1004

Organic Acids in Aquatic Ecosystems
eds. E.M. Perdue and E.T. Gjessing, pp. 261–279
John Wiley & Sons Ltd

Spatial and Temporal Scales of Dissolved Organic Carbon in Streams and Rivers

J.R. Sedell[1] and C.N. Dahm[2]

[1]*USDA Forest Service*
Pacific Northwest Research Station
FSL Laboratory, 3200 Jefferson Way
Corvallis, OR 97331, U.S.A.

[2]*Department of Biology*
University of New Mexico
Albuquerque, NM 87131, U.S.A.

Abstract. Regional variation in riverine ecosystem dissolved organic carbon (DOC) concentration generally ranges from 0.5–40 mg C/l. Downstream concentrations of DOC within a catchment show no predictable general trends. Where anthropogenic activity increases as a river becomes larger, a general increase in DOC is apparent. In less disturbed river basins there does not appear to be a strong link between stream size and DOC concentration. The amount of swamps and wetlands within a basin strongly influences the amount of DOC. Small streams are more variable in DOC concentrations than larger streams and rivers. Historically, river floodplains and small streams retained more water and supported greater primary production which contributed more DOC to riverine ecosystems.

INTRODUCTION

Dissolved organic carbon (DOC) in freshwater ecosystems, normally the largest fraction of organic matter present, has long been a topic of interest to geochemists, limnologists, and stream ecologists (Thurman 1985). Quantification of specific components, structural characteristics, utilization as an energy resource by microbes, interaction with metals, and effects on the light spectrum are topics that have received considerable attention. Much, however, remains to be learned about the chemical structure of DOC in natural waters and the roles that DOC plays in the functioning of aquatic ecosystems. Recently, one role played by the largest component of DOC, the organic acids, has come under closer scrutiny. The role of organic acids as a source of acidity in natural waters has generally been considered to be relatively constant temporally. It has been suggested, however, that DOC is not temporally constant over the long term in areas receiving strong acid deposition and that DOC concentrations decrease as acidification proceeds.

Support for the hypothesis of decreasing organic acids in surface waters draining catchments with increasing, strong acid deposition has been presented from a lake survey of the eastern United States (Sullivan et al. 1988). The concentration of DOC decreased in the northeastern and upper Midwest sections of the United States across a gradient of increasing wet sulfur deposition. Paleolimnological evidence has also been put forth to argue that lake acidification is accompanied by a loss of organic matter (Davis et al. 1985). In other areas, notably eastern Canada and much of Scandinavia, a link between acidification of catchments and a decline in DOC has not been found. Historical changes in the amount and type of DOC within a drainage basin are difficult to infer or quantify and unequivocal linkage of long-term changes in DOC to acid deposition is still to be proven. In particular, distinguishing between DOC differences which are linked to varying land use patterns, vegetation type, soil type, and/or agricultural activities from those due to strong acid deposition can be problematic.

In this chapter, we will focus on sources of DOC, spatial variation in DOC concentration, and the temporal variability in concentration of DOC in streams and rivers in a variety of lotic environments worldwide. In addition, we will highlight historical changes in streams, rivers, riparian zones, and catchments which are very likely to have influenced the type and amount of DOC in surface waters over temporal scales comparable to those attributed to long-term acidification.

SPATIAL PATTERNS OF DOC IN STREAMS AND RIVERS

Meybeck (1982) estimated DOC transport by world rivers to the oceans. An average DOC concentration of 5.75 mg C/l was calculated from available data for large rivers. This is equivalent to a transport of 2150 kg of carbon as DOC annually from each square kilometer of land surface. This estimate of DOC concentration and transport was based upon data from only a few major rivers. These values, however, have held up well to a growing data set for rivers in a wide variety of climatic zones. A global average value for DOC of approximately 5 mg C/l remains a good estimate.

Regional variation in the concentration of DOC can range from less than 1 mg C/l to upwards of 30 mg C/l. For example, in North America, DOC concentrations in excess of 10 mg C/l commonly occur in streams and rivers draining regions with extensive wetlands such as swamps of the Atlantic Coastal Plain (Mulholland and Kuenzler 1979) or northern bogs (McKnight et al. 1985). Meyer (1986) has also studied blackwater streams and rivers in the southeastern United States where mean monthly concentrations of

DOC in the Ogeechee River ranged from 6–17 mg C/l. A small tributary to the Ogeechee, Black Creek, had an annual average DOC concentration of 30.8 mg C/l with occasional mean monthly concentrations exceeding 40 mg C/l. Streams draining forested upland catchments of the southeastern United States contained much lower concentrations of DOC. Mean annual discharge-weighted concentration of DOC for four small streams at Coweeta in North Carolina ranged from 0.60 to 2.33 mg C/l (Tate and Meyer 1983). Tate and Meyer (1983) also summarized mean discharge-weighted concentration of DOC from 14 montane catchments throughout North America. All 14 sites fell below the mean worldwide river average of 5 mg C/l with a range from 0.56–3.9 mg C/l. Other forested areas, such as boreal forest streams, have somewhat higher concentrations of DOC on average with typical DOC concentrations from 5–15 mg C/l.

Mulholland and Watts (1982) synthesized existing data from rivers and streams throughout North America to come up with an estimate of organic carbon transport to the oceans. Although their data are presented as total organic carbon (TOC), the bulk of the material in transport for most systems was probably in the DOC fraction. A range of TOC concentrations from 1.6–21.7 mg C/l was found for 1977 and 1978. Regional variation in annual export was primarily attributed to differences in annual runoff, but the concentration of DOC in various streams and rivers was not strongly correlated to discharge alone. In general, regional variations in DOC concentration can span the range from about 0.5–40 mg C/l.

The concentration of DOC also changes substantially as water is routed through a basin. McDowell and Likens (1988) have summarized the concentration data for DOC for precipitation, throughfall, soil solution, streamside seeps, and stream water in the Hubbard Brook Valley of New Hampshire. Precipitation contained on average 1 mg C/l. Throughfall concentrations averaged 12 and 34 mg C/l during two years of sampling. Upper eluvial soil horizons had an average DOC concentration of 28 and 38 mg C/l during two years of measurement. The upper B soil horizon had a DOC concentration of 6 mg C/l and the B horizon at 30 cm was 3 mg C/l. Seeps feeding Bear Brook had an average DOC concentration of 1.7 mg C/l while the stream average was 1.8 mg C/l. A dynamic range of DOC concentrations of about 40 times precipitation averages occurred within various zones of the catchment, but the average concentration of DOC in the stream was only 0.8 mg C/l above the precipitation average.

Spatial variation in DOC along the length of the Amazon River has been reported by Richey et al. (1980). During both rising and high water, the concentration of DOC was relatively uniform, averaging 4.2 and 6.5 mg C/l, respectively. The range of DOC values along a 2000 km transect during rising water was from 3.4–6.0. The range along a 3400 km transect during high water was from 3.9–9.9. Waters from the Rio Negro, a lowland region with an expansive floodplain, were normally about a factor of two higher than those in the mainstem Amazon. Overall, the water in the Amazon ranged from 3.4–9.9 mg C/l during these two cruises. No discernible downstream pattern was seen and a somewhat smaller range of DOC concentrations was found relative to North America or Europe. Downstream concentrations of DOC within a catchment have been observed to increase, decrease, or show no predictable changes dependent on the specific study. A general trend has not emerged. Where anthropogenic activity increases as streams and rivers grow larger, a general increase in DOC has been observed. In less disturbed environments, there does not appear to be a strong link between stream order and DOC concentration. Streams and rivers need not be accumulators of soluble organic material as they progress to the sea.

Streams are connected with their watersheds primarily through their interaction with the riparian component of the watershed. The nature of the river systems dictates that the form of this coupling is different between small streams and large rivers.

Small streams are linked to the landscape by virtue of their small size, relatively large surface area/volume ratio, and their great abundance relative to larger water courses. Changes in the hydrologic coupling and any degradation most often occur through removal of the riparian forest. Changes in the riparian forest affect throughfall, litter fall, and retention of organic inputs.

Large streams are often linked to the landscape by virtue of extensive floodplains and complex channel patterns. Because of their greater width and relatively short length, direct riparian inputs can be minimal under low flow conditions. Hydrologic decoupling and degradation occur through channelization or flow regulation, confining the river to a single channel and denying it annual or more frequent access to its floodplain. Many riparian litter and tree inputs that were referred to for small streams occur in an analogous way on the floodplain of large rivers. Large rivers go to the forest, rather than wait for forest inputs.

Rivers and streams have many different geomorphic reaches. Those reaches have varying abilities to influence DOC concentration. For example, gorges on highly constrained reaches of rivers do not interact with a floodplain, have high velocities, and have relatively small natural organic inputs into the reach from the edges. In a braided section, the river system is characterized by multiple channels, bars, and unstable islands, and the expected organic inputs and biomass from the floodplain are medium. In a meandering section of a river, a great diversity of abandoned channels, cut off meanders (oxbow lakes), side-arm sloughs, and marshes allows a mosaic of floodplain wetlands usually well connected hydrologically with the main with an expansive floodplain, were normally about a factor of two higher than those in the mainstem Amazon. Overall, the water in the Amazon ranged from 3.4–9.9 mg C/l during these two cruises. No discernible downstream pattern was seen and a somewhat smaller range of DOC concentrations was found relative to North America or Europe. Downstream concentrations of DOC within a catchment have been observed to increase, decrease, or show no predictable changes dependent on the specific study. A general trend has not emerged. Where anthropogenic activity increases as streams and rivers grow larger, a general increase in DOC has been observed. In less disturbed environments, there does not appear to be a strong link between stream order and DOC concentration. Streams and rivers need not be accumulators of soluble organic material as they progress to the sea.

Streams are connected with their watersheds primarily through their interaction with the riparian component of the watershed. The nature of the river systems dictates that the form of this coupling is different between small streams and large rivers.

Small streams are linked to the landscape by virtue of their small size, relatively large surface area/volume ratio, and their great abundance relative to larger water courses. Changes in the hydrologic coupling and any degradation most often occur through removal of the riparian forest. Changes in the riparian forest affect throughfall, litter fall, and retention of organic inputs.

