



Limnology

Lake and River Ecosystems

Third Edition

ROBERT G. WETZEL



ACADEMIC PRESS

A Harcourt Science and Technology Company

San Diego San Francisco New York Boston London Sydney Tokyo

TABLE 23-3 Annual Average Particulate, Colloidal, and Dissolved Organic Fractions of Lake Furesø, Denmark^a

Organic fraction ^b	Total dry weight ^c (mg liter ⁻¹)	Organic weight ^c (mg liter ⁻¹)	Crude protein (%)	Lipid material (%)	Carbohydrate (%)
Particulate	2.1	1.56	53.2	9.9	36.9
Colloidal	3.6	0.67	41.5	11.7	46.8
Dissolved	Approx. 70	8.8	37.5	—	62.5

^a After Krogh and Lange (1932).

^b Colloidal and dissolved fractions separated by ultrafiltration.

^c Based on a limited number of largely surface and near-sediment samples.

with moderate-to-high concentrations of dissolved organic matter (see p. 734). Nitrogen content decreases and carbon content increases in the progression from particulate to colloidal to truly dissolved organic matter fractions (Table 23-3). The colloidal fraction is high in lakes rich in DOC, such as bog waters, and in hard waters in which organic compounds are adsorbed onto carbonate particles (cf. Ohle, 1934b; White, 1974; White and Wetzel, 1975).

Both allochthonous and autochthonous sources of detrital particulate organic matter (POM) and dissolved organic matter (DOM), therefore, constitute variable inputs to aquatic ecosystems. As is emphasized repeatedly in this synthesis, POM tends to remain near sites of production. Lateral transport of POM is small, relative to DOM transport, in terrestrial soils, and in land-water interface zones such as flood plains, wetlands, and littoral areas. As we have seen earlier (Chap. 21), even in streams, large POM is often retained (snags and debris dams) and transport is mainly via DOM and fine POM. Transport of DOM is the primary movement of allochthonous organic carbon and energy to all aquatic ecosystems (Wetzel, 1993, 1995).

Autochthonous sources within the lake or river supplement the allochthonous inputs and include

1. Littoral photosynthetic sources of POM and of DOM by active secretion, decomposition, and lysis of the macrophytes and attached algae and cyanobacteria
2. Primary producers of the open-water zone, primarily the algal and cyanobacterial phytoplankton. Under some circumstances, sulfur photosynthetic and chemosynthetic bacteria are also significant sources of organic carbon.

Rapid transformations between POC and DOC by heterotrophic microflora progressively degrade organic matter to CO₂ and heat. The amount of organic carbon utilized and transformed by animals is a quantitatively small portion (<10%) of that of the whole ecosystem. Most of the heterotrophic metabolism, which is almost

entirely microbial, occurs both in the open water and in the sediments. Because so much detrital organic matter from pelagic and littoral sources is displaced to the sediments, much heterotrophic decomposition occurs in benthic sediments. The benthic region is the dominant site of organic carbon transformation to CO₂ in most lake ecosystems, especially as depth and volume decrease, in most reservoir ecosystems, and in all river ecosystems.

A. Allochthonous Organic Matter from Terrestrial Sources and within Streams

Terrestrial plants form much of the allochthonous organic matter of aquatic ecosystems. The organic carbon of residues of plant structural tissues is transformed variously by microbial utilization and degradation both at the sites of growth and while the organic matter is being transported by runoff ground water and vadose-surface water. Most (>95%) of the organic matter produced in the terrestrial portions of the drainage basin remains at the sites of production and is largely decomposed (Fisher and Likens, 1977; Dosskey and Bertsch, 1994). Little is stored permanently. Export of nondecomposed organic matter is largely as dissolved organic compounds in runoff and ground water. There is large variability in dissolved organic carbon (DOC) concentrations in terrestrial soils along this flow path (Cronan and Aiken, 1985; McDowell and Likens, 1988; Mulholland *et al.*, 1990; Nelson *et al.*, 1993; Hope *et al.*, 1994; Webster *et al.*, 1995; Kalbitz *et al.*, 2000; Magill and Aber, 2000).

