a few days after mixing with seawater and that low concentrations of Ca^{++} and Mg^{++} (1 mM/l) are able to precipitate 80 % of the " brown color ". Formation of particulate organic material by such pathways can represent a significant contribution to the organic material deposited in estuarine sediments (Swanson et al., 1972). However, Sholkovitz (1976) claims that only 3 - 10% of the dissolved organic matter from riverwater if flocculated during the mixing with seawater.

Biological processes may also drastically affect the transfer of organic matter within the estuarine zone. In long-residence-time types of estuaries, the nonrefractory organic matter is almost completely mineralized by the heterotrophic bacteria. If the organic load is high, this leads to the formation of zones of anoxic water. For instance, in the Scheld estuary, about 40% of the organic load is respired, affecting mainly the dissolved fraction. On the other hand, in the Zaire River, the anoxic zone is restricted to the bottom water near the head of the canyon where the detritus of terrestrial plants accumulate. Approximately 1% of this load is respired before settling (Van Bennekom _et al_., 1978). However, in this case the terrigenous material discharged by the river serves as food for polychaetes and crustaceans which are in turn eaten by carnivorous fish species (Cadée, 1978). Odum and Heald (1975) conclude that the detritus food web often dominates in shallow and muddy estuaries.

Finally, the high nutrient content of estuarine waters promotes the development of high productivity zones as soon as the turbidity caused by the terrigenous suspended matter drops as a result of flocculation and sedimentation. The diatom bloom in the Amazon estuary reaches its maximum already at a salinity lower than 10‰. In the case of the Zaire, the algae start to develop at much higher salinities but the dilution of nutrients has reached levels too low to produce an algal bloom of importance (Cadée, 1978).

In the case of the Scheldt estuary, the large supply of nutrients produces a phytoplankton bloom during the Spring and as a result, during that period, the organic matter produced by photosynthesis in the lower part of the estuary equals almost exactly the amount of detrital organic carbon removed by respiration in the upper part (Wollast and Peters, 1978). Most of this fresh organic matter is transferred to the coastal zone where it is often difficult to distinguish it from the coastal primary production.

ORGANIC MATTER CYCLING IN COASTAL ECOSYSTEMS

Both in oceanic and in costal systems, organic carbon flows mostly through biological processes. The main stocks involved are listed in Table I along with typical values of their size and turnover times. The distinctions applied within these various stocks need the following comments.

- The distinction between particulate organic carbon (POC) and dissolved organic carbon (DOC) is based on the classical definition using filtration through 0.45 μm membranes. Living zooplankton and phytoplankton belong entirely to POC. Many bacteria are smaller than .45 μm although few pass through these filters. On the other hand, small colloïdal detritus may be classified as DOC. This colloïdal detritus can constitute up to 15% of the DOC (Sharp, 1973; Cauwet, 1977; Ogura, 1977). This distinction is especially important for organic matter from soil origin which is colloïdal rather than dissolved. A further separation of organic matter into dissolved, colloïdal and particulate is thus highly desirable.

- The chemical composition of DOC remains a major problem in marine organic chemistry. The "characterized fraction", made of free or combined amino-acids, carbohydrates, fatty acids, urea and so on, accounts for only 10 - 20% of total DOC (Williams, 1975).

Within this fraction, we still distinguish "directly utilizable organic matter" (DUOM) (Billen *et al.*, 1980), made only of the free small organic substrates that can be taken up by microorganisms directly, the rest requiring exoenzymatic - or spontaneous - hydrolysis before microbial utilization. The turnover times of these individual substrates, as measured by tracer experiments, are very short (a few hours to a few days) and reflect their very rapid utilization by microorganisms.

TABLE 1.

	Coastal Ecosystems		Oceanic Ecosystems			
			PHOTIC LAYER		DEEP LAYER	
	Pool Size (mgC/l)	Turnover Time (years)	Pool Size (mgC/l)	Turnover Time (years)	Pool Size (mgC/l)	Turnover Time (years)
DISSOLVED ORGANIC CARBON						
Bulk wet oxidation (b)	1-5	-	.6-1	.1-1.2 10^{3}(a)	4-6 10^{-1}	3.4-6.6 10^{3} (a)
dry oxidation (b)	2-10	-	1.5-2	-	1-1.3	-
Directly usable O.M. (b)	.2	.2-1 10^{-4}(e)	.1-.2	.1-2 10^{-3}	0-.1	.3
PARTICULATE ORGANIC CARBON						
Bulk (c)	.1-1	-	.5-1 10^{-1}	-	.1-1 10^{-1}	-
Phytoplankton	1-2 10^{-1}(i)	.3-2 10^{-2}(i)	4 10^{-2}(h)	2-4 10^{-2}	-	-
Zooplankton	.05-1 10^{-1}(i)	.1-5 10^{-1}(i)	-	-	-	-
Bacteria	.05-1 10^{-3}(i)	.1-8 10^{-2}(i)	3 10^{-3}(h)	.2-3 10^{-2}(g)	-	-
ORGANIC MATTER IN SEDIMENTS	(gC/kg)				(gC/kg)	
Surface layer (0-10cm)	.1-1 10^{2}(f)	1-2 (d)			15 (f)	-
Deep layer	15	-			5 (f)	3 10^{8} (g)

References :

a) Williams et al., 1969; Arhelger et al., 1974; Bada and Lee, 1977.
b) Williams, 1975.
c) Parsons, 1975
d) Berner, 1980; Billen, in press; Turekian et al., 1980.
e) Billen et al., 1980.
f) Wollast, in press; Degens and Mopper, 1976.
g) Hagström et al., 1979; Jannasch, 1969.
h) Cauwet, 1978.
i) Nihoul and Polk, 1977.

No convincing evidence exists concerning the nature of the large "uncharacterized fraction". The very low turnover time of DOC as a whole (Williams et al., 1969; Arhelger et al., 1974; Bada and Lee, 1977) and direct experiments with concentrated seawater (Barber, 1968) suggest that it consists mostly of biologically refractory compounds.

Ultrafiltration or dialysis shows that 70 - 90% of DOC has a molecular weight higher than 1,000 (Ogura, 1974; Wheeler, 1975), and that an increase in molecular weight occurs with depth (Ogura, 1974; Maurer, 1971; Mopper and Degens, 1979).

- Although particulate organic matter obviously dominates in sediments, the same kind of comments as for DOC could be made for organic matter dissolved in the interstitial phase. Thus Krom and Sholkovitz (1977) have also found an increase of molecular weight with depth in the organic matter of the pore-water of coastal sediments.

Table I shows that although the size of most stocks of organic matter in coastal systems does not differ more than a factor of 10 from those in oceanic systems, their turnover times are often several order of magnitude more rapid. Rapidity of organic matter cycling is therefore a characteristic feature of coastal ecosystems.

The main processes involved in this cycling are briefly discussed below. Fig. 1 shows as an example the budget of organic carbon circulation established for the coastal North-Sea, off Belgium. It shows for this particular environment the relative importance of the various processes described.