Large streams are often linked to the landscape by virtue of extensive floodplains and complex channel patterns. Because of their greater width and relatively short length, direct riparian inputs can be minimal under low flow conditions. Hydrologic decoupling and degradation occur through channelization or flow regulation, confining the river to a single channel and denying it annual or more frequent access to its floodplain. Many riparian litter and tree inputs that were referred to for small streams occur in an analogous way on the floodplain of large rivers. Large rivers go to the forest, rather than wait for forest inputs.

Rivers and streams have many different geomorphic reaches. Those reaches have varying abilities to influence DOC concentration. For example, gorges on highly constrained reaches of rivers do not interact with a floodplain, have high velocities, and have relatively small natural organic inputs into the reach from the edges. In a braided section, the river system is characterized by multiple channels, bars, and unstable islands, and the expected organic inputs and biomass from the floodplain are medium. In a meandering section of a river, a great diversity of abandoned channels, cut off meanders (oxbow lakes), side-arm sloughs, and marshes allows a mosaic of floodplain wetlands usually well connected hydrologically with the main channel and with the aquifer. Because of the geomorphic stability and varied riparian forests, there is a high production of biomass.

Unconstrained reaches which have a high valley width/channel width ratio are more hydrologically retentive regardless of stream size. Both subsurface flow and surface area of water are greater in these areas. The primary production of the stream and floodplain vegetation is also high in these areas. These metabolic hotspots along a stream are characterized by lower gradients and often aggrading channels indicating reduced stream power.

TEMPORAL VARIATION IN DOC CONCENTRATION

Large Rivers

Annual variation in concentration of DOC in large rivers tends to be dampened by the hydrologic regime (Welcomme 1985). Spatial variations within the basin are often integrated into values which change only minimally during the year. Occasionally, however, hydrologic processes linking the expansive riparian areas to the main channels can contribute significantly to the concentration of DOC within the river. This can occur either during initial inundation of the riparian zones or during the falling limb of the hydrograph when stored water along the main channels drains back into the river. Examples of annual patterns of DOC concentrations in four large rivers are shown in Fig. 1. The four rivers are the Columbia, Ganges, Gambia, and Amazon and they drain large portions of the North American, Asian, African, and South American continents. Sampling locations and details of sampling methods and chemical analyses are given in Richey et al. (1980), Dahm et al. (1981), Lesack et al. (1984), and Ittekkot et al. (1985).

The Columbia River has a remarkably constant concentration of DOC throughout an annual cycle. A small increase in DOC concentration occurred in the late spring when runoff was peaking, but total variability was small. The entire range of DOC measured in 1973 and 1974 was from 1.81–2.47 mg C/l. The extensive network of large dams on the lower reaches of the river is a likely cause for the limited variation in the concentration of DOC on an annual basis. The other factor influencing the low DOC would be the limited floodplain area within this canyon-dominated river basin.

The Ganges River showed a much wider range of DOC values than the Columbia River (1.3–9.3 mg C/l). Oxbow lakes, ponds, and topographic depressions in the lower reaches of the river are hypothesized as major sources for increased DOC such as occurred in July 1981 (Ittekkot et al. 1985). When discharge is low, biogeochemical processes occurring within the wetted margins of the river, often under anaerobic conditions, result in

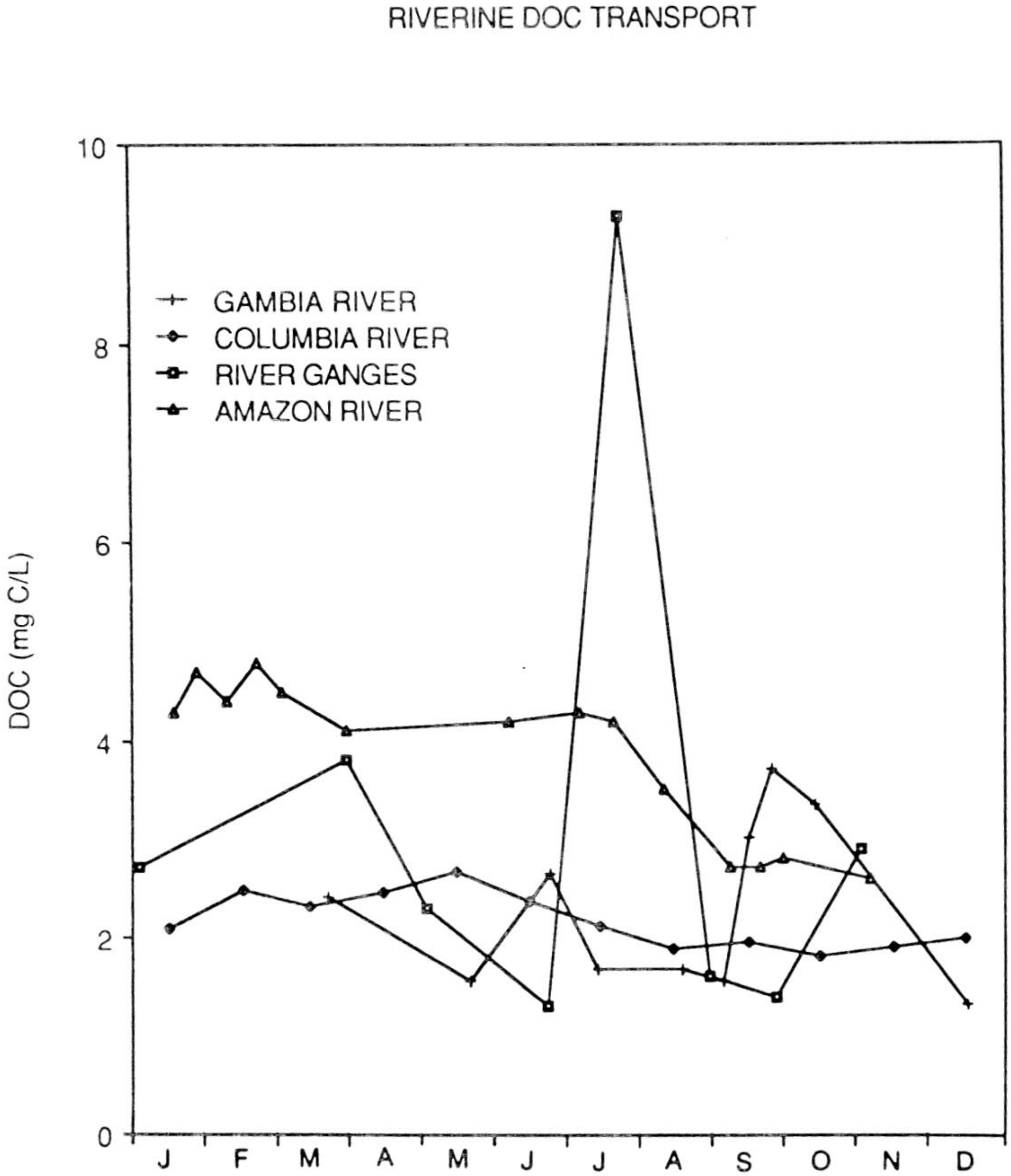

Fig. 1—Riverine concentration of DOC from the Amazon, Ganges, Gambia, and Columbia rivers over an annual cycle.

increased concentrations of DOC in those waters. With increasing water discharge from the river, the accumulated DOC is flushed out into the main channel through thorough mixing of river water with the previously isolated floodplain features. Chemical characterization of the DOC during various times of the year supports the conclusion that the wetlands adjacent to the main channel are major contributors of DOC to the river during periods of rising and high water.

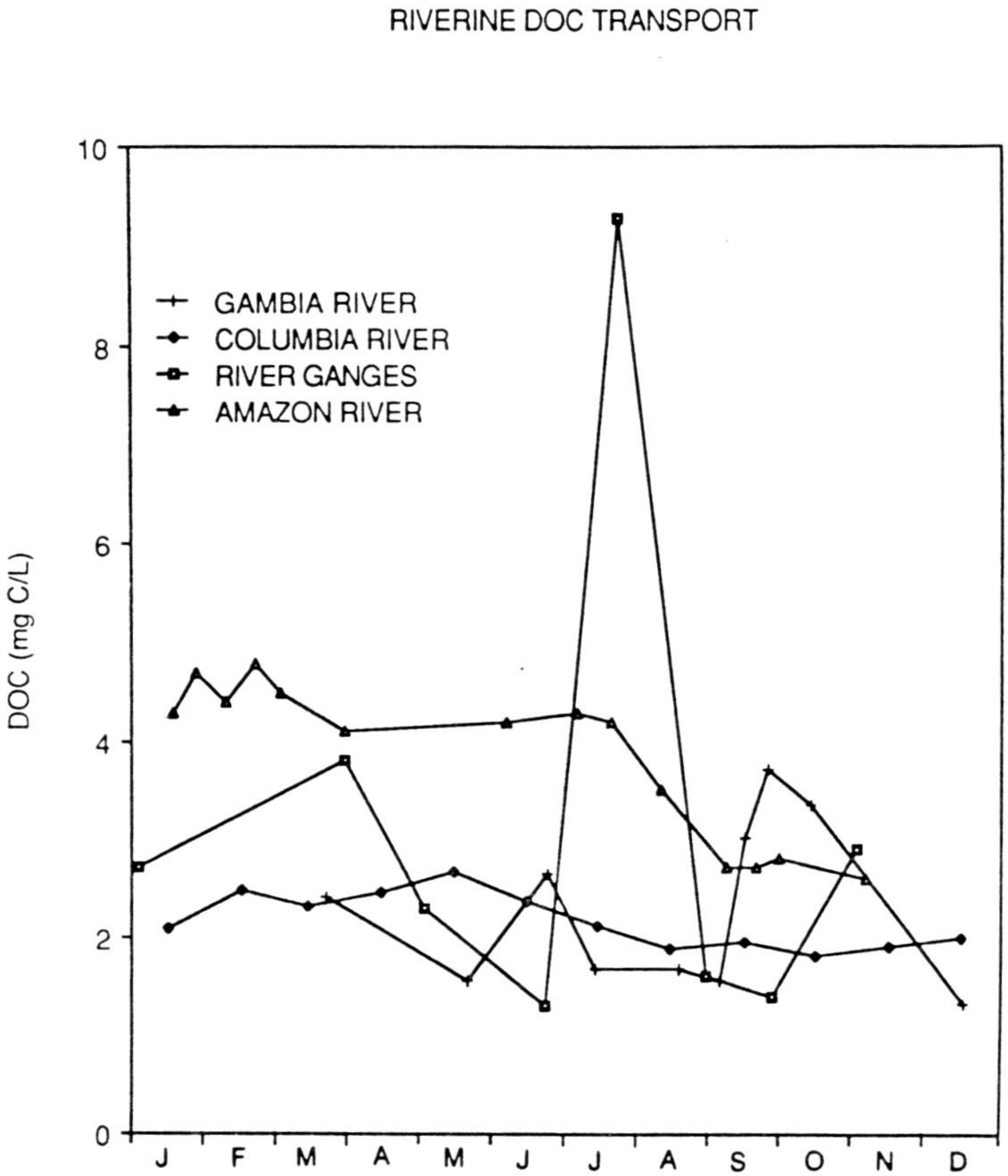

Fig. 1—Riverine concentration of DOC from the Amazon, Ganges, Gambia, and Columbia rivers over an annual cycle.

increased concentrations of DOC in those waters. With increasing water discharge from the river, the accumulated DOC is flushed out into the main channel through thorough mixing of river water with the previously isolated floodplain features. Chemical characterization of the DOC during various times of the year supports the conclusion that the wetlands adjacent to the main channel are major contributors of DOC to the river during periods of rising and high water.