When anthropogenic inputs of organic matter are low to rivers, concentrations of inorganic nitrogen are usually low and dissolved organic nitrogen (DON) is the primary form of nitrogen (Hedin *et al.*, 1995; Stepanauskas *et al.*, 1999, 2000). Much of that DON (to 70%) is bioavailable. Spring flooding from snowmelt is frequently a major hydrological event, and in some boreal rivers >50% of the annual water discharge may occur in a few weeks. During spring floods,

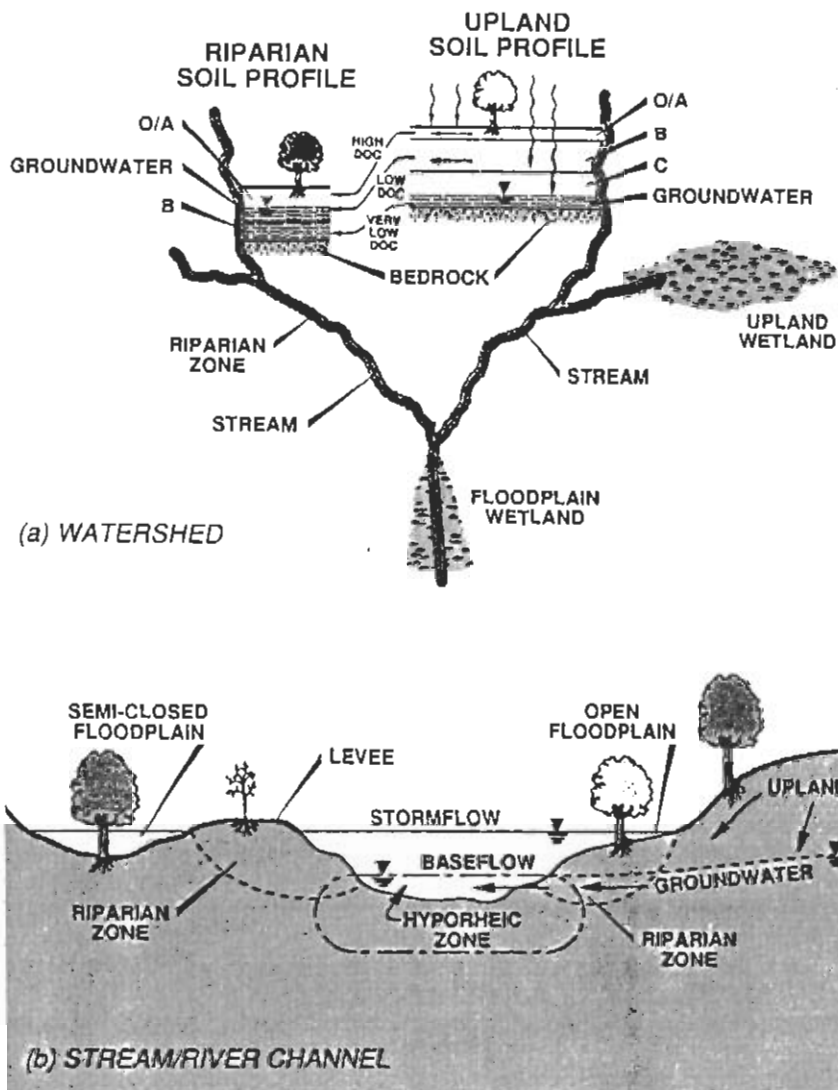


FIGURE 23-1 Potential dissolved organic carbon sources and hydrologic linkages with the stream/river at (a) the drainage basin (watershed) and (b) floodplain/channel spatial scales. (Extracted from Mulholland *et al.*, 1990.)

DON fluxes may exceed the baseflow fluxes by several orders of magnitude. During the flooding period, DON bioavailability increases markedly and has been correlated directly with increased concentrations of amino acids and related compounds.