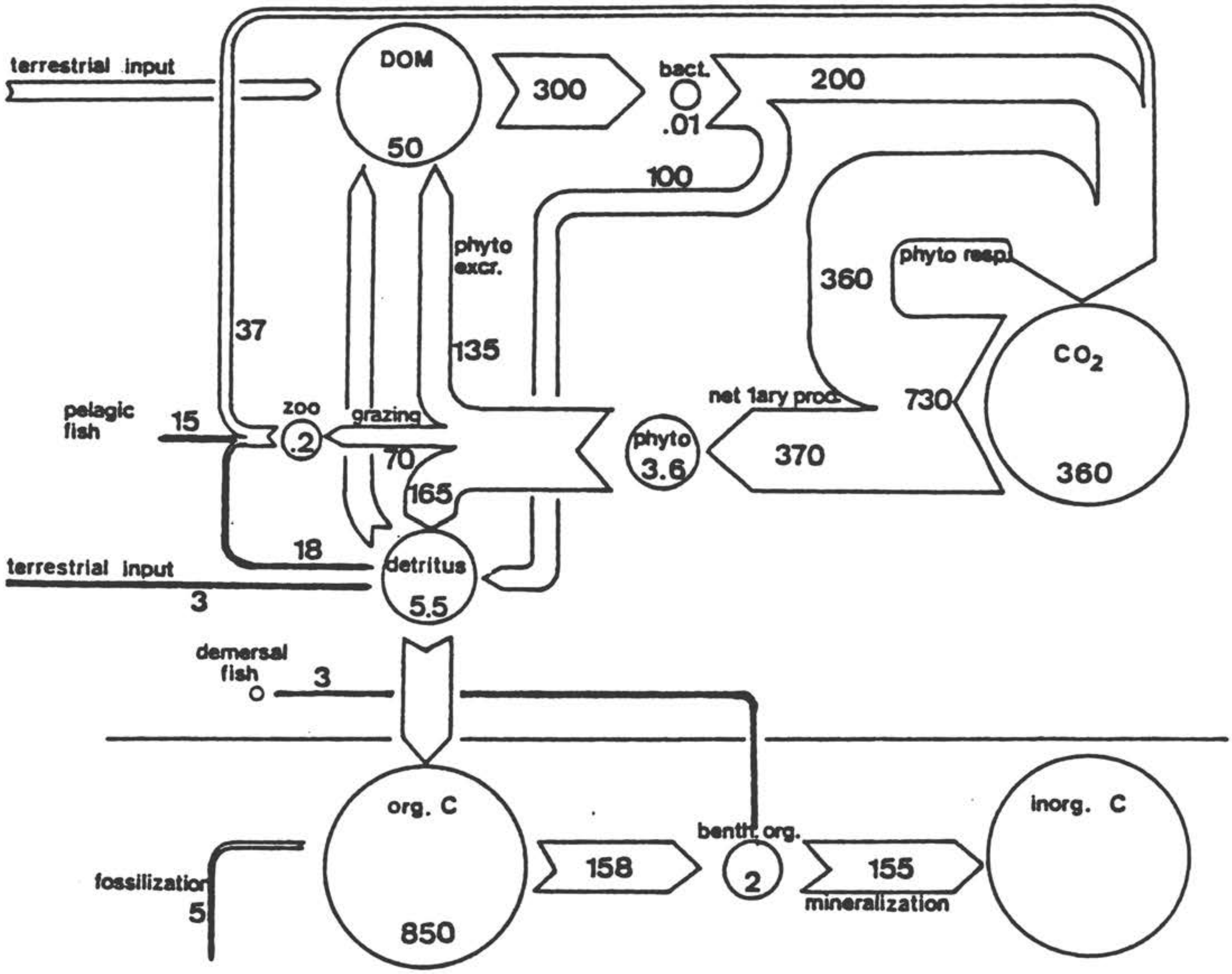

Figure 1: Schematic representation of organic matter cycling in the Belgian coastal region of the North Sea.
Fluxes in g C/m^{2}year; reservoirs in g C/m^2.
All figures given have been independently estimated so that the good balance of the overall circulation is not all trivial.
(Calculated from data of Organic Matter Group of the Actions de Recherche Concertées en Océanographie; Lancelot et al. (1980); Billen (1976); Nihoul et Polk (1976).

Primary Production

Primary production in coastal environments is generally much more important than in the ocean owing to a much greater nutrient availability. This results not only from external imports by river input or from upwelling but also from a greater efficiency in nutrient recycling in shallow systems. It is now well established that a considerable part (about 30%) of primary production is released in a dissolved form (phytoplanktonic excretion) (Lancelot, 1979).

By ultrafiltration techniques, Lancelot (in preparation) showed that 50 - 85% of dissolved primary production consists of high molecular weight (> 500) material.

Planktonic Heterotrophic Consumption

Heterotrophic consumption in the water column comprises zooplankton and bacterial activity.

Zooplankton graze living phytoplankton cells, but ingestion of detrital particles can also be of significance (Heinle et al., 1973; Poulet, 1976). As pointed out above, bacteria can use only dissolved low molecular weight substrates; detritus and high molecular weight dissolved organic matter can be ultimately degraded by bacteria only through the action of exoenzymes which hydrolyze them into smaller substrates.

The importance of direct grazing with respect of primary production has often been considered as a characteristic feature of marine ecosystems in contrast with terrestrial ecosystems (Odum, 1962; Crisp, 1964; Wiegert and Owen, 1971). However, it now becomes evident that, a least in coastal environments, zooplankton grazing does not account for all the phytoplankton mortality and that important pathways of organic matter recycling through detritus and bacteria exist in parallel with the pathway through herbivorous zooplankton (Banse, 1974; Pomeroy and Johannes, 1966, 1968; Joiris, 1978; Joiris et al., 1979). On the other hand, bacterial biomass systhesis can be an important process of particulate organic matter formation from DOC (fig. 1). Nothing is known, however, about the extent of grazing on bacteria in the marine environment.

Benthic Heterotrophic Consumption

Figure 2 summarizes the available data about the quantitative importance of organic matter degradation in marine sediments with respect to primary production. The decrease observed with water depth is obviously explained by the fact that with increasing depth, a higher percentage of the organic matter is degraded within the water volume. This leaves less nonrefractory organic matter available for recycling in the benthos. In shallow environments, up to 50% of the primary production can be recycled in the benthos. Fecal pellets and dead zooplankton have been generally considered as the most important source of organic material for the benthos (Steele, 1974). Balance calculations show, however, that for many shallow areas these sources cannot account for all the benthic activity. Direct input of phytoplanktonic material to the bottom occurs, either by passive sedimentation (Davies, in press), by feeding of benthic macroorganisms (Daro and Polk, 1973) or by processes like wave induced percolation of sea-water through the interstitial space of sediments (Steele _et_ _al_., 1970; Reidl _et_ _al_., 1972).

Most of the biological degradation of organic matter in sediments occurs in the upper 10 or 30 cm. Below this depth, a large concentration of biologically less available or inert organic matter remains and the bacterial population is dramatically reduced. The slow burial of organic matter within the sedimentary column constitutes a net loss of carbon for the marine environment.

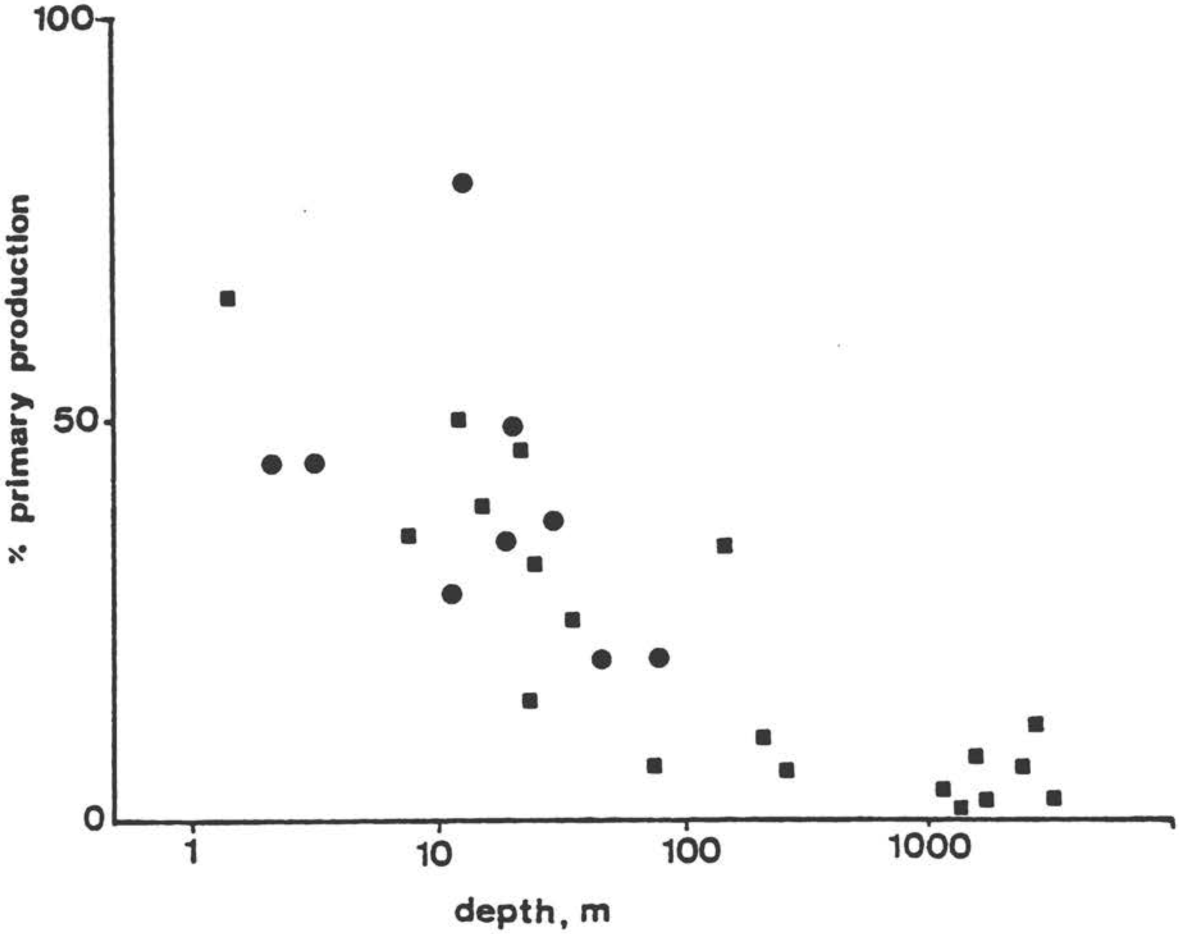

Figure 2: Amount of organic matter degraded by microbial activity in the sediments expressed in percentage of primary production in the water column, for marine (■) and lacustrine (●) environments as a function of the water depth. Data from Hargrave, 1973 and Billen, 1976.

Nonbiological Processes

In addition to the biological processes mentioned above, some physical or chemical processes can play a role in organic matter cycling.

Chemical reactions involving the organic constituents of seawater can be important in transforming labile substrates into refractory compounds as will be indicated later.

A possibly important physical process is particle formation from DOC. The possible role of bubbles in this process has been emphasized by many authors (Barber, 1966; Wheeler, 1975; Johnson, 1976). Adsorption on mineral particles may also be of significance (Suess, 1970; Meyers and Quinn, 1973).