The Gambia River had a somewhat smaller dynamic range of DOC concentrations than the Ganges, but much more variability than the Columbia River. The concentration range for DOC on an annual basis was 1.3–3.7 mg C/l in 1980–1981. A period of elevated DOC concentrations occurred from August to October while the minimum value occurred in December (Lesack et al. 1984). The concentration of DOC displayed counterclockwise hysteresis with rising and falling discharge (Fig. 2). Concentration of DOC peaked in late September (3.7 mg C/l) when discharge had fallen to about one-half the maximum level. Little change in DOC concentration was measured during the rising limb of the hydrograph. Minimum DOC

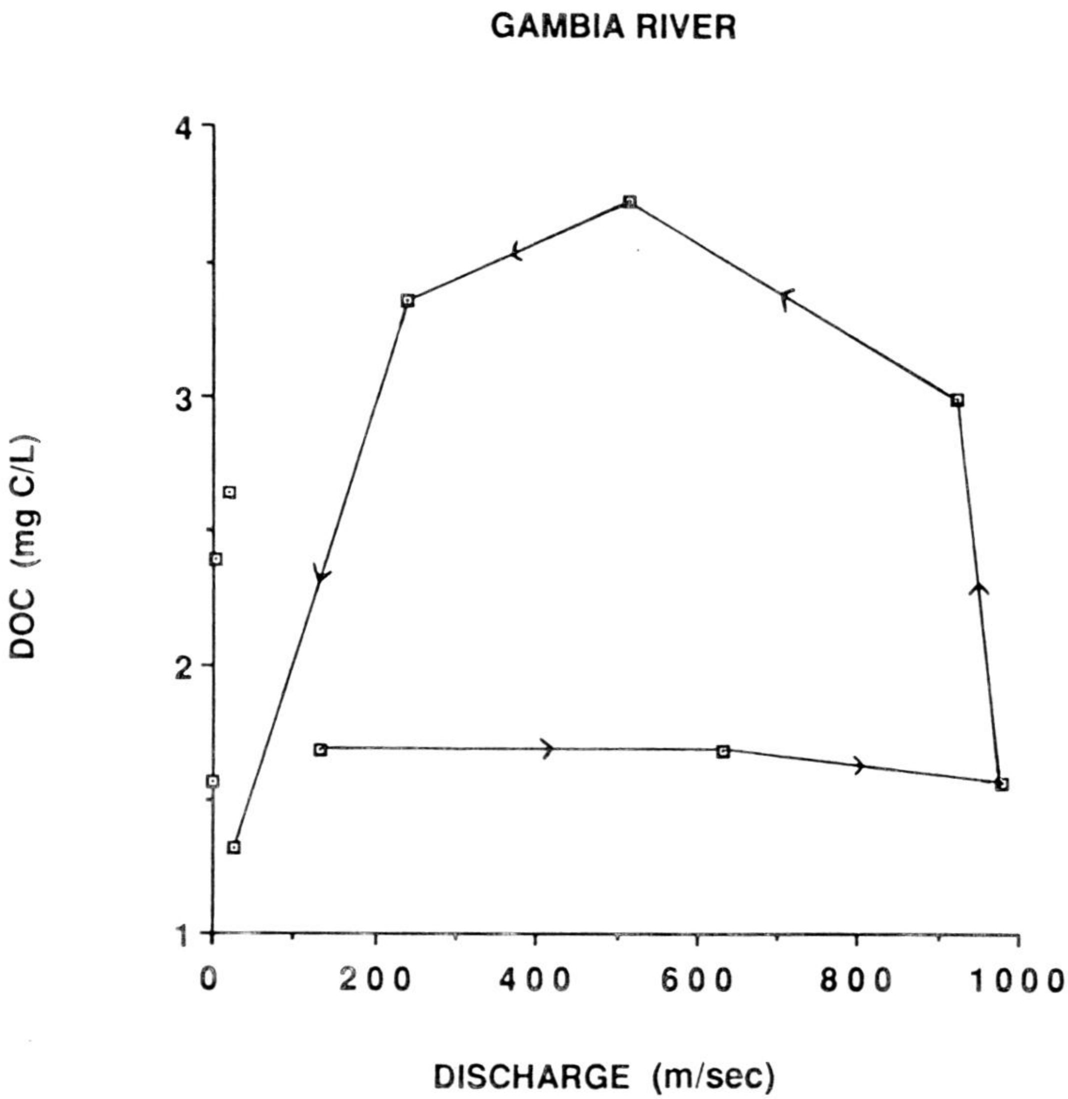

Fig. 2—DOC concentrations in the Gambia River display a counterclockwise hysteresis with rising and falling discharges due to draining DOC-enriched wetlands.

concentration was found to occur near lowest discharge rates for the river. In this river, the draining of DOC-enriched wetlands, marshes, and backwaters in the margins of the river, after peak discharge, as the likely source for the increased DOC and counterclockwise hysteresis with discharge.

The annual pattern for DOC concentrations in the Amazon River in 1983 upstream of the Rio Negro is shown in Fig. 1, and the relationship between riverine discharge and DOC is shown in Fig. 3 (unpublished data provided by A.H. Devol and J.E. Richey, University of Washington, Seattle, WA). The patterns are very compatible with those reported by Furch (1985).

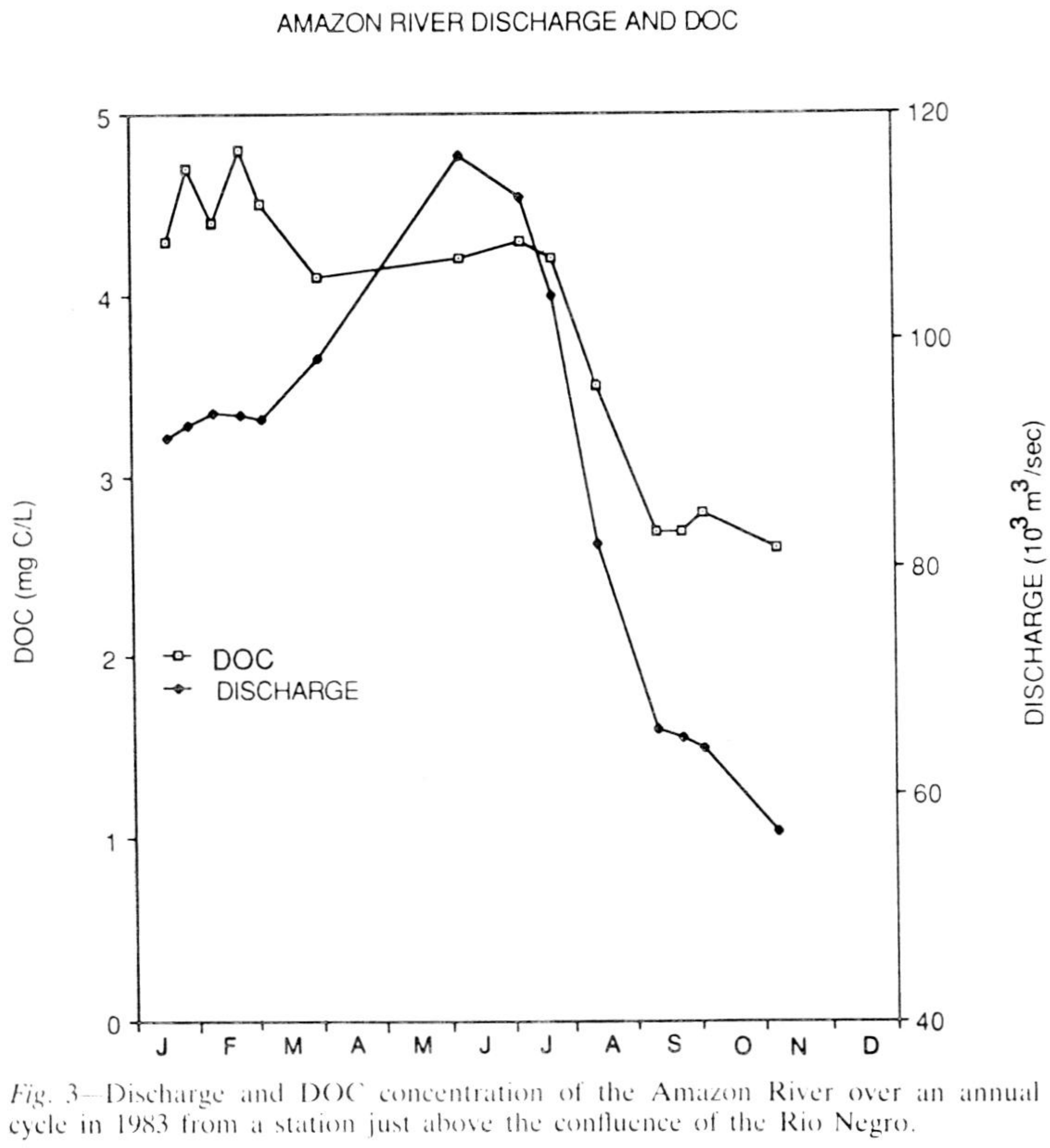

Fig. 3—Discharge and DOC concentration of the Amazon River over an annual cycle in 1983 from a station just above the confluence of the Rio Negro.

concentration was found to occur near lowest discharge rates for the river. In this river, the draining of DOC-enriched wetlands, marshes, and backwaters in the margins of the river, after peak discharge, as the likely source for the increased DOC and counterclockwise hysteresis with discharge.