Highest DOC concentrations occur in surface soil horizons (O and A) as a result of inputs from throughfall of the vegetation canopy and decomposition of surface POM (Fig. 23-1a), and tend to be much greater in forest soils among coniferous vegetation than among hardwood trees. Many humic substances of plant origins form microaggregates with clay-sized particles, which tend to reduce alteration by microbes (Clapp and Hayes, 1999). Removal of terrestrial vegetation, such as by clear cutting of forests of a drainage basin

or removal of riparian vegetation for agriculture, reduces the inputs of organic matter to the soils and reduces the release of DOC in runoff to streams (Meyer and Tate, 1983; Delong and Brusven, 1994; Guyot and Wasson, 1994).

Seasonally, the concentration of DOC in soil leachates is inversely correlated with temperature. Additionally, warm temperate and tropical communities are more productive than those of temperate regions, but oxidation of organic matter of forest origin is rapid and reduces DOC concentrations in leachates. Hence, the mean DOC concentrations of streams among the taiga is much greater (ca. 10 mg liter^{-1}) than from other upland habits (see Table 23-1), exceeded only by the DOC of swamps and wetlands (Thurman, 1985).

Concentrations of DOC decline steeply in lower soil horizons (B and C), primarily because of adsorption and coprecipitation in mineral soils with iron and aluminum sesquioxides (McDowell and Wood, 1984; David and Vance, 1991; Kaiser and Zech, 1998). Rates of microbial respiration in the upper soil horizons, especially B, indicate constant renewal of adsorption sites occurs as adsorbed DOC is utilized. Where soils, such as tropical podsoils, do not have an iron-rich clay horizon, large quantities of DOC, particularly hydrophobic DOC, can be released. It is also probable that organic acids of root exudates from terrestrial vegetation can alter stereochemical hydrophobic arrangements within micellelike conformations of humic substances (Piccolo *et al.*, 1996; Nardi *et al.*, 2000). Organic compounds adsorbed to the soil can then be mobilized and released.

As DOC moves laterally within soils in gravity flows along decreasing elevation levels and reaches the floodplain and riparian soils, further changes occur (Fig. 23-1b). The DOC moving through soil particles is subject to continual microbial degradation and becomes progressively more recalcitrant. For example, over half of the DOC leached from soils was found to be readily biodegradable by soil microbes (Baker *et al.*, 2000). Indeed, the concentrations of DOC are reduced appreciably by microbial degradation. Despite this utilization in soil and groundwater flows, concentrations of dissolved organic carbon and nitrogen are often significantly higher in ground water than in surface water (Ford and Naiman, 1989).

During baseflow conditions of low-flow inflows, microbial activity of flood plain and subsurface ground water can be limited by DOC availability. DOC concentrations of subsurface flows tend to be positively correlated with discharge within the river channels and decrease with greater distances from the head of entry places, such as the head of gravel bars (Vervier and Naiman, 1992). DOC from these soil and groundwater sources is augmented by formation of DOC in small streams by both abiotic processes, such as leaching from particulate materials, and biotic, soluble processes and leaches rapidly (<24 h) from detrital particulate terrestrial vegetation.

During low-flow periods, DOC concentrations in the soils increase. Subsequent rapid declines in DOC concentrations are roughly proportional to increased water percolation through the soils such as is released from rapid snowmelt and from precipitation events (see p. 747) (Lewis and Saunders, 1989; Ciaio and McDuffett, 1990; Clair *et al.*, 1994; Hornberger *et al.*, 1994; Jones, *et al.*, 1996). Maximum DOC concentrations appear in receiving streams and rivers soon thereafter and rapidly decline as the rivers return to base flows. As the area of flood plains increases in lowland river

ecosystems, stream DOC concentrations often increase during high flows as DOC-rich water originating in wetlands is transported to the channel (e.g., Dalva and Moore, 1991).