THE IMPORTANCE OF RIVERBORNE ORGANIC CARBON IN C CYCLING OF COASTAL AREAS

In order to elucidate the behavior of dissolved and particulate organic carbon of terrestrial origin in shallow coastal waters, let us first evaluate the relative input of carbon transported by major rivers to these regions compared with the coastal primary production.

We have already underlined the differences that one may encounter with respect to the characteristics of the estuarine zone and similar effects are responsible for large variations in the primary production in the coastal zone. These include river input of nutrients, intensity of upwelling, high turbidity patches and instability of water masses due to local currents and turbulence. It is possible, however, to estimate a general trend by considering the problem on a global scale.

We have first selected the mean concentration of organic matter carried by rivers to the sea from independent but coherent evaluations found in the literature (Table II). Degens and Mopper (1976) consider that on the basis of a total concentration of organic matter in fresh water of 5 mg C/l, the transfer to the oceans may be 1.8×10^{14} g C/y. Garrels et al. (1975) have distinguished between particulate and dissolved organic carbon and propose river fluxes equal to 1.28 and 0.70×10^{14} g C/y respectively (total 1.98×10^{14} g C/y). Sharp (1975), on the basis of a few but well studied cases, considers that 2.0 mg C/l and 2.9 mg C/l are representative values for the concentrations of particulate and dissolved organic matter in estuarine waters reaching the sea. This would give fluxes of 0.64×10^{14} g C/y for POM and 0.93×10^{14} g C/y for DOM and a total of 1.57×10^{14} g C/y for a global river flow of 32×10^{12} m^3/y.

Duce and Duursma (1977) estimated that the global fluxes carried by rivers are equal to 1.1×10^{14} g C/y for the DOM, and 0.6×10^{14} g C/y for the POM. Taking into account the partial removal of this organic matter before reaching the sea, they proposed a maximum flux of organic matter ranging from 1 to 1.5×10^{14} g C/y.

TABLE II.

EVALUATION OF THE INPUT OF ORGANIC CARBON TRANSPORTED BY RIVERS TO THE COASTAL AREA (in 10^{14} c C/y)

AUTHORS	DISSOLVED INPUT	PARTICULATE INPUT	TOTAL INPUT
Garrels *et al.* (1975)	0.70	1.28	1.98
Sharp (1975)	0.93	0.64	1.57
Degens and Mopper (1976)	-	-	1.8
Duce and Duursma (1977)	1.10	0.60	1.70
Meybeck (this volume)	2.15	1.80	3.95

Finally, Meybeck (this volume) detailed calculations of the river fluxes and obtained an input of 2.15 x 10^{14} g C/y as dissolved organic matter and of 1.8 x 10^{14} g C/y as particulate organic matter. This study is by far the most abundantly documented and is therefore selected here.

If we compare the flux of particulate organic matter to the total suspended matter carried by rivers as given by Martin and Meybeck (1978) (15.5 x 10^{15} g C/y), we obtain a mean content of about 1% of organic carbon for the suspensions in the streams.

There are numerous measurements of primary production in coastal zones and several evaluations of regional annual productivities. Platt and Subba Rao (1975) have estimated the annual productivity of the marine microphytes divided into inshore and offshore zones. Their estimate of the average annual primary production of shelf regions (< 200 meters) is 183 g C/m^2 y. However, Fogg (1975) pointed out that Platt and Subba Rao have not taken extracellular products into account and their estimates may therefore be too low. To adjust for this contribution, Vooys (1979) found an overall correction of 20% for extracellular excretion, which would then correspond to a mean value of 37 g C/m^2 y of dissolved organic carbon produced in the shelf region. The planktonic primary production for the total coastal area extended to 30 x 10^6 km^2 becomes then 5.5 x 10^{15} g C/y.

On the other hand, Woodwell et al. (1973) calculated the global primary production of coastal marshes and open water regions in estuaries. According to these authors estuary production including the marshes would be 1.4 x 10^{15} g C/y. The total production of fresh organic matter in the coastal zone including all biotic elements would then be 8.0 x 10^{15}g C/y.

The comparison of this flux with the river flux shows that the terrestrial contribution of organic carbon in the coastal zone is only about 5% of the net primary production.

THE FATE OF TERRIGENOUS CARBON WITHIN COASTAL SYSTEMS

It follows from the preceding section that the flux of terrigenous organic matter to coastal systems is generally too low, with respect to primary production, to have more than a local influence on the structure of the food web of these systems.

The question now arising is whether the small flux of terrestrial organic matter is simply "metabolized" within the trophic chains of coastal systems or whether it accumulates to a large extent in some inert compartment. The fact that the terrigenous material reaching the sea has crossed the biologically very active estuarine system supports the idea that it is largely refractory organic carbon. As pointed out above, two big reservoirs of inert organic matter exist in coastal marine systems: refractory dissolved organic carbon and organic matter burried in deep sediments.

We will now examine to what extent terrigenous material contributes to the fluxes feeding these two inportant reservoirs.

Contribution of Terrigenous Organic Matter to Refractory Dissolved Organic Matter

It has been believed in the past that "gelbstoff" present in seawater simply consists at the terrigenous humic material transported by rivers (Shapiro, 1964). Some authors have even suggested the use of "gelbstoff" as a conservative tracer of the mixing of freshwater masses in seawater. This idea has been largely disproved on the basis of the following arguments:

On the one hand, as discussed above, it has been shown that most of the humic material present in river water flocculates at low salinities and does not reach the marine environment.

On the other hand, more detailed studies on the structure of marine "gelbstoff" have shown basic differences with terrestrial humic and fulvic acids. For instance, Sieburth and Jensen (1968) isolated yellow dissolved substances from coastal seawater and freshwater by adsorption on nylon and subsequent alkaline elution. The paper chromatogram from the two samples differed markedly. Khailov and Finenko (1970) made similar observations. Sieburth and Jensen (1969) suggested condensation of phenolic, proteinaceous and carbohydrate compounds present in seaweeds and excreta as a possible mechanism for the formation of marine "gelbstoff". Stuermer and Harvey (1974) isolated dissolved fulvic acid from the Sargasso Sea and from coastal Pacific water. Both of them differed markedly from soil fulvic acids and from marine sedimentary fulvic acids. The $\delta\ ^{13}C$ values (- 22.76 to - 23.7 %) indicated a marine origin.

"Gelbstoff" does not of course account for all refractory DOC. Processes other than formation of high molecular weight humiclike compounds have been suggested which could lead to biologically inert organic matter: metal ion complexes and intermolecular condensation reactions. No reason exists for believing that terrigenous organic matter could be preferentially involved in these processes. In fact, as shown by Williams and Gordon (1970) $\delta\ ^{13}C$ values of the bulk dissolved organic matter from various marine locations are in the range - 21.2 to - 24.4, and do not reflect the values found for dissolved and particulate organic matter transported by rivers (- 28.5 to 29.4 for the Amazon river).

Accumulation of Terrigenous Organic Carbon in Coastal Sediments

The mean content of organic carbon in coastal sediments is 1 - 5% (Degens and Mopper, 1976). If we consider 5% as a typical value for the freshly deposited material at the sediments interface, the global flux of POM from the water column to the sediment may be estimated by multiplying this value by the rate of sedimentation in the coastal zone. We know that the present day sedimentation rate on the shelf is unusually high due to the high sea-level and we estimate it close to 30 cm/1000 y. This gives a rate of deposition of 16×10^{15} g/y for the coastal zone which represents 80% of the present day total river input to the oceans (Martin and Meybeck, 1978). The rate of deposition of organic carbon would then be 8×10^{14} g C/y which corresponds to 10% of the primary production of the coastal zone. This evaluation is supported by the data presented in Figure 2, which suggests that for a mean depth of 100 meters corresponding to the mean water depth of the coastal zone, approximately 10% of the degradation occurs in the sediments whereas the remaining 90% occurs in the water column.

One can assume that the terrestrial particulate organic matter transferred by the streams into the sea is relatively refractory and thus not very much affected by biological degradation during its residence in the water column. A significant proportion of the particulate terrestrial organic carbon consists of the remains of plants (Gearing et al., 1977; Cadée , 1978) which are rather refractory to mineralization. For example, Van Bennekom et al. (1978) showed that only 1% of the organic matter transported by the Zaire is mineralized before sedimentation. Thus if we assume that all the terrestrial organic matter transferred by the rivers is deposited in the coastal zone, the flux, equal to 2×10^{14} g/y of particulate terrestrial organic matter represents approximately 25% of the total organic matter deposited.

This evaluation is well sustained by the distribution of $\delta\ ^{13}C$ in continental margin sediments (Nissenbaum and Kaplan, 1972; Gearing et al., 1977). The $^{13}C/^{12}C$ ratios reflect a definite terrestrial input very close to land; they decrease in an approximately logarithmic fashion with distance from shore (Gearing et al., 1977). As a mean, $\delta\ ^{13}C$ values of organic C in the coastal region (up to a few tens of kilometers off the coast) are about - 22‰, indicating a 20 - 30%

contribution of terrestrial material.

After deposition, the degradation of organic matter during the early diagenetic processes progressively reduces the organic carbon content. Even in anoxic sediments this reaction is quite fast. Berner (1980) showed that the mean residence time of organic matter in Long Island Sound sediments,a system dominated by sulfate reduction, was only 20 months. This value agrees well with independent measurements, based on ^{14}C material balance, of Turekian _et al_. (1980) in the same region. These authors obtained a mean residence time of 2.2 years and found no appreciable amounts of plankton derived carbon below 5 cm depth.