The annual pattern for DOC concentrations in the Amazon River in 1983 upstream of the Rio Negro is shown in Fig. 1, and the relationship between riverine discharge and DOC is shown in Fig. 3 (unpublished data provided by A.H. Devol and J.E. Richey, University of Washington, Seattle, WA). The patterns are very compatible with those reported by Furch (1985).

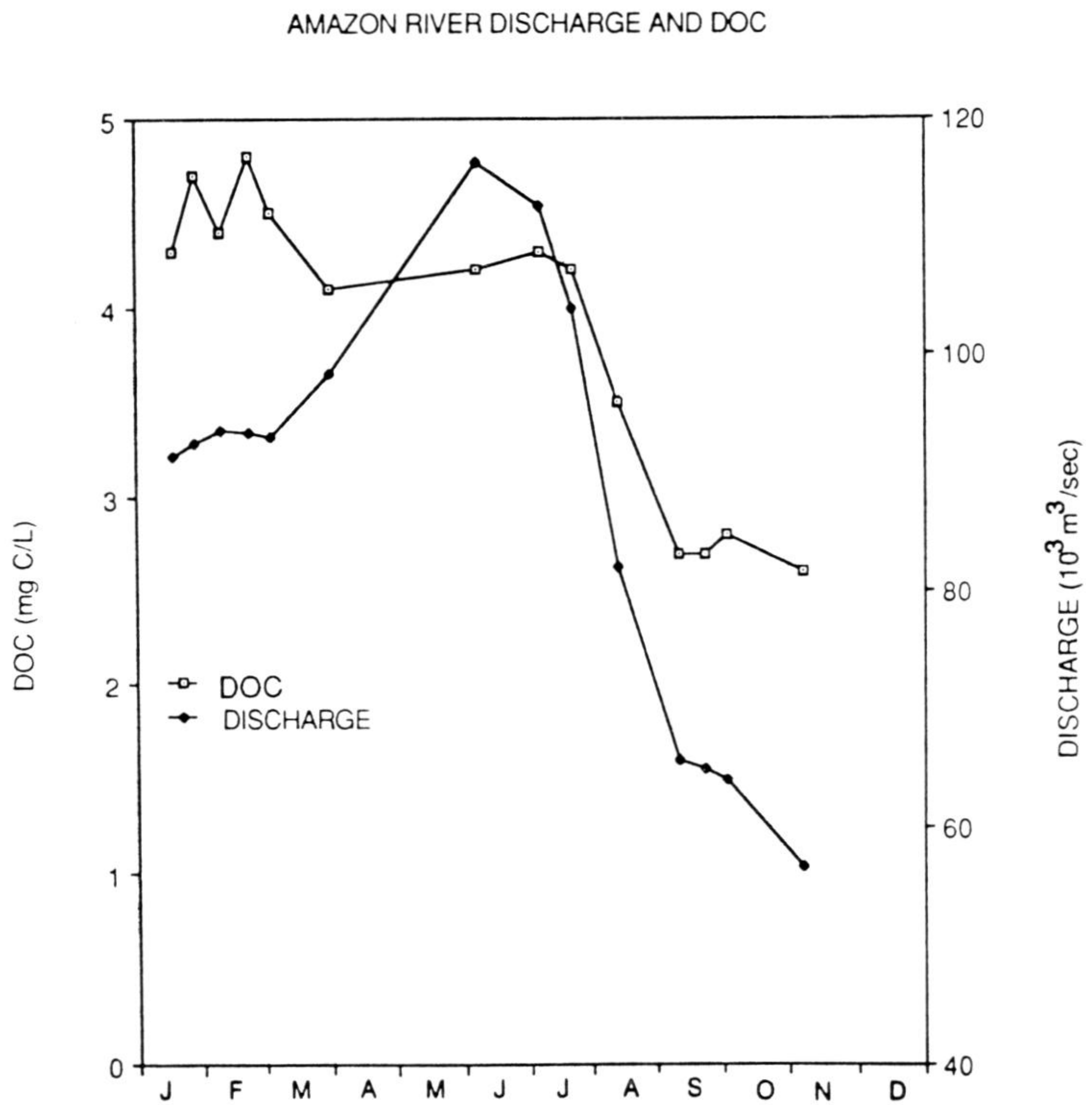

Fig. 3—Discharge and DOC concentration of the Amazon River over an annual cycle in 1983 from a station just above the confluence of the Rio Negro.

Concentrations of DOC are above 4.0 mg C/l during the rising limb and high water times of the hydrograph. As the river recedes, DOC concentrations decline to values consistently less than 3.0 mg C/l during the low water phase. Hysteresis in this section of the Amazon is clockwise with increases in DOC during rising discharge and decreases in DOC as discharge declines.

Intermediate-sized Rivers

We define intermediate-sized rivers on the basis of catchment areas between 10^2–10^5 km^2. Examination of the hydrographs for intermediate-sized rivers indicates discharge spikes which are more accentuated than those of large rivers and which persist for days to weeks. The variation of DOC on an annual basis shows a wider dynamic range than for big rivers but a smaller range than for little streams and small rivers. Mean DOC levels in this river size reflect both water storage in adjacent wetlands and primary production on the floodplain.

Good examples of the annual variation of DOC in intermediate-sized rivers are found in the northeastern and southeastern U.S. In the northeastern U.S., Fisher (1977), studying the Fort River (107 km^2), and Klotz and Matson (1978), investigating the Shetucket River (1330 km^2), found that DOC levels varied inversely with discharge and ranged from 1.7–14.8 and 2.1–18.3 mg C/l, respectively. Generally, the summer and fall low flows had high DOC levels. Both of these rivers are moderately urbanized and have extensive woodlots in the catchment area.

In the southern U.S., DOC levels can average from between 2–4 mg C/l in semiarid areas to between 10–27.6 mg C/l in the productive bottomland hardwood forests of the Southeastern and Gulf Coast. Aside from the climate, which drives higher or lower rates of primary production, river floodplain interactions play a role in the annual DOC variation. For example, the Brazos River (90,000 km^2) drains a semiarid region that is dewatered, channelized, dammed, and has had much of its riparian vegetation removed. The mean annual DOC concentration is about 3.3 mg C/l, and its annual variability is 1.7–7.7 mg C/l (Malcolm and Durum 1976). The DOC levels on an annual basis reflect a clockwise hysteresis with DOC increasing with discharge to a maximum peak point, then declining before peak discharge. This river is highly eutrophic, and there is a suggestion that DOC concentrations are low because of enhanced bacterial activity, but a limited source region of terrestrial vegetation adjacent to the channel may be a likely reason. The Sopchoppy River (264 km^2) in a rich bottomland hardwood forest varies annually between 6.2–52.0 mg C/l and has a mean of 27 mg C/l (Malcolm and Durum 1976). This river exhibits an annual

DOC pattern that has an almost direct relationship with discharge. This indicates to us a wide, rich floodplain with very little levee development and hence a higher hydrologic connectivity between the river channel and floodplain.

We use these data to illustrate the comparison with big river DOC, showing accentuated annual variability and high terragenic primary production results in higher concentrations of DOC.

Small Streams and Rivers

Streams also show distinctive variability in the concentration of DOC on the scale of hours to a few days in addition to the weekly and seasonal patterns common to rivers. Storms are important regulators of DOC concentration in streams. In general, DOC concentrations increase during the rising limb of a hydrograph. The relative response of the concentration of DOC during a storm is also linked to antecedent precipitation within the basin, season, and hydrology of the catchment during storms. Mechanisms which have been postulated to explain the observed increase in DOC during storms include (*a*) channel flushing and elongation, (*b*) changes in the flow path of water through the soil, (*c*) input of throughfall directly entering the stream, and (*d*) flushing of the hyporheic zone into the stream.

Figure 4 shows an example of the response of DOC concentrations within a first-order stream in western Oregon to a series of small storms over a two-week period in September 1977. The storms followed a time of dry weather when the concentration of DOC was generally 2–3 mg C/l. An initial gradual increase in discharge to approximately four times baseline was accompanied by an increase in DOC to 7–9 mg C/l. A more intense storm increased discharge more than an order of magnitude from baseline and a maximum concentration of DOC was measured during the rising limb of the hydrograph during this storm. The concentration of DOC reached 24.6 mg C/l and then decreased to 4.47 mg C/l on the falling limb of the hydrograph after the storm ended. Increases in the concentration of DOC up to one order of magnitude above background values can occur in association with storm flows.

Another factor which has been shown to cause daily fluctuations in the concentration of DOC in small streams is algal primary production (Kuserk et al. 1984). Early morning minima were followed by a mid-afternoon peak in a second-order stream in a pasture with a verdant streambed community. Diel increases in DOC of 35–66% were measured at six stations along the stream. Photochemical reactions might also produce diel patterns in DOC concentrations in some streams, but such a linkage has yet to be shown conclusively.

DOC pattern that has an almost direct relationship with discharge. This indicates to us a wide, rich floodplain with very little levee development and hence a higher hydrologic connectivity between the river channel and floodplain.

We use these data to illustrate the comparison with big river DOC, showing accentuated annual variability and high terragenic primary production results in higher concentrations of DOC.

Small Streams and Rivers

Streams also show distinctive variability in the concentration of DOC on the scale of hours to a few days in addition to the weekly and seasonal patterns common to rivers. Storms are important regulators of DOC concentration in streams. In general, DOC concentrations increase during the rising limb of a hydrograph. The relative response of the concentration of DOC during a storm is also linked to antecedent precipitation within the basin, season, and hydrology of the catchment during storms. Mechanisms which have been postulated to explain the observed increase in DOC during storms include (*a*) channel flushing and elongation, (*b*) changes in the flow path of water through the soil, (*c*) input of throughfall directly entering the stream, and (*d*) flushing of the hyporheic zone into the stream.

Figure 4 shows an example of the response of DOC concentrations within a first-order stream in western Oregon to a series of small storms over a two-week period in September 1977. The storms followed a time of dry weather when the concentration of DOC was generally 2–3 mg C/l. An initial gradual increase in discharge to approximately four times baseline was accompanied by an increase in DOC to 7–9 mg C/l. A more intense storm increased discharge more than an order of magnitude from baseline and a maximum concentration of DOC was measured during the rising limb of the hydrograph during this storm. The concentration of DOC reached 24.6 mg C/l and then decreased to 4.47 mg C/l on the falling limb of the hydrograph after the storm ended. Increases in the concentration of DOC up to one order of magnitude above background values can occur in association with storm flows.