The DOM input from terrestrial organic matter to streams results from direct leaching from living vegetation or from soluble compounds carried in runoff from dead plant material in various stages of decomposition (Fig. 23-2). POM, again mostly of plant origin, can fall directly into stream water from overhanging tree canopies, be transported by runoff water, particularly from flood plains, or be windblown into the stream. Foliage from trees and ground vegetation can provide very significant inputs of organic matter to streams, both as POM and as leached DOM from the dead POM. The variability in the ratios of DOC:POC in streams and rivers is very large (range between 0.09 to 70; Moeller *et al.*, 1979).

Total transport of organic carbon in the world's rivers from land masses to the ocean in both dissolved and particulate forms is ca. $0.37-0.41 \times 10^{15}$ g C yr⁻¹ (Schlesinger and Melack, 1981; Meybeck, 1993c). Although this organic carbon transport is a small flux in the global carbon cycle, fluxes from land can be significant, though highly variable. Transport losses range from <1 g C m⁻² yr⁻¹ in grassland ecosystems to 10 g C m⁻² yr⁻¹ from some cultivated forests. Wetlands tend to release appreciably greater amounts of organic carbon (to ca. 20 g C m⁻² yr⁻¹) (Table 23-4).

1. Transformations

The large (coarse) as well as fine particulate matter of terrestrial vegetation entering streams is leached of a significant portion of its organic content as dissolved compounds (Fig. 23-2). The amount and degradability varies with the plant species. For example, slower uptake by stream bacteria of DOC in an old-growth forest could be a result of a more limited supply of labile DOC as well as a greater concentration of inhibitory compounds such as polyphenolic and terpene compounds in the stream water (Dahm, 1984). Much of this DOM leachate, however, is metabolized very rapidly. As a result, bacterial populations in the water, attached on sediments, and in the hyporheic zone within the sediments increase markedly in response to the DOM loading. For example, in large experimental streams, leaf leachate was demonstrated to have a bacteriologically labile dissolved organic carbon (DOC) fraction that was decomposed rapidly ($T_{1/2} = 2$ days) and a recalcitrant DOC fraction ($T_{1/2} = 80$ days) (Wetzel and Manny, 1972b). Most of the recalcitrant dissolved organic nitrogen compounds persisted in a relatively unmodified state for at least 24 days. As the DOC mixtures from natural sources are degraded,