Billen (in press) calculated the rate of degradation of organic matter in the coastal sediments of the North Sea based on the rate of mineralization of nitrogen. It appears that the half life of organic nitrogen in the sediments is only one year in these less anoxic sediments and that only 20% of the initial amount of organic nitrogen is preserved.

On the other hand, one can expect that the organic fraction of the sediments is enriched in terrigenous organic matter burried, owing to the refractory nature of this material. Sweeney _et al_. (1976) have shown that this is indeed the case by measuring the isotopic composition of organic nitrogen in coastal sediments. Their results show that in sediment of the Santa Barbara Basin on the California continental shelf, where the input of terrestrial organic nitrogen has been estimated to be 25 - 50% of the total nitrogen input, it is the marine-derived nitrogen which is preferentially utilized by bacteria during early diagenesis. Terrestrial organic nitrogen seems to be entirely preserved.

To summarize, the various fluxes discussed here are presented in Figure 3 as a tentative global mass balance of organic carbon in the coastal zone.

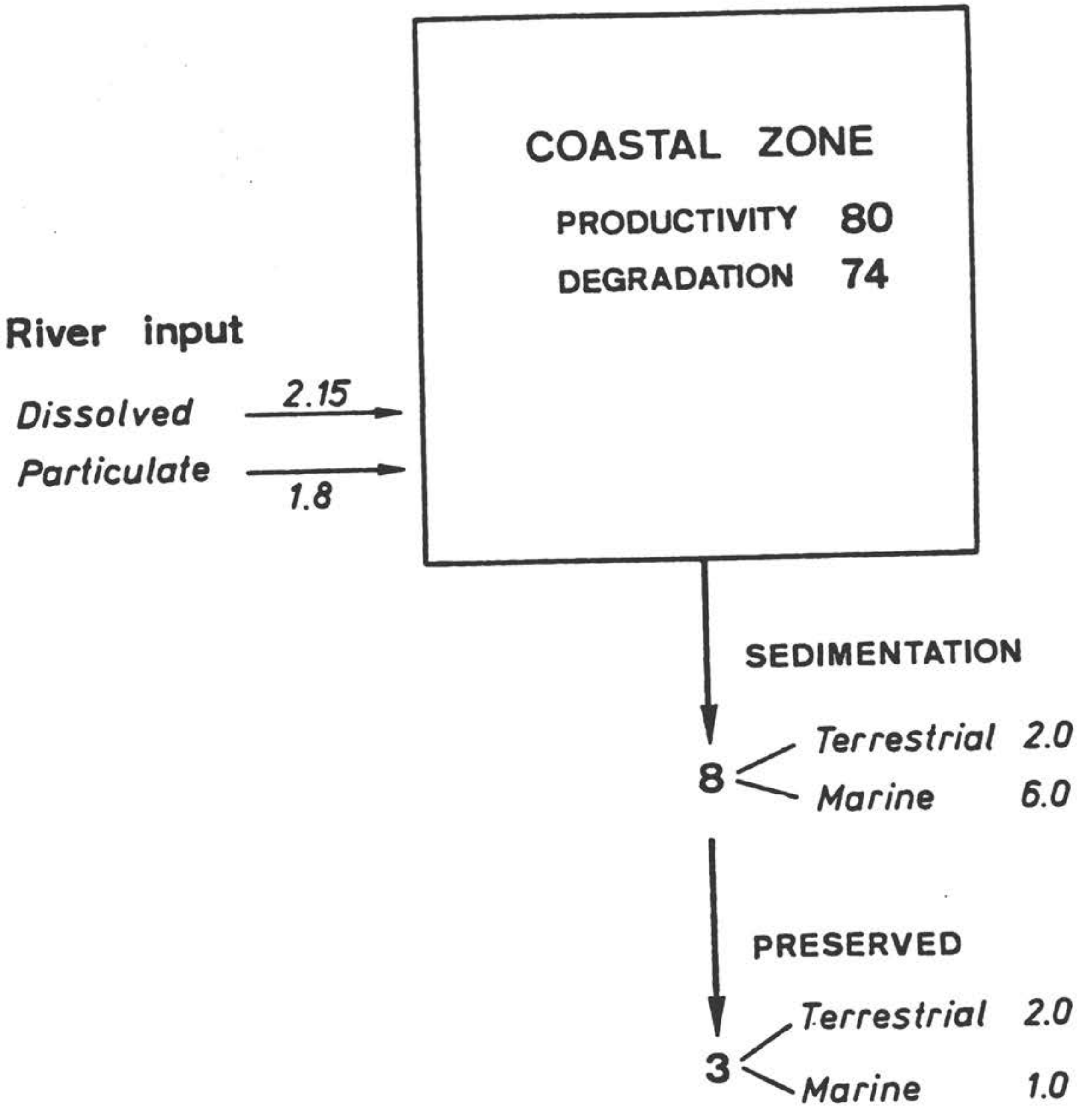

Figure 3: Tentative global mass balance of organic carbon in the coastal zone (in 10^{14} g C/y). The exportation of organic carbon to the open ocean is assumed to be negligeable at the present time except for dissolved organic carbon.

CONCLUSIONS

Terrigenous organic matter appears to play only a minor role in coastal marine systems:

Most of the material transported by rivers is either mineralized or sedimented within the estuarine zones.

The amount of this material which ultimately reaches the sea constitutes only a minor flux (about 3%) compared to the flux of organic matter produced in situ by primary production.

Terrestrial organic matter does not significantly modify, unless locally, the structure of the trophic web of caostal systems. Moreover, it consists essentially of refractory organic matter.

The particulate fraction of this refractory organic matter seems to have only a very limited residence time in the water column of the coastal environment. It is almost quantitatively deposited in sediments near to the coast, where it is preferentially accumulated.

The fate of dissolved organic matter from terrestrial origin in the coastal system is far less understood. However, it does not seem to influence significantly the composition of dissolved organic matter in the sea.

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GLOBAL CARBON CYCLE:

SOME MINOR SINKS FOR CO_2

Fred T. Mackenzie

Since about 1975, it has become evident that sinks other than the ocean and atmosphere may be responsible for storage of some CO_2 produced by activities of society. It is not likely that the increased fluxes of carbon associated with these minor sinks are substantial. However, a number of small sinks could play a role in alleviating what seems to be a present small imbalance in the estimates of the carbon cycle. The purpose of this paper is to assess the role of some minor sinks in storage of CO_2 produced from fossil fuel burning and other sources.

BACKGROUND

The burning of fossil fuels--coal, oil, and gas--and other anthropogenic sources of CO_2, such as net oxidation of the terrestrial biosphere because of deforestation, are responsible for an estimated increase in atmospheric CO_2 of about 14% during the last 100 years. The rate of atmospheric CO_2 increase is now about 1.5 ppmv per year. However, fossil fuel burning alone over the last century is estimated to have released to the atmosphere about twice as much CO_2 as the total atmospheric increase. There is considerable controversy concerning the role of the terrestrial biosphere as a net source or sink for atmospheric CO_2.

Estimates of annual biospheric CO_2 fluxes to the atmosphere range from about equal to that from fossil fuels to zero; some authors have the biosphere as a net sink. It seems likely that the terrestrial biosphere may have vacillated between acting as a source and as a sink of atmospheric CO_2 within the last century, although its exact role is a hotly debated topic today. The biosphere's role in the global carbon balance during the last two decades and on into the twenty-first century is critical to models that predict future atmospheric CO_2 levels.

Whatever the case, models of ocean uptake of CO_2 yield estimates of annual uptake over the last two decades of between 70 and 100% of the annual CO_2 increase in the atmosphere. Broecker's (1980 personal communication at a Department of Energy meeting, Washington, D.C.) most recent estimate of ocean uptake based on the GEOSECS (Geochemical Ocean Sections) transient tracer data leaves about 5 to 10% of the total fossil fuel CO_2 additions to the atmosphere unaccounted for (Table 1). All these ocean models currently assume that CO_2 simply dissolves into seawater and include no provision for CO_2 uptake as a result of reactions with carbonate solids in contact with shallow ocean waters, or organic carbon buried in sediments.

If Broecker's estimate is correct, the ocean as currently modeled is an inadequate or barely adequate sink for fossil fuel CO_2. If the terrestrial biosphere is a significant source of CO_2 for the atmosphere, the problem of the ocean as the only major sink of the missing CO_2 is exacerbated. Thus, it recently has become apparent that potential sinks other than the open ocean deserve attention.

Table 1 summarizes the balance problem for anthropogenic CO_2 and includes some flux estimates evaluated in this report or recently elsewhere (Broecker et al., 1979; Garrels and Mackenzie, in press). An important point to remember is that known additions of CO_2 to the atmosphere due to society's activities should be balanced by an equivalent increase in atmospheric CO_2 unless these societal contributions lead to a negative feedback and also increase fluxes of CO_2 out of the atmosphere. In terms of the CO_2 problem, it is necessary not only to determine the relative magnitudes of fluxes involved in the global cycle of CO_2 but also to demonstrate that fluxes into reservoirs other than the atmosphere have increased in magnitude since ancient times. If this can be shown, the fluxes associated with these processes can act as CO_2 sinks.