Another factor which has been shown to cause daily fluctuations in the concentration of DOC in small streams is algal primary production (Kuserk et al. 1984). Early morning minima were followed by a mid-afternoon peak in a second-order stream in a pasture with a verdant streambed community. Diel increases in DOC of 35–66% were measured at six stations along the stream. Photochemical reactions might also produce diel patterns in DOC concentrations in some streams, but such a linkage has yet to be shown conclusively.

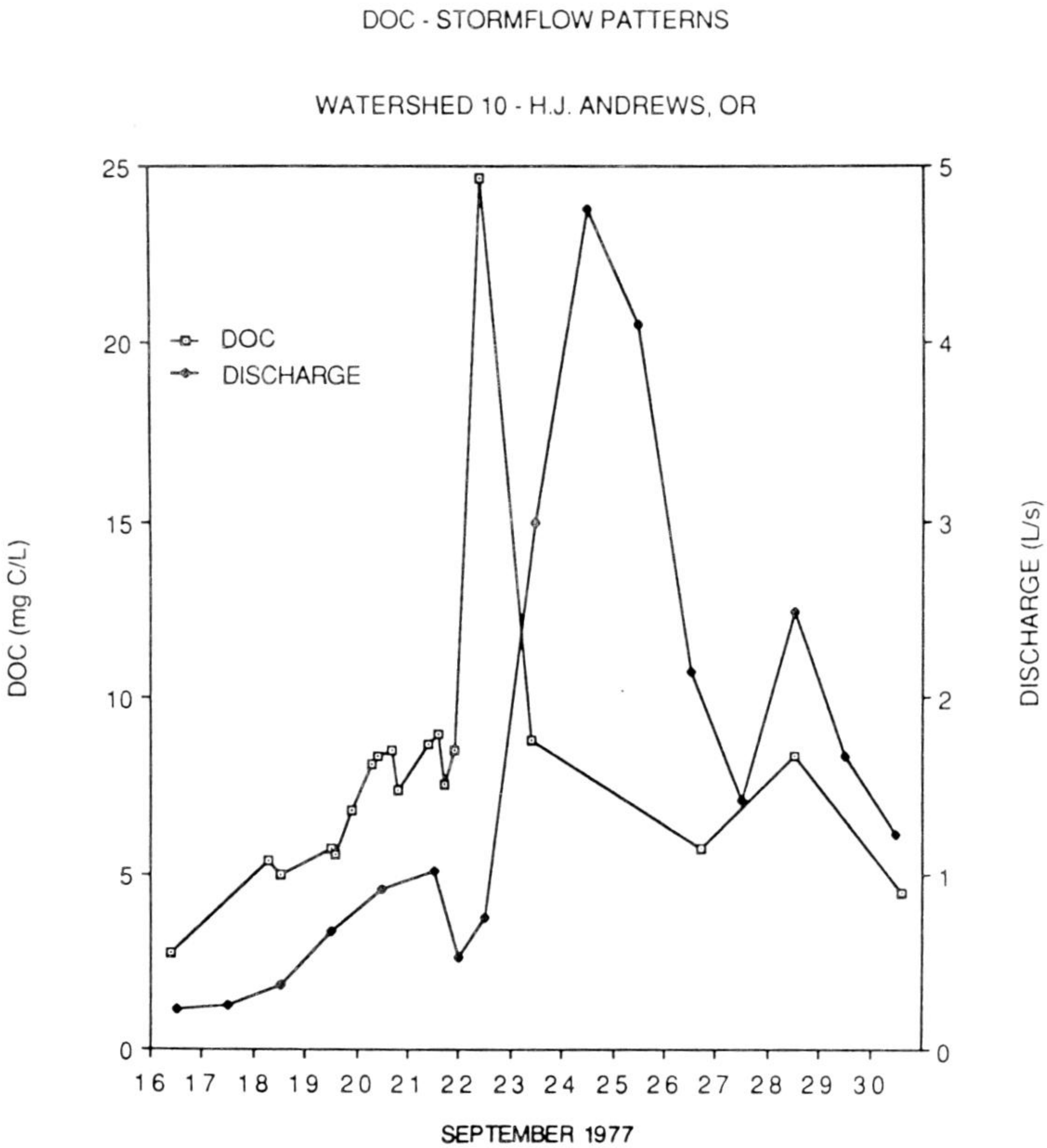

Fig. 4—Discharge and DOC concentration in a small stream in western Oregon over a two-week period during which a series of storms added precipitation to the catchment.

Historical Changes in Hydrologic Retention and Floodplain Vegetation

The river system and its associated floodplain vegetation are shaped by the physical energy of water moving downhill and the sediment load. Schafer (1973) superbly illustrates these concepts for the Rhine River in Germany where the size, shape, location, and migration rates of oxbow lakes along the floodplain respond to changes in sediment loads and discharge.

Sedell and Froggatt (1984) documented such a change for 25 km of the Willamette River, Oregon. Between 1854 and 1967, the Willamette River became increasingly isolated from its floodplain as a result of channelization and agricultural modification of the riparian forests. In 1854, the riparian forest was 1.5–3 km wide and in contact with >250 km of river edge on oxbow lakes and cutoff sloughs. By 1967 the length of river edge was systematically decreased to 64 km, a reduction of 74 percent, and the riparian forest was restricted to the adjacent bank. Much of the change in riparian forest interaction was completed by 1910 owing to snag removal and river navigation improvements (levees). These changes have resulted in a severe reduction in the ability of alluvial reaches to retain sediments and organics, the quantity of organic inputs, and primary production on the floodplain.

Hesse et al. (1989) dramatically illustrate this point on the lower Missouri River from Sioux City, Iowa, to the mouth at St. Louis. Channelization of this reach of the Missouri River directly eliminated over 192,000 ha of aquatic habitat and wetlands from the active erosional zone of the river. Channelization, along with the flood protection provided by mainstem and tributary reservoirs, fostered agricultural, urban, and industrial encroachment on 95% (728,460 ha) of the floodplain. This extensive development dramatically changed the composition of the natural plant communities that formerly colonized the floodplain and reduced available supplies of organic material by at least 65%. Native floodplain vegetation plus increased water retention on the floodplain will produce more DOC (tea bag effect). Native plant communities contribute large amounts of DOC (Moore 1987) from throughfall, stemflow, and root decomposition as well as 20–25% of the litter fall leaching out as DOC. Although agricultural production on the floodplain can reach 9 t/ha/yr of biomass (Ovington et al. 1963), much of this production is physically removed from the cropped field (floodplain) in the form of grain, forage, or domestic livestock. Native plant communities, which are periodically flooded, can contribute biomass from 6 t/ha/yr for grasslands to 16 t/ha/yr for cattail marshes to the ecosystem.

The total of worldwide wetland areas has drastically decreased in the last 40 years. The conterminous U.S. has only 46% of the original 8.7×10^7 ha of wetlands remaining (Tiner 1984). In a twenty-year period between the mid-1950s and mid-1970s, there was a net 3.6×10^6 ha loss (for every ha of wetland gained about 5.5 ha were lost). Tiner (1984) further estimates that about 2.0×10^5 ha of wetlands continue to be lost annually to agriculture and estuarine filling.

Gains in wetlands in the U.S. have come in the form of open water habitat from reservoirs, farm ponds, and coastal subsidence and total 0.8×10^6 ha. These open water gains were both modest in area and biological productivity as compared to the 4.45×10^6 ha losses in the productive

Sedell and Froggatt (1984) documented such a change for 25 km of the Willamette River, Oregon. Between 1854 and 1967, the Willamette River became increasingly isolated from its floodplain as a result of channelization and agricultural modification of the riparian forests. In 1854, the riparian forest was 1.5–3 km wide and in contact with >250 km of river edge on oxbow lakes and cutoff sloughs. By 1967 the length of river edge was systematically decreased to 64 km, a reduction of 74 percent, and the riparian forest was restricted to the adjacent bank. Much of the change in riparian forest interaction was completed by 1910 owing to snag removal and river navigation improvements (levees). These changes have resulted in a severe reduction in the ability of alluvial reaches to retain sediments and organics, the quantity of organic inputs, and primary production on the floodplain.

Hesse et al. (1989) dramatically illustrate this point on the lower Missouri River from Sioux City, Iowa, to the mouth at St. Louis. Channelization of this reach of the Missouri River directly eliminated over 192,000 ha of aquatic habitat and wetlands from the active erosional zone of the river. Channelization, along with the flood protection provided by mainstem and tributary reservoirs, fostered agricultural, urban, and industrial encroachment on 95% (728,460 ha) of the floodplain. This extensive development dramatically changed the composition of the natural plant communities that formerly colonized the floodplain and reduced available supplies of organic material by at least 65%. Native floodplain vegetation plus increased water retention on the floodplain will produce more DOC (tea bag effect). Native plant communities contribute large amounts of DOC (Moore 1987) from throughfall, stemflow, and root decomposition as well as 20–25% of the litter fall leaching out as DOC. Although agricultural production on the floodplain can reach 9 t/ha/yr of biomass (Ovington et al. 1963), much of this production is physically removed from the cropped field (floodplain) in the form of grain, forage, or domestic livestock. Native plant communities, which are periodically flooded, can contribute biomass from 6 t/ha/yr for grasslands to 16 t/ha/yr for cattail marshes to the ecosystem.

The total of worldwide wetland areas has drastically decreased in the last 40 years. The conterminous U.S. has only 46% of the original 8.7×10^7 ha of wetlands remaining (Tiner 1984). In a twenty-year period between the mid-1950s and mid-1970s, there was a net 3.6×10^6 ha loss (for every ha of wetland gained about 5.5 ha were lost). Tiner (1984) further estimates that about 2.0×10^5 ha of wetlands continue to be lost annually to agriculture and estuarine filling.

Gains in wetlands in the U.S. have come in the form of open water habitat from reservoirs, farm ponds, and coastal subsidence and total 0.8×10^6 ha. These open water gains were both modest in area and biological productivity as compared to the 4.45×10^6 ha losses in the productive forested and emergent wetlands during the same period. As an illustration, the lower Mississippi River floodplain originally included over 9.7×10^6 ha of bottomland forested wetlands. By 1937, only 4.7×10^6 or <50% of these remained. In the 1980s, there are less than 2.1×10^6 ha remaining—roughly 20% of the original acreage (Hefner and Brown 1984; Tiner 1984).