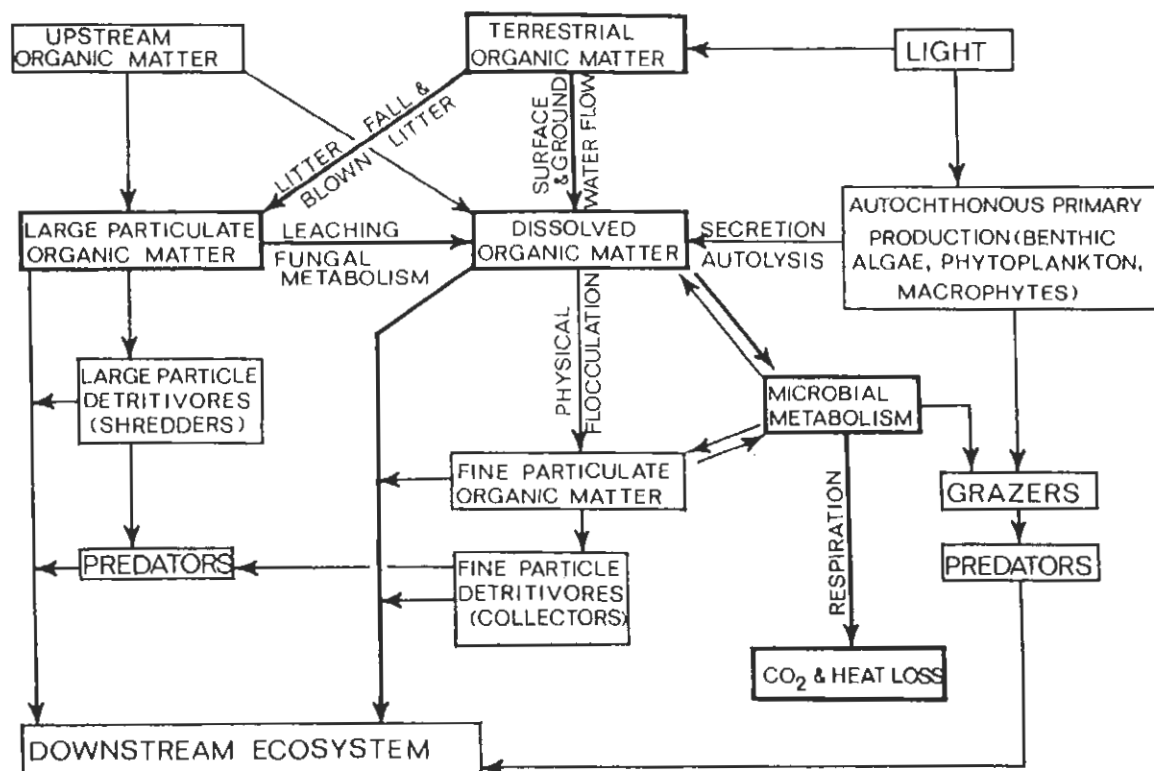


FIGURE 23-2 Simplified compartment model of the structure of an idealized stream ecosystem. Heavier lines indicate dominant transport and metabolic pathways of organic matter. (Composite of modified figures after Fisher and Likens, 1973; Cummins *et al.*, 1973.)

TABLE 23-4 Annual Riverine DOC Flux from Different Soils and Vegetation Habitat^a

Biome	Soil C:N	Observed DOC flux (g C m ⁻² yr ⁻¹) ^b
Cool grasslands	13.5	0.386
Tropical savannah	13.6	1.090
Taiga	13.8	0.700
Siberian steppe	14.7	1.290
Warm deciduous forests	15.3	1.410
Warm mixed woodlands	16.7	1.714
Cool deciduous forests	17.1	1.927
Warm conifer forests	21.0	3.684
Cool conifer forests	21.0	4.226
Northern mixed forests	23.2	5.260
Heath/moorlands	24.6	5.650
Tropical forests	25.0	6.336
Boreal/peat mix	25.7	6.349
Peatlands	30.1	8.567
Swamp forests	32.4	9.913

^a From data reviewed by Aitkenhead and McDowell (2000).

^b $\times 10 - \text{kg C ha}^{-1} \text{ yr}^{-1}$.

largely by benthic microbes, aliphatic compounds such as organic acids are being released as degradation products along with CO₂ and CH₄ (Schindler and Krabbenhoft, 1998). These gaseous products either oxidize or evade to the atmosphere.

A quantity of the dissolved leachate precipitates to particulate form (Lush and Hynes, 1973); the rate of precipitation and the size of the resulting particles depend upon leaf species and water chemistry. As will be discussed later, a portion of the DOC can be photolysed upon exposure to sunlight to simple organic substrates readily utilizable by bacteria or to CO₂.

Aggregations of large POM, such as leaf packs trapped among stream sediments, rocks, and large woody debris undergo colonization by fungi in complex successional patterns within the detrital microhabitats (cf. detailed discussion in Chap. 21). As the resistant plant material is degraded, solubilized products of decomposition are utilized by bacteria living in highly stratified populations in the steep redox gradients of the compacted plant material (Fig. 23-2). The detrital material and its associated microflora serve as a major nutritive source for numerous aquatic invertebrates, especially the immature insect fauna (Kaushik and Hynes,