GLOBAL CARBON CYCLE

Figure 1 shows an updated version of the global carbon cycle, as derived from compilations of data from many sources, Fossil fuel burning alone results in release to the atmosphere of 420×10^{12} moles carbon per year; about 52 (± 0.04) % of this amount remains in the atmosphere, and 37 (± 0.04) % is taken up in the sea according to:

$$CO_{2(g)} + H_2O + CO_3^{=} = 2HCO_3^{-}.$$

TABLE 1 Man-related Fluxes of CO_2 to the Atmosphere Compared with Estimates of Increases in Fluxes of CO_2 to Potential Sinks (units of 10^{12} moles C y^{-1}) [a]

	Flux	Source	Sink (increase since ancient times; 100-200 to 1000 yrs. B.P.)
(1)	Fossil fuel burning	412-428	
(2)	Land use	0-415	
(3)	CO_2 solution in ocean		149-161
(4)	Dissolution of Mg-calcites in ocean mixed layer		0-8
(5)	Sequestering of organic C in continental and marine aquatic systems because of N and P additions to these systems (maximum from Walsh, in press)		0-60
(6)	Terrestrial organic C transport to marine systems and storage in marine sediments [b]		0-18
(7)	Terrestrial organic carbon storage in continental systems such as floodplains (crude estimate of increased flux based on present-day range of deposition of organic carbon in these systems)		0-7
(8)	Atmospheric increase		209-227
	TOTAL RANGE	412-843	358-456

[a] Estimates adapted from Bolin, 1977; Broecker et al., 1979; Garrels and Mackenzie, in press; Walsh, in press; Woodwell and Houghton, 1977; and this paper.

[b] See summary of estimates, no. 3, in section "Sequestering of Organic carbon." All the calculated organic carbon increased flux to sediments is considered to be due to this process. Because processes (6) and (7) are not resolvable from (5), their ranges are included in (5) and not included in total range.

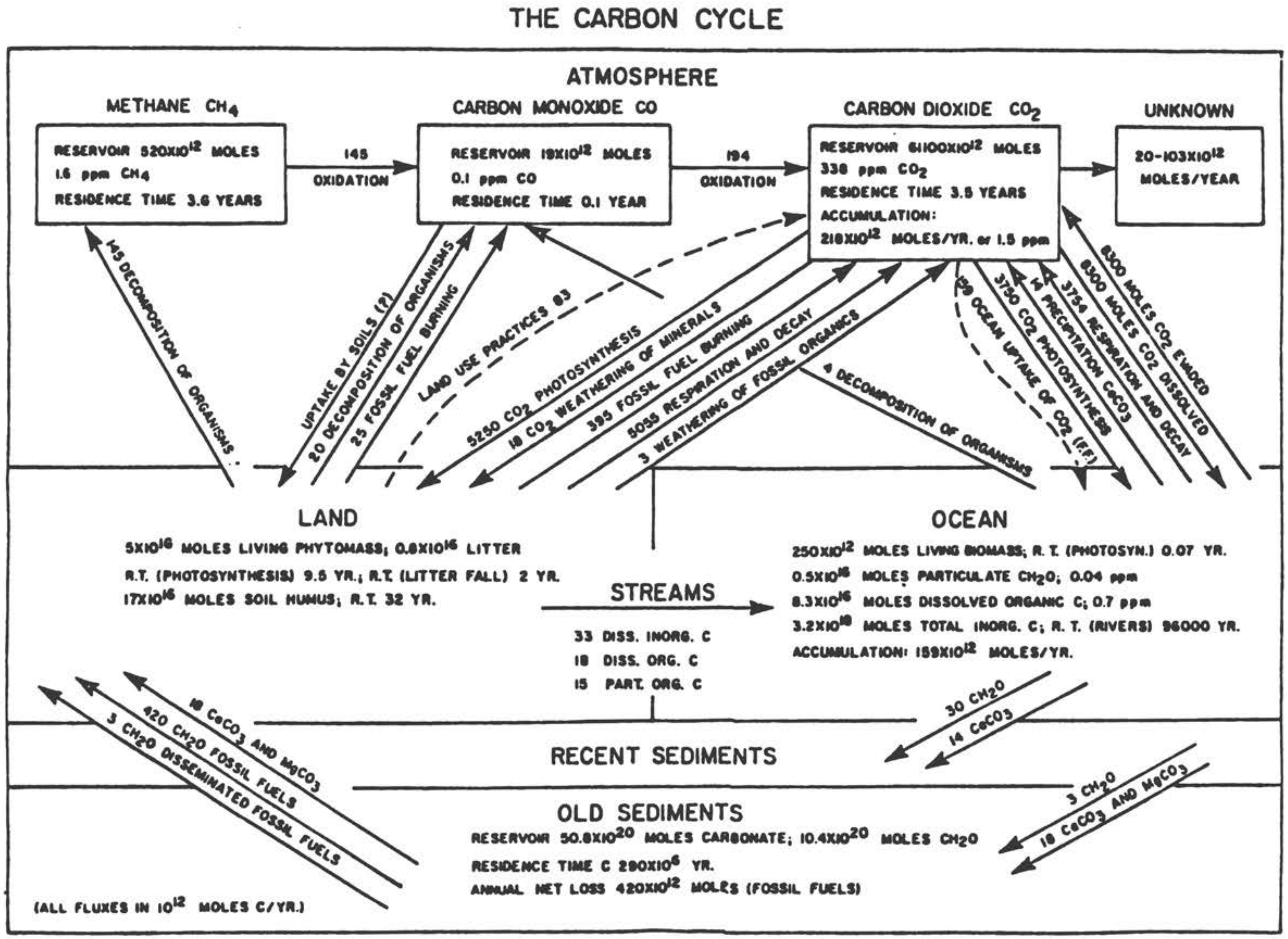

FIGURE 1 Global cycle of carbon. Compilation of data from several sources. Updated version of Figure 30, Garrels, Mackenzie, and Hunt, 1975.

The balance accounts for 89% of the annual release of carbon to the atmosphere from fossil fuel burning, leaving about 11% , or 47 x 10^{12} moles of carbon per year unaccounted for. Broecker et al. (1979(estimate that if carbon sequestered in sediments because of excess anthropogenic phosphorus (Garrels, Mackenzie, and Hunt, 1975; Mackenzie, 1975) is taken into account, then about 91 (± 0.07) % of the CO_2 released by the burning of fossil fuels can be taken care of by the processes of CO_2 solution in the ocean and organic carbon burial.

However, if during the recent past, practices involving land plants, such as deforestation and cultivation, have led to a net release of CO_2 to the atmosphere, the problem of balancing the carbon cycle is more difficult than the above scenario indicates. Using Bolin's (1977) estimate of 83 x 10^{12} moles C/y as the net release from the terrestrial biota, we find that the imbalance in the cycle could be as much as 130 x 10^{12} moles C/y. Thus, the possible range in imbalance of the global carbon cycle is 47-130 x 10^{12} moles C/y. (Figure 1; this figure shows a smaller range because of correction for estimates of increased fluxes of CO_2 due to solution of Mg-calcites in the ocean and organic carbon burial). This imbalance seems large for the last two decades. The question is whether any carbon dioxide sinks, in terms of increased CO_2 fluxes from the atmosphere, have been significantly underestimated or whether, heretofore, unevaluated sinks have played a significant role in resolving the balance. It may be a matter of a number of small fluxes due to different processes giving rise to a composite important flux.

SOME MINOR SINKS AND THEIR ROLE IN THE CARBON CYCLE

Inorganic Carbonate Reactions

The details of this sink are explained in a recent Department of Energy report (Garrels and Mackenzie, in press). In summary, reactions of CO_2 dissolved into the oceans according to

$$CO_2 \text{ increase} + \text{Mg-calcite} \dashrightarrow \text{increased dissolved } (Ca^{++} + Mg^{++}) + \text{increased dissolved C}$$

may amount to a few percentage points of the annual atmospheric increase. Probably an upper estimate of the flux associated with this sink is about 8×10^{12} moles C/y.

Sequestering of Organic Carbon

Following are various estimates of potential increases in organic carbon fluxes as a means of sequestering CO_2 generated by activities related to society. These increased organic carbon flux estimates are on the order of 10^{12}—10^{13} moles C/y, and could play a significant role in bringing the global carbon cycle into balance.