Figure 5a provides a cross-sectional view of a degraded small stream system. In this example, the stream has cut down through previously deposited alluvium. As a result, the channel and associated vegetation have changed dramatically. Species typical of wetland conditions have largely disappeared and the channel continues to erode laterally. There is little subsurface storage of water and the stream is characterized by intermittent flow. In contrast, Fig. 5b illustrates a previously eroded channel that supports a diversity of riparian vegetation and has undergone recovery. The vegetation provides relative stability to stream banks and causes deposition of sediment; over time the channel has undergone aggradation. Such aggradation is often a natural consequence of allowing streamside vegetation that may have been modified by historical grazing, logging, agriculture, or other management practices an opportunity to again function and exert its influence on flow conditions, characteristics of the channel, and DOC concentrations. A consequence of this aggradation process is that the water table will similarly rise. In some cases, a formerly intermittent stream may flow perennially.

The DOC concentration, retention, and production both on the surface and in the saturated zone are much higher in Fig. 5b than in Fig. 5a because of greater primary production and fine root biomass (Fig. 5c). The subsurface riparian soils have concentrations 4–10 times that of stream water (Moore 1987; C. Dahm, unpublished). For large rivers, the lowering of the water table in river valleys in both Europe and North America is well documented by Decamps et al. (1988). This lowering of the water table below the rooting zones is a result of gravel mining, trapping of sediments by upstream dams, and channelization. The retention of water in the area, as well as the carbon inputs, contributes to higher DOC (Naiman et al. 1988).

The landscape processes of deforestation, combined with floodplain levee systems, tend to isolate the river from the floodplain and accelerate the runoff of storm events. Figure 6 illustrates the relationship between increasing area of freely flooding floodplain and stage/discharge ratios expressed as degree of deviation from "pristine" (100%) conditions. As illustrated by Belt (1975) for the Mississippi River, long-term mean stage/discharge ratios increase as freely flooding floodplains decrease in area or become unavailable to floodwaters. Simultaneously, the annual variation about the long-term mean stage/discharge ratio increases with the decrease in freely flooding bottomlands, resulting in significant hydrologic changes in the river and in the adjacent bottomland hardwood wetlands. Such changes in hydrologic conveyance do not occur in response to elimination of a single site from

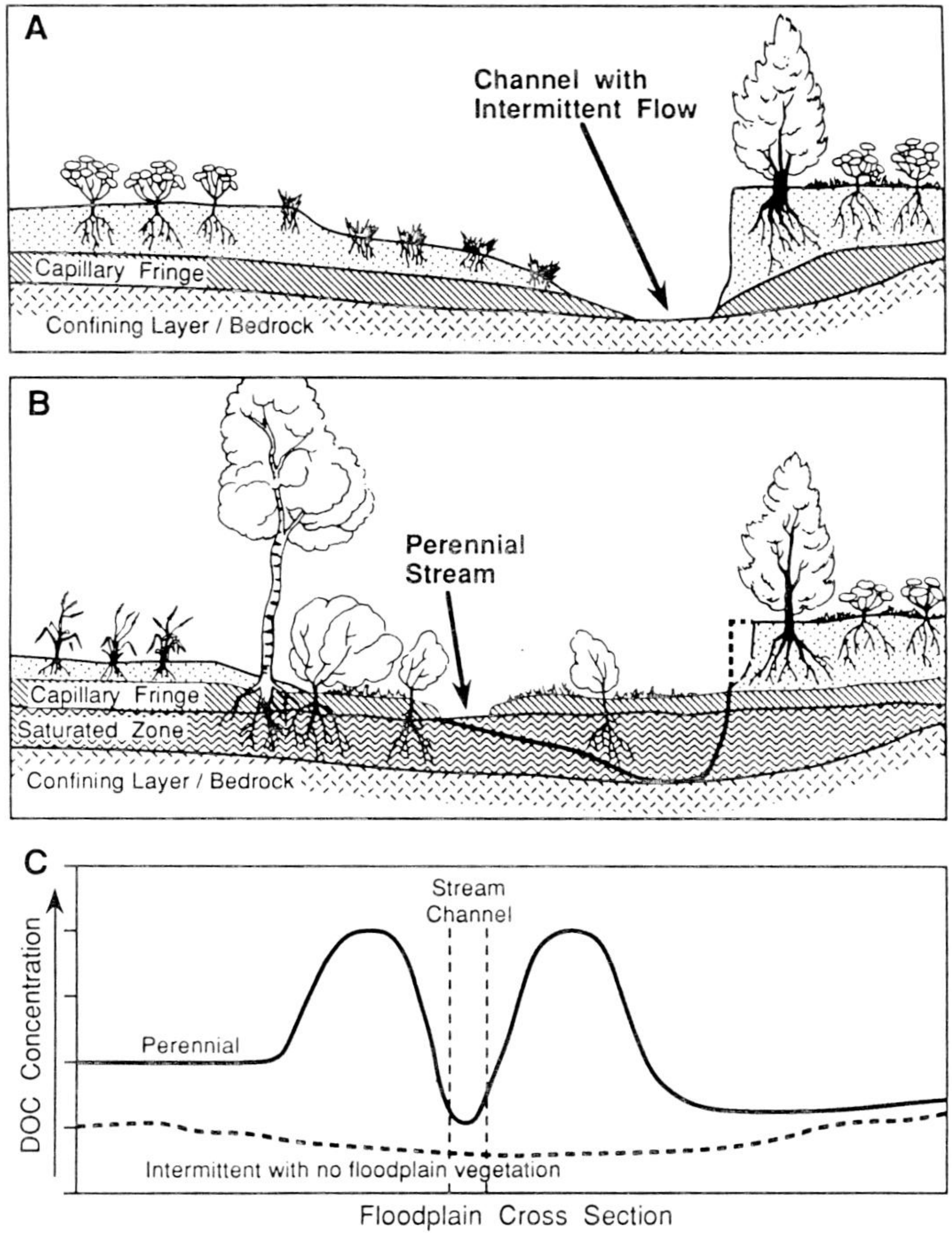

Fig. 5—General characteristics and DOC functions of riparian areas associated with rangeland streams (adapted from Elmore and Beschta 1987).

the bottomlands, but emerge as a result of incremental decreases in freely flooding bottomland. This type of alteration in the hydrologic regime of a channel network results from landscape-level processes (Lee and Gosselink 1988).

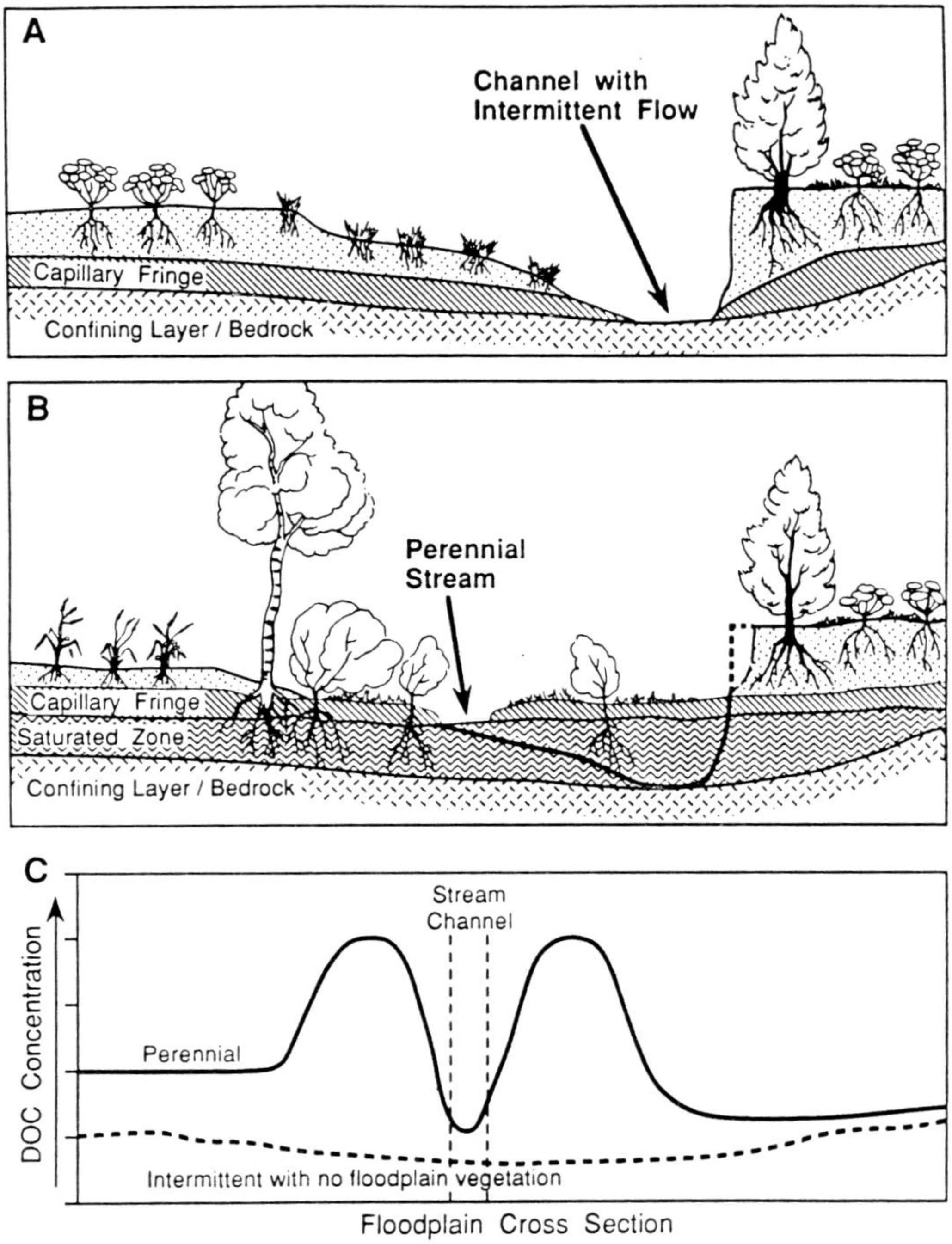

Fig. 5—General characteristics and DOC functions of riparian areas associated with rangeland streams (adapted from Elmore and Beschta 1987).

the bottomlands, but emerge as a result of incremental decreases in freely flooding bottomland. This type of alteration in the hydrologic regime of a channel network results from landscape-level processes (Lee and Gosselink 1988).