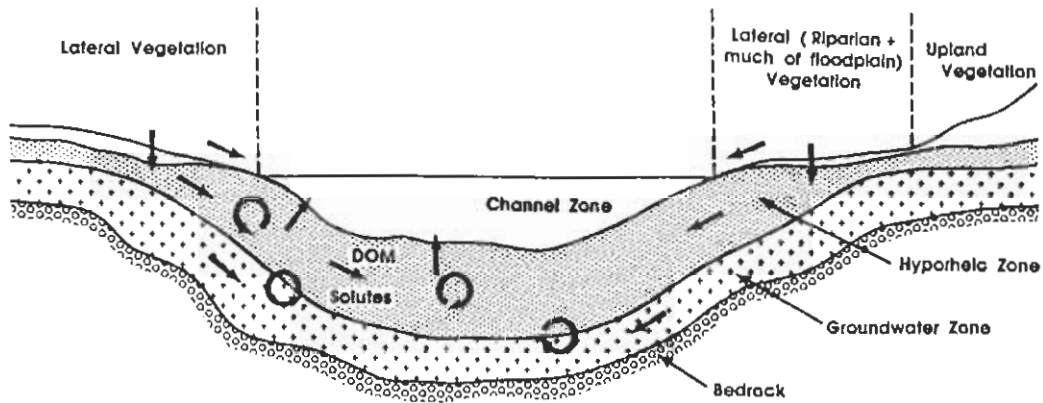


FIGURE 23-3 Conceptualization of lateral and vertical boundaries of running water ecosystems. The stream ecosystem boundary is defined as the hyporheic/groundwater interface and thereby includes a substantial volume beneath and lateral to the main channel. Vegetation rooted in the hyporheic zone is therefore part of the stream ecosystem primary production. Arrows indicate flow pathways of dissolved organic matter and inorganic solutes derived from plants and plant detritus within the stream ecosystem and flood plain. (From Wetzel and Ward, 1992; extensively modified from Triska *et al.*, 1989.)

1971; Cummins, 1973; Cummins *et al.*, 1973; Iversen, 1973; Anderson and Sedell, 1979) (see Chap. 22). There is no question that the shredding, collecting, and grazing activities of aquatic insects play a role in quickening the reduction of the size of POM and increasing the surface area for subsequent microbial degradation. It is also clear that a major portion of the animal nutrition is obtained from the microflora attached to the resistant detrital POM. Only a few animals are adapted with symbiotic gut microflora to utilize the particulate plant material directly (see Chap. 22).

Most of the lateral streamside and floodplain vegetation, however, will fall to the ground or hydrosols beside the main channel and be incorporated into subsurface soil regions, including lateral hyporheic zones. Both organic matter stored and/or produced within the main channel, as well as that which feeds into the hyporheic zone from lateral regions, can fuel microbially active subsurface regions, where both aerobic and anaerobic processes further transform the detrital organic material (Fig. 23-3). Some of the dissolved organic and solute material eventually reemerges in the main channel, where it can serve as nutrient sources to within-channel microbial communities (e.g., Crocker and Meyer, 1987; Dahm *et al.*, 1987; Triska *et al.*, 1989; Coleman and Dahm, 1990; DeAngelis *et al.*, 1990; Leff and Meyer, 1991; Kaplan and Newbold, 1993).

There are few detailed analyses of the metabolism of organic carbon in streams. However, there is sufficient evidence to indicate that

1. Allochthonous inputs of terrestrial organic matter, in the form of detrital DOM and POM, commonly

form the dominant source of material and energy for stream and river ecosystems (Tables 23-5 and 23-6). Much of that DOC is released from soils into groundwater and from anaerobic processes in adjoining wetlands (e.g., Dahm *et al.*, 1987; Eckhardt and Moore, 1990; Dillon and Molot, 1997b).

2. From 10 to 25 times more organic matter occurs as DOM than occurs in particulate form on an annual basis (e.g., Table 23-5).

3. Groundwater inputs of DOM are the major source to upland streams, and most of the water reaching the streams passes through soil strata and is exposed to microbial degradation (e.g., Wallis *et al.*, 1981; Rutherford and Hynes, 1987).

4. The rates of decomposition of DOM are rapid (days) in comparison to those for much of the POM (leaves in weeks and woody material in years).

5. Bacteria rapidly metabolize the labile components of DOC and DON, but more recalcitrant components are decomposed at slower rates and are exported downstream (Wetzel and Manny, 1972; McDowell and Fisher, 1976; Leff and Meyer, 1991; Perdue, 1998; Findlay and Sinsabaugh, 1999; Stepanauskas *et al.*, 1999, 2000). Proteinaceous moieties in