1. Phosphorus Balance

A. 4×10^{12} moles C y^{-1} organic carbon storage in coastal marine environments as a result of eutrophication. Based on the assumptions that 20% of the phosphorus input to the ocean of 0.12×10^{12} moles P y^{-1} (Pierrou, 1976) is derived from fertilizers and municipal wastes = 0.024×10^{12} moles P y^{-1} and that this phosphorus results in burial of sedimentary organic matter with an average C/P ratio of 150/1 (Simpson et al., 1977):

$$4 \times 10^{12} \cong 0.12 \times 10^{12} \times 0.20 \times 150.$$

B. 23×10^{12} moles C y^{-1} carbon storage in aquatic systems as a result of eutrophication. Phosphorus applied as fertilizer to soils (human excreta plus industrial fertilizers) is $\sim 0.4 \times 10^{12}$ moles P y^{-1}. An agricultural area of 14.7×10^{16} cm^2, from which is leached annually about 10 μg P cm^{-2} (Pierrou, 1976, Table 1) is used, and the total amount of phosphorus that enters aquatic systems because of fertilizer application is found to be 0.05×10^{12} moles P y^{-1}, or 12.5% of fertilizer phosphorus applied to the land's surface. Phosphorus injected directly into aquatic systems as sewage (0.04×10^{12} moles P y^{-1}) (Pierrou, 1976) is added to this value, and the total phosphorus entering aquatic systems is found to be 0.09×10^{12} moles P y^{-1}. If all this phosphorus led to growth and burial of organic matter with an average C/P of 250/1 (Broecker et al., 1979), this increased flux (23×10^{12} moles C y^{-1}) would be about 11% of the annual increase of CO_2 in the atmosphere:

$$23 \times 10^{12} \cong (0.05 \times 10^{12} + 0.04 \times 10^{12}) \times 250.$$

2. Nitrogen Balance

9×10^{12} moles C y^{-1} carbon storage in marine systems because of eutrophication. Based on global river discharge to the ocean of nitrate and organic nitrogen of 0.5×10^{12} and 0.4×10^{12} moles N y^{-1}, respectively, from agricultural areas (Söderlund and Svensson, 1976), and the assumption that <u>all</u> this nitrogen is consumed as nutrient to produce sedimentary organic matter with an average C/N of 10/1 (Simpson <u>et</u> <u>al</u>., 1977):

$$9 \times 10^{12} = (0.5 \times 10^{12} + 0.4 \times 10^{12}) \times 10.$$

Walsh (in press) estimates 60×10^{12} moles C y^{-1} storage in marine systems because of increased production of organic matter due to addition of nutrients to the ocean from man's activities. This value is 28% of the yearly increase of atmospheric CO_2.

3. Organic Carbon Storage in Marine Sediments

18×10^{12} moles C y^{-1} increased rate of organic carbon storage in coastal marine systems because of man's activities. Total coastal and nearshore sedimentation rate today is 154×10^{14}g y^{-1} (assuming 80% of total river suspended load of 183×10^{14} g y^{-1} is deposited in these regions and Milliman's (1974) estimate of

7×10^{14}g $CaCO_3$ y^{-1} Holocene shelf and reef deposition of carbonates). This total accumulation rate is equivalent to $50cm/10^3y$ distributed over an area of 30×10^{16} cm^2. Freshly deposited marine sediments contain about 5 - 6 wt% organic carbon (Heath _et al_, 1977, Figure 3; (Wollast and Billen, this volume); thus, the maximum rate of organic carbon sedimentation in coastal and shelf environments today is $\sim 80 \times 10^{12}$ moles C y^{-1}, which is equivalent to 13% of organic carbon production in these environments.

About 30% of the freshly deposited organic carbon is preserved in sediments (Wollast and Billen, this volume); the rest is returned to the water column by oxidation. Therefore, _accumulation_ of organic carbon in nearshore areas today is about 24×10^{12} moles C y^{-1}.

Organic carbon accumulation in pelagic and hemipelagic areas over the last few thousands of years may be estimated from the product of the areas of 268 and 63×10^{16} cm^2 for these environments, and their organic carbon accumulation rates of 10^{-3} and 10^{-1}g C $cm^{-2}/10^3y$ (Heath _et al_., 1977, Figure 3). The value obtained is $\sim 6 \times 10^{12}$ moles C y^{-1}. If we use the minimum Holocene estimate of Hay and Southam (1977) of 12×10^{12} moles C y^{-1} for total accumulation of organic carbon in oceanic sediments, the average Holocene nearshore accumulation rate is found to be 6×10^{12} moles C y^{-1}.

Calculations of this type indicate that the present coastal and nearshore organic carbon accumulation rate may be about 2-4 times greater than that of the recent past. The value of this increased flux is about 3-8% of the annual increase of atmospheric CO_2.

4. 7×10^{12} moles C y^{-1} stored in continental sediments resulting from increased carbon fluxes due to deforestation, agricultural cropping, and nitrogen and phosphorus fertilization activities of man.

5. Sewage
1×10^{12} moles C y^{-1} carbon storage in marine environment because of direct input of urban sewage to oceans. Based on New York City per capita sewage production of 1×10^3 moles carbon per year and a world urban coastal population of 1×10^9 people:

$$1 \times 10^{12} = 1 \times 10^9 \times 1 \times 10^3.$$

6. 13×10^{12} moles of carbon yr^{-1} produced as manure; mostly volatilized but a little stored.

7. Direct introduction of man-related CO_2 taken up in plant debris (terrestrial) to aquatic systems. Estimates 3 and 4 include this potentially increased flux.

8. Agricultural Crop Production
Potential for carbon storage is 9.1×10^{15}g crops y^{-1} with a carbon content of 50%; 12% harvested gives ∿ 46×10^{12} moles C y^{-1}; detritus represents 334×10^{12} moles C y^{-1}—

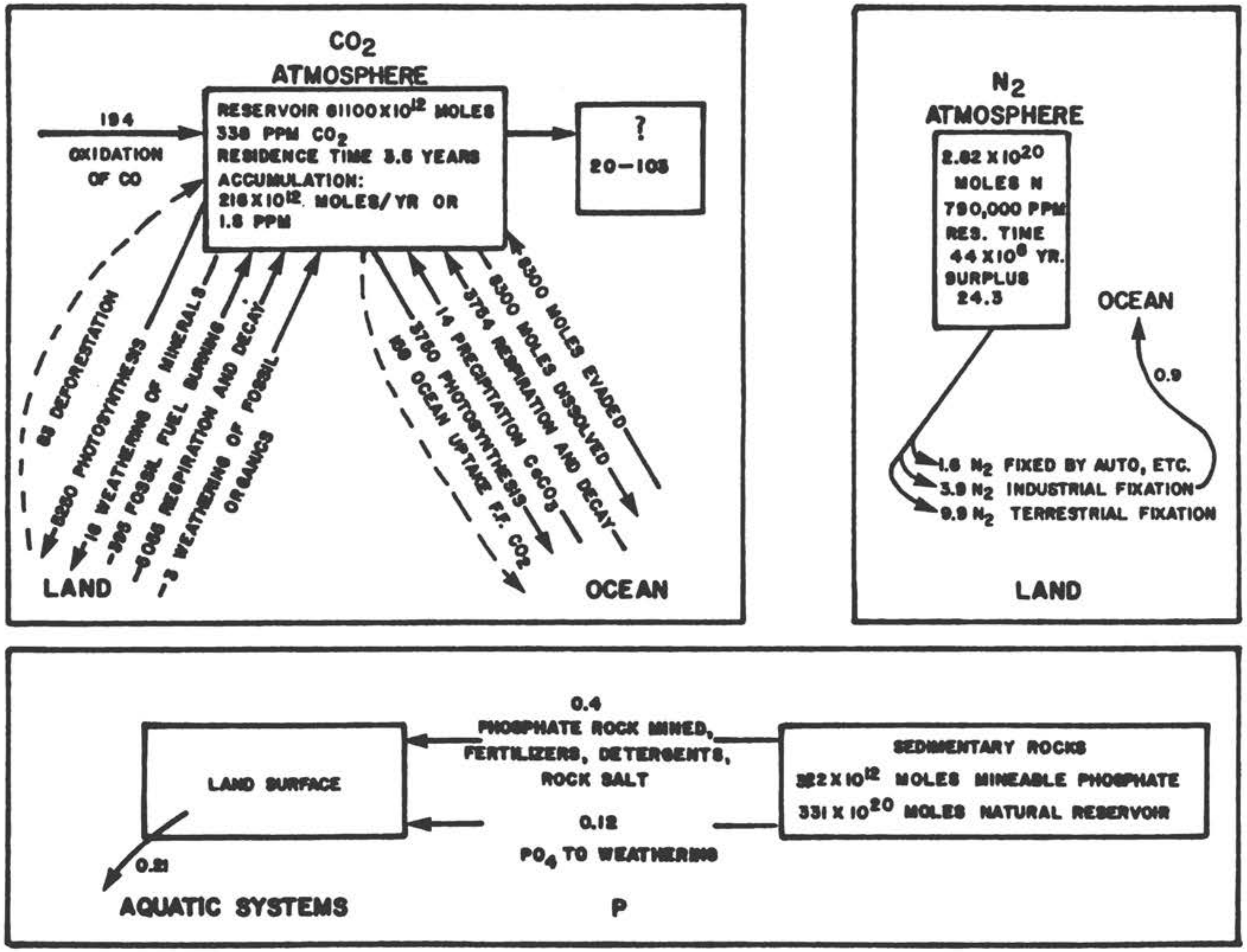

FIGURE 2 Portions of the global cycles of carbon, nitrogen, and phosphorus as related to increased fluxes of organic carbon to sediments because of addition of nutrients to the surface environment. All fluxes in units of 10^{12} moles y^{-1}. Adapted from Garrels, Mackenzie, and Hunt, 1975; Mackenzie, 1975.

small leakage from this system could be significant.