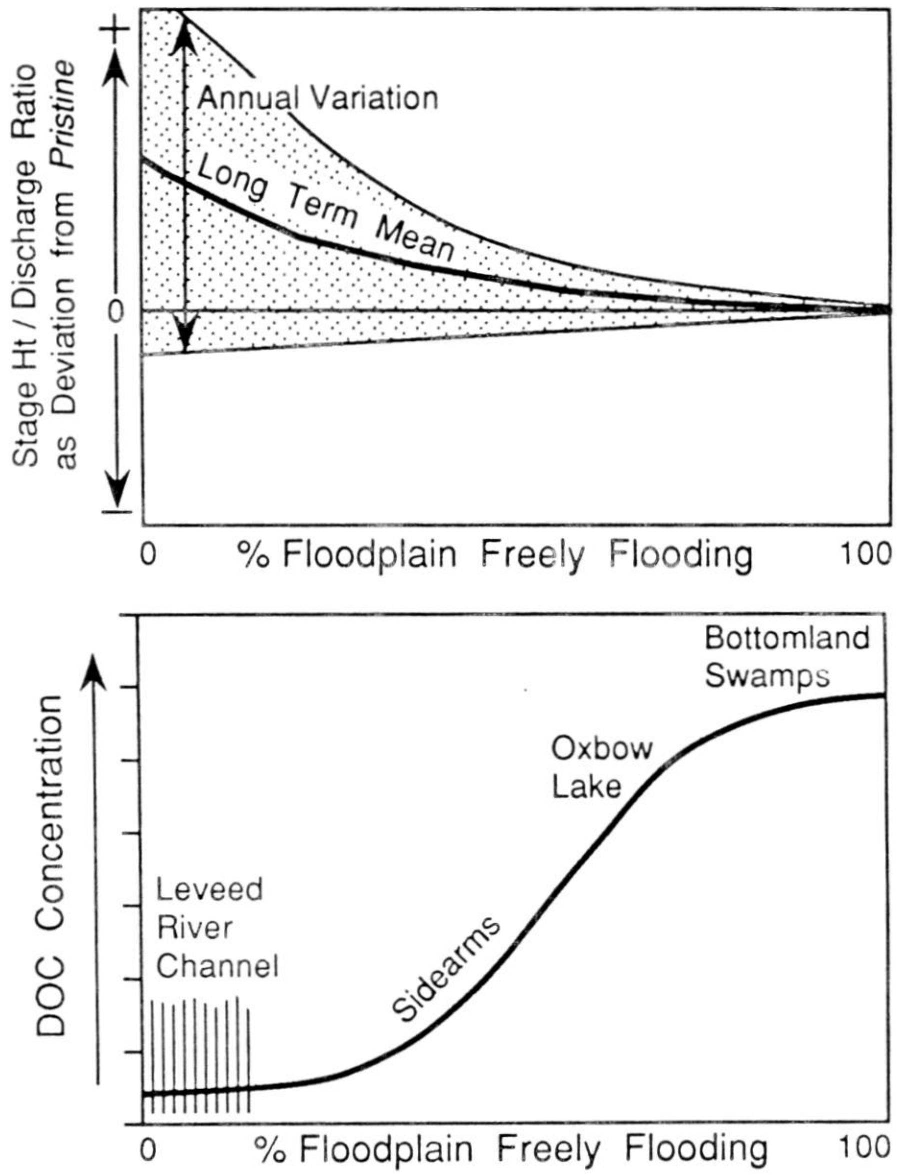

Fig. 6—Increased hydrologic conveyance from disconnecting the floodplain from the river channel (adapted from Lee and Gosselink 1988).

Changes in DOC concentration are hypothesized to vary directly with change in hydrologic conveyance within systems which have not been drastically urbanized or receive significant human effluents (Fig. 6b). The different floodplain features display a trend in DOC concentrations which increase with distance and connectivity with the main channels or aerial extent of the floodable floodplain or wetlands.

Not only is the floodplain becoming less productive in terms of primary production, but also the retention of water on the land is greatly reduced. This results in a potential reduction in DOC.

DISCUSSION – POSSIBLE ISSUES FOR CONSIDERATION

Concentrations of DOC in natural waters range over approximately two orders of magnitude. The causes behind this variability are important to the energetics, buffering characteristics, and nutrient dynamics of these ecosystems. The causal mechanisms which control the concentration and quality of DOC in various aquatic ecosystems are important to elucidate. Hypotheses that predict declining concentrations of DOC in regions receiving strong acid deposition need to be evaluated mechanistically in addition to the correlative procedures used to date. Therefore, we present the following questions as possible topics for further discussion.

1. What are the sources and routing of DOC in different types of surface waters?
2. What factors predispose some natural waters to contain high or low concentrations of DOC?
3. What is the relative importance of anthropogenic changes to surface water runoff in altering the quantity and characteristics of DOC?
4. What is the effect on the aquatic ecosystem of changing from a complex deciduous and coniferous leaf litter source to an algal-macrophyte-dominated DOC source?
5. What is the effect on the aquatic ecosystem of DOC derived from anaerobic processes as opposed to aerobic processes?
6. How do structural differences in the types of organic acids affect availability of limiting nutrients?

Question 1 includes such topics as (*a*) the relative contribution of soil organic matter versus autochthonous sources of DOC to the soluble organic carbon pool; (*b*) the importance of riparian, wetland, hyporheic, and main channel contributions to total DOC; and (*c*) spatial and temporal variability in the source areas for DOC within a catchment. Historically, there has been a general consensus among organic geochemists that DOC in surface waters is derived mainly from soil organic matter. The variability of the concentration of DOC in time and space and the generally higher concentrations of DOC in waters which drain regions with extensive wetlands, riparian zones, and gallery forests suggest a major contribution from the floodplains of streams and rivers. Is the geomorphology of the catchment, particularly along the drainage network, a strong determinant of the average DOC concentration? Which river ecosystems derive the majority of their DOC from upland terrestrial environments and which ecosystems are primarily dependent on carbon sources within the permanently saturated wetland areas of the floodplain?

Question 2 focuses on what the major sources and sinks of DOC are within a catchment. Two major potential sources of DOC for most surface

DISCUSSION – POSSIBLE ISSUES FOR CONSIDERATION

Concentrations of DOC in natural waters range over approximately two orders of magnitude. The causes behind this variability are important to the energetics, buffering characteristics, and nutrient dynamics of these ecosystems. The causal mechanisms which control the concentration and quality of DOC in various aquatic ecosystems are important to elucidate. Hypotheses that predict declining concentrations of DOC in regions receiving strong acid deposition need to be evaluated mechanistically in addition to the correlative procedures used to date. Therefore, we present the following questions as possible topics for further discussion.

1. What are the sources and routing of DOC in different types of surface waters?
2. What factors predispose some natural waters to contain high or low concentrations of DOC?
3. What is the relative importance of anthropogenic changes to surface water runoff in altering the quantity and characteristics of DOC?
4. What is the effect on the aquatic ecosystem of changing from a complex deciduous and coniferous leaf litter source to an algal-macrophyte-dominated DOC source?
5. What is the effect on the aquatic ecosystem of DOC derived from anaerobic processes as opposed to aerobic processes?
6. How do structural differences in the types of organic acids affect availability of limiting nutrients?

Question 1 includes such topics as (*a*) the relative contribution of soil organic matter versus autochthonous sources of DOC to the soluble organic carbon pool; (*b*) the importance of riparian, wetland, hyporheic, and main channel contributions to total DOC; and (*c*) spatial and temporal variability in the source areas for DOC within a catchment. Historically, there has been a general consensus among organic geochemists that DOC in surface waters is derived mainly from soil organic matter. The variability of the concentration of DOC in time and space and the generally higher concentrations of DOC in waters which drain regions with extensive wetlands, riparian zones, and gallery forests suggest a major contribution from the floodplains of streams and rivers. Is the geomorphology of the catchment, particularly along the drainage network, a strong determinant of the average DOC concentration? Which river ecosystems derive the majority of their DOC from upland terrestrial environments and which ecosystems are primarily dependent on carbon sources within the permanently saturated wetland areas of the floodplain?

Question 2 focuses on what the major sources and sinks of DOC are within a catchment. Two major potential sources of DOC for most surface waters are the upper organic-rich horizons of upland soils and organic-rich depositional zones within the floodplain. Two major potential sinks for DOC are the lower horizons of upland soils and bacterial metabolism. The interplay of these sources and sinks, coupled with the hydrologic pathways of water in the basin, produces the array of DOC concentrations measured worldwide.

Question 3 encompasses the wide range of impacts that human activities can potentially exert on DOC dynamics within a catchment over temporal scales ranging from hours to millennia. Anthropogenic activities may result in changes which could either increase or decrease DOC concentrations in the water. Possible mechanisms which are postulated to decrease DOC include (*a*) structures which accelerate the rate of runoff (e.g., levees, channelized streams and rivers, large organic debris removal, drainage canals and ditches, etc.); (*b*) lowered water table through wetland removal, enhanced erosion, dredging, etc.; (*c*) vegetation reduction within the riparian corridor; (*d*) large reservoirs; and (*e*) acid deposition throughout the basin.

Human activities which can lead to a possible increase in DOC concentrations within streams and rivers include: (*a*) eutrophication associated with urban, industrial, or agricultural loading of nutrients; (*b*) increased rice production throughout much of the world; (*c*) riparian zone protection and reestablishment; (*d*) wetland zone protection and reestablishment; and (*e*) increased channel complexity from such agents as large organic debris and beaver activity. A wide variety of human impacts, both enhancing or restricting DOC inputs into streams and rivers, are often occurring within a basin simultaneously. Differentiating between the major effects of human intervention within a catchment is critical for assigning an unequivocal dominant mechanism to explain a directional shift in DOC concentration through time.

Questions 4–6 address the fact that vast areas of DOC-producing features have been disconnected and removed from influencing rivers. The sources of organic acids have changed along with the processes from which DOC is derived. In general there is greater in-channel production of algae and less structurally complex organic material entering streams. Algal organics would have more carbohydrates and proteins. Leaf litter has more polymeric forms, such as phenolics, terpenes, and alkaloids. We, as well as M. Perdue (pers. comm.), have suggested that those systems with extensive floodplains and adjacent wetlands have a large proportion of DOC derived from anaerobic decomposition.

What are the structural differences in DOC derived from anaerobic processes as compared to more prevalent aerobic processes today? If there are major structural differences in DOC caused by both differences in organic sources as well as decomposition processes, what are the effects on limiting nutrient availability? There are suggestions that some DOC makes limiting nutrients more available and countersuggestions that DOC from wetlands may suppress blue-green algal blooms in adjacent water bodies.

The general question of temporal and spatial variations of organic acids at the ecosystem level has been discussed above in terms of DOC. Implicit in the discussion is the assumption that most of the DOC is in the form of organic acids and that the equivalents of carboxyl groups per gram of DOC are relatively constant. An additional topic for discussion, one for which a much smaller set of data is presently available, is the temporal and spatial variation of organic acids within the larger DOC pool. Can it be generally assumed that the concentration of organic acids closely follows the concentration of DOC in most aquatic ecosystems?

Acknowledgements. The National Science Foundation supports ecosystem-level research at Oregon State University (grants BSR-8414325 and BSR-8508356) and University of New Mexico (BSR-8616438) which we gratefully appreciate. J. Barnett, D. Coor, and L. Nelson prepared the figures. Special thanks to M. Meybeck for a thorough review.

REFERENCES

Belt, C.B., Jr. 1975. The 1973 flood and man's construction of the Mississippi River. *Science* 189:681–684.

Dahm, C.N., S.V. Gregory, and P.K. Park. 1981. Organic carbon transport in the Columbia River. *Est. Coast. Shelf Sci.* 13:645–658.

Davis, R.B., D.S. Anderson, and F. Berge. 1985. Palaeolimnological evidence that lake acidification is accompanied by loss of organic matter. *Nature* 316:436–438.

Decamps, H., M. Fortune, F. Gazell, and G. Pautau. 1988. Historical influence of man on the riparian dynamics in a fluvial landscape. *Landsc. Ecol.* 1:163–173.

Elmore, W., and R.L. Beschta. 1987. Riparian areas: perceptions in management. *Rangelands* 9(6):260–265.

Fisher, S.G. 1977. Organic matter processing by a stream segment ecosystem: Fort River, Massachusetts, U.S.A. *Int. Rev. Ges. Hydrobiol.* 62:701–727.

Furch, K. 1985. Dissolved carbon in a floodplain lake of the Amazon and in the river channel. *Mitt. Geol.-Paläont. Inst. Univ. Hamburg*:285–298.

Hefner, J.M., and J.D. Brown. 1984. Wetland trends in the southeastern United States. *Wetlands* 4:1–12.

Hesse, L.W., G.R. Chaffink, and J. Brabender. 1989. Missouri River mitigation: a system approach. *Fisheries* 14:11–15.

Ittekkot, V., S. Safiullah, B. Mycke, and R. Seifert. 1985. Seasonal variability and geochemical significance of organic matter in the River Ganges, Bangladesh. *Nature* 317:800–802.

Klotz, R.L., and E.A. Matson. 1978. Dissolved organic carbon fluxes in the Shetucket River of eastern Connecticut, U.S.A. *Freshwat. Biol.* 8:347–355.

Kuserk, F.T., L.A. Kaplan, and T.L. Bott. 1984. *In situ* measures of dissolved organic carbon flux in a rural stream. *Can. J. Fish. Aq. Sci.* 41:964–973.

Lee, L.C., and J.G. Gosselink. 1988. Cumulative impacts on wetlands: linking scientific assessments and regulatory alternatives. *Envir. Manag.* 12(5):519–602.

limiting nutrients more available and countersuggestions that DOC from wetlands may suppress blue-green algal blooms in adjacent water bodies.

The general question of temporal and spatial variations of organic acids at the ecosystem level has been discussed above in terms of DOC. Implicit in the discussion is the assumption that most of the DOC is in the form of organic acids and that the equivalents of carboxyl groups per gram of DOC are relatively constant. An additional topic for discussion, one for which a much smaller set of data is presently available, is the temporal and spatial variation of organic acids within the larger DOC pool. Can it be generally assumed that the concentration of organic acids closely follows the concentration of DOC in most aquatic ecosystems?

Acknowledgements. The National Science Foundation supports ecosystem-level research at Oregon State University (grants BSR-8414325 and BSR-8508356) and University of New Mexico (BSR-8616438) which we gratefully appreciate. J. Barnett, D. Coor, and L. Nelson prepared the figures. Special thanks to M. Meybeck for a thorough review.

REFERENCES

Belt, C.B., Jr. 1975. The 1973 flood and man's construction of the Mississippi River. *Science* 189:681–684.

Dahm, C.N., S.V. Gregory, and P.K. Park. 1981. Organic carbon transport in the Columbia River. *Est. Coast. Shelf Sci.* 13:645–658.

Davis, R.B., D.S. Anderson, and F. Berge. 1985. Palaeolimnological evidence that lake acidification is accompanied by loss of organic matter. *Nature* 316:436–438.

Decamps, H., M. Fortune, F. Gazell, and G. Pautau. 1988. Historical influence of man on the riparian dynamics in a fluvial landscape. *Landsc. Ecol.* 1:163–173.

Elmore, W., and R.L. Beschta. 1987. Riparian areas: perceptions in management. *Rangelands* 9(6):260–265.

Fisher, S.G. 1977. Organic matter processing by a stream segment ecosystem: Fort River, Massachusetts, U.S.A. *Int. Rev. Ges. Hydrobiol.* 62:701–727.

Furch, K. 1985. Dissolved carbon in a floodplain lake of the Amazon and in the river channel. *Mitt. Geol.-Paläont. Inst. Univ. Hamburg*:285–298.

Hefner, J.M., and J.D. Brown. 1984. Wetland trends in the southeastern United States. *Wetlands* 4:1–12.

Hesse, L.W., G.R. Chaffink, and J. Brabender. 1989. Missouri River mitigation: a system approach. *Fisheries* 14:11–15.

Ittekkot, V., S. Safiullah, B. Mycke, and R. Seifert. 1985. Seasonal variability and geochemical significance of organic matter in the River Ganges, Bangladesh. *Nature* 317:800–802.

Klotz, R.L., and E.A. Matson. 1978. Dissolved organic carbon fluxes in the Shetucket River of eastern Connecticut, U.S.A. *Freshwat. Biol.* 8:347–355.

Kuserk, F.T., L.A. Kaplan, and T.L. Bott. 1984. *In situ* measures of dissolved organic carbon flux in a rural stream. *Can. J. Fish. Aq. Sci.* 41:964–973.

Lee, L.C., and J.G. Gosselink. 1988. Cumulative impacts on wetlands: linking scientific assessments and regulatory alternatives. *Envir. Manag.* 12(5):519–602.

Lesack, L.F.W., R.E. Hecky, and J.M. Melack. 1984. Transport of carbon, nitrogen, phosphorus, and major solutes in the Gambia River, West Africa. *Limnol. Ocean.* 29:816–830.

Malcolm, R.L., and W.H. Durum. 1976. Organic carbon and nitrogen concentrations and annual organic carbon load of six selected rivers of the United States. USDI-Geological Survey, Water Supply Paper 1817-F, Washington, D.C.

McDowell, W.H., and G.E. Likens. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. *Ecol. Monogr.* 58:177–195.

McKnight, D., E.M. Thurman, R.L. Wershaw, and H. Hemond. 1985. Biogeochemistry of aquatic humic substances in Thoreau's Bog, Concord, Massachusetts. *Ecology* 66:1339–1352.

Meybeck, M. 1982. Carbon, nitrogen, and phosphorus transport by world rivers. *Am. J. Sci.* 282:401–450.

Meyer, J.L. 1986. Dissolved organic carbon dynamics in two subtropical blackwater rivers. *Arch. Hydrobiol.* 108:119–134.

Moore, T.R. 1987. Dissolved organic carbon in forested and cutover drainage basins, Westland, New Zealand. *Int. Ass. Sci. Hydrol. Publ.* 167:481–487.

Mulholland, P.J., and E.J. Kuenzler. 1979. Organic carbon export from upland and forested wetland watersheds. *Limnol. Ocean.* 24:960–966.

Mulholland, P.J., and J.A. Watts. 1982. Transport of organic carbon to the oceans by rivers of North America: a synthesis of existing data. *Tellus* 34:176–186.

Naiman, R.J., H. Decamps, J. Pastor, and C.A. Johnston. 1988. The potential importance of boundaries to fluvial ecosystems. *J. N. Am. Benthol. Soc.* 7(4):289–306.

Ovington, J.D., D. Heitkamp, and D.B. Lawrence. 1963. Plant biomass and productivity of prairie, savanna, oakwood and maize field ecosystems in central Minnesota. *Ecology* 44:52–63.

Richey, J.E., J.T. Brock, R.J. Naiman, R.C. Wissmar, and R.F. Stallard. 1980. Organic carbon: oxidation and transport in the Amazon River. *Science* 207:1348–1351.

Schafer, W. 1973. Alkrhein Verbund am Nördlichen Oberrhein. *Cour. Forsch. Senckenberg* 7:1–63.

Sedell, J.R., and J.L. Froggatt. 1984. Importance of streamside vegetation to large rivers: the isolation of the Willamette River, Oregon, U.S.A., from its floodplain. *Verh. Int. Verein. Limnol.* 22:1828–1834.

Sullivan, T.J., J.M. Eilers, M.R. Church, D.J. Blick, K.N. Eshleman, D.H. Landers, and M.S. De Hann. 1988. Atmospheric wet sulphate deposition and lakewater chemistry. *Nature* 331:607–609.

Tate, C.M., and J.L. Meyer. 1983. The influence of hydrologic conditions and successional state on dissolved organic carbon export from forested watersheds. *Ecology* 64:25–32.

Thurman, E.M. 1985. Organic Geochemistry of Natural Waters. Dordrecht:Nijhoff.

Tiner, R.W. 1984. Wetlands of the United States: current status and recent trends. National Wetlands Inventory 1984-439-855-814/10870. Washington, D.C.:U.S. Fish and Wildlife Service.

Welcomme, R.L. 1985. River Fisheries. Fisheries Technical Paper 262. Rome: FAO.