Phosphorus and Nitrogen Fertilization

The situation with respect to the interactions of the C, N, and P cycles and organic carbon as a sink for anthropogenic CO_2 is shown in Figure 2. For example, an estimate of phosphorus added to aquatic systems from municipal wastes and leaching of phosphate fertilizers is 0.09×10^{12} moles P/yr. If this P is used in plant photosynthesis with an average atomic ratio of C/P of 250:1, about 23×10^{12} moles of carbon would be utilized. If this carbon were "permanently" stored in sediments, the global sink of organic carbon would be increased by this amount. The range of values associated with this flux depends on the average C/P ratio used and the amount of phosphorus released to aquatic systems via fertilizers and municipal wastes. Walsh (in press) estimates that increased nutrient supply to the ocean because of runoff from agricultural lands and sewage discharge may have increased the flux of organic carbon to slope sediments by as much as 60×10^{12} moles C/y. This value seems to be an upper estimate.

It is possible that the tie between C, P, and N could result in a substantially increased flux of organic carbon in freshwater and marine systems. Thus, in terms of the "unknown" sinks, this item is an important loose end to nail down.

Marine Macrophytes

Smith (in press) notes that marine macrophytes may be an additional minor sink of carbon. The residence time of carbon

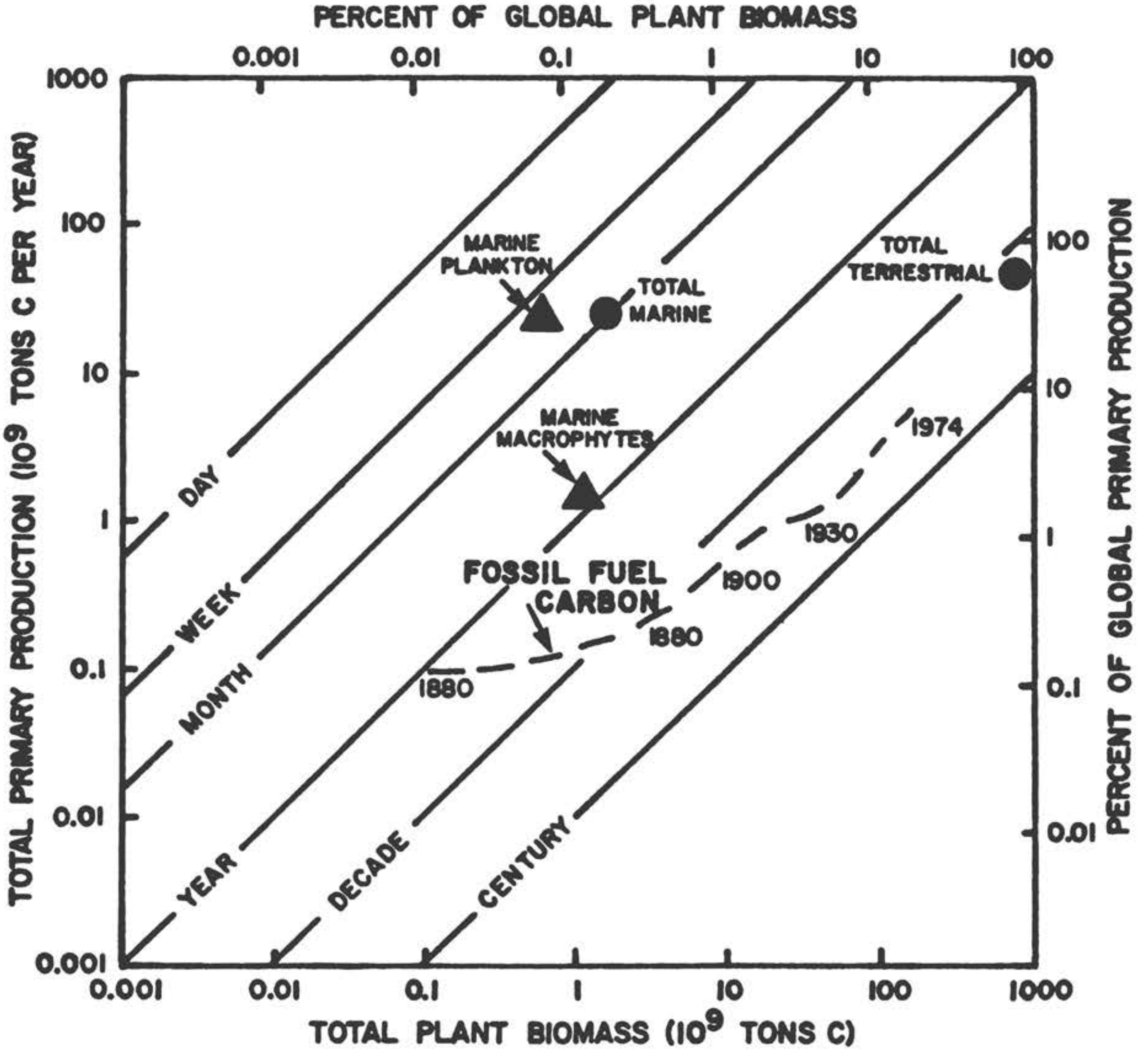

FIGURE 3 Primary production, biomass, and turnover time of carbon in the biosphere. Smith, 1980; adapted from Whittaker and Likens, 1973.

in the macrophyte (algae plus seaweed) reservoir is about 1 year, and its biomass is about 83 x 10^{12} moles C (Figure 3). The main question is whether net carbon input into this system has increased over the last 100 years or so by accelerated gas exchange across the air--sea interface and has thus increased production and burial of organic carbon. If the organic carbon in sediments has bacterially oxidized to CO_2, and if, in turn, this CO_2 has reacted with carbonate minerals to produce dissolved HCO_3^-, then the oxidation process need not result in CO_2 return during early diagenesis.

Soil Humus

Because of the size of the soil humus reservoir (170,000 x 10^{12} moles C) and its relatively long residence time with respect to organic C, small net changes in the size of this reservoir implies a large net flux. For example, changes in land use could result in changes in the magnitude of organic carbon fluxes related to the humus layer. It can be seen from Figure 4 that increases in desert and cultivated regions should result in shrinkage of the humus reservoir and an increase in the flux of carbon from the humus layer. Bolin (1977) suggested that cultivation practices have led to a net average carbon input to the atmosphere of about 25 x 10^{12} moles annually since the early nineteenth century. Current annual release of carbon from organic soils undergoing drainage as a result of man's activities is 3 to 31 x 10^{12} moles, whereas sequestering of organic carbon by undrained organic soils is estimated within an order of magnitude at 4 x 10^{12}

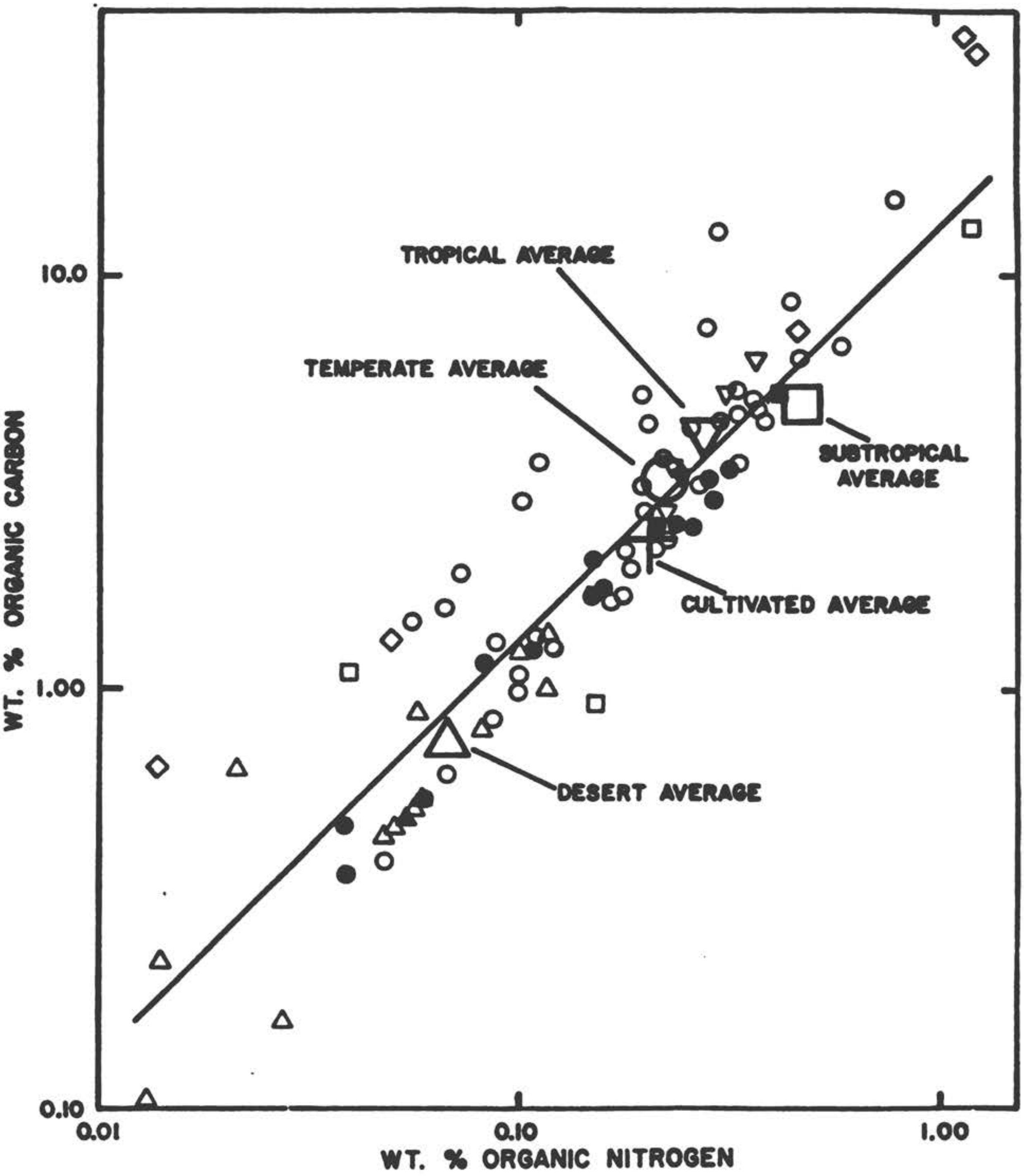

FIGURE 4 Relationship of carbon to nitrogen contents of soil organic matter.

Data from a variety of sources

	Uncultivated	Cultivated
Subtropical	□	■
Tropical	▽	▼
Temperate	○	●
Desert	△	▲
Arctic	◇	◆

moles (Armentano, 1980). Thus, the net exchange of carbon today from organic soils could be zero.

The organic carbon content of tropical-subtropical, temperate, and desert soils is related to the net primary production of these areas. Desert areas are least productive, and their soils are carbon-poor, whereas tropical-subtropical regions are most productive and have carbon-rich soils. Temperate production and soil organic carbon contents lie between these extremes. In general, the total organic carbon transported by streams draining these climatic areas reflects the organic content of the soils and primary production of these areas. Streams of arid areas carry little TOC, whereas streams of tropical wet regions are rich in TOC (Meybeck, this volume).

It is interesting to note that the average wt % C/N ratio of organic material in soils is about 13 (Figure 4). Recent marine sediments average 8-10 (Trask, 1932; Toth, 1976), whereas ancient sediments average 12-15 (Trask and Patnode, 1937). This similarity in C/N ratios of various types of organic materials makes it difficult to distinguish the sources of sedimentary organic matter on the basis of C/N ratios alone.

The important point is that the soil humus reservoir of organic carbon is large, and small changes in it could substantially affect the global carbon cycle.

EROSION RATES AND ATMOSPHERIC CO_2

Man has significantly increased the average erosional rate of land by agricultural and deforestation practices. In comparison with the erosional rates that prevailed during the immediate past, today's rates are a factor of two to three times greater (Judson, 1968; Garrels and Mackenzie, 1972). This increased erosional rate has presumably led to an increased rate of consumption of oxygen from the atmosphere, with a concomitant increase in the rate of CO_2 release to the atmosphere because of weathering of fossil organics.

Garrels et al. (1976) attempted to evaluate the effects of increased erosion on atmospheric CO_2. The changes in the CO_2 content of the atmosphere due to a threefold increase in the rate of land erosion as calculated from the Garrels-Lerman-Mackenzie model are shown in Figure 5. It can be seen from the figure that trebling the erosional rate can result in an increase in atmospheric CO_2 of about 2 1/2 times its present value, over a period of 2 million years. Thus, the effects of accelerated erosion, even though they must be considered on a time scale of several million years, are possibly greater than those due to fossil fuel burning in terms of O_2 depletion and CO_2 increase. Perhaps man's greatest long-term pollutional effects on the global environment may result from his practices leading to large changes in erosional rates on land.

Although the above model illustrates what can happen on a long-term basis, it has implications for the shorter term also. In the model, the cause of increased atmospheric CO_2

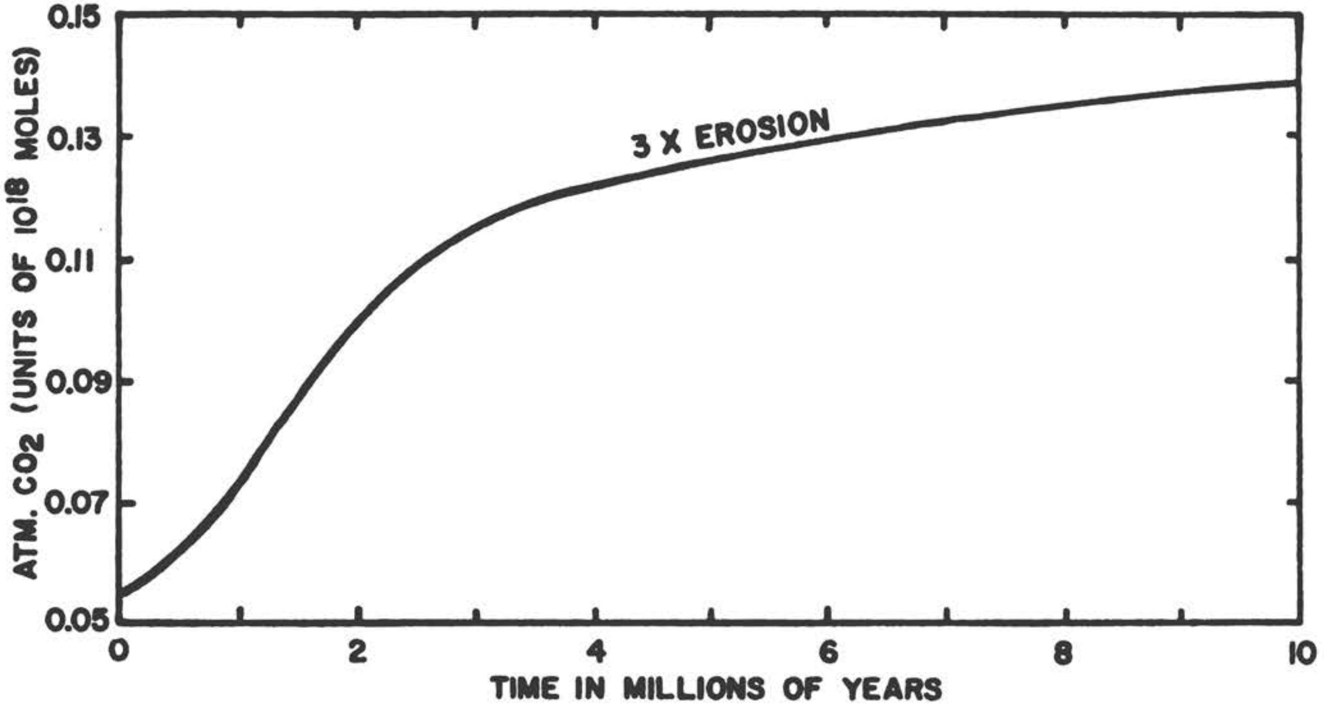

FIGURE 5 Increase in the CO_2 content of the atmosphere due to a threefold increase in the rate of erosion derived from Garrels <u>et</u> <u>al</u>., 1976.

is oxidation of fossil sedimentary organics in rocks. However, land use practices may lead to similar results on a shorter time scale. Cultivation, overgrazing, and deforestation practices leading to increased erosional rates may increase not only the weathering rate of fossil organics, which constitute a very small portion of the organic material in soils, but also that of the more abundant, younger humus matter in soils. This increased oxidation rate accounts for soils being a potential source of CO_2 to the atmosphere.

CONCLUSIONS AND RECOMMENDATIONS

The assessment of the global cycle of carbon indicates it may be out of balance by 0 to several hundred x 10^{12} moles C/y. If deforestation practices had not been important over the last two decades, the situation is much less acute. It is then possible to balance the cycle (Table 1): 52% (± 4%) of the fossil fuel CO_2 remains airborne; 37% (± 4%) dissolves into the ocean; 7% (± 7%) is sequestered as organic C in sediments of aquatic systems because of direct input of terrestrial organic carbon or because of increased organic production and burial resulting from increased nutrient supply to these systems; and 1% (± 1%) enters the oceanic mixed layer via dissolution reactions with Mg-calcites. If deforestation and cultivation practices were an important net source of carbon to the atmosphere in the past, or if these practices become important in the future, as anticipated, the balance situation is more complex, and the search for sinks more critical. However, even with our present crude knowledge of the nature of minor sinks of man-related CO_2 released to the atmosphere, and an optimistic estimate of the present collective magnitude of the fluxes related to these sinks, as much as 44 x 10^{12} moles carbon y^{-1} biospheric release to the atmosphere can be accounted for in the present global balance sheet for CO_2 (Table 1).

It appears that the minor sinks of anthropogenic CO_2 bear further investigation as to their nature and the amounts of increased carbon fluxes to them. In particular, we should investigate the source and fate of organic carbon in riverine and coastal marine ecosystems and the relationships among organic productivity, carbon burial, and increased nutrient supply to continental and marine systems becuase of man's activities. The problem is difficult; if all the 44 x 10^{12} moles C/y were sequestered in nearshore marine systems as organic carbon, this would amount to a layer only about 0.02 mm thick spread over the area of these systems. Total sedimentation in nearshore marine environments may be as much as 0.05 cm/y, or 25 times the thickness of the layer mentioned here. It is, indeed, like "looking for a needle in a haystack."

Acknowledgement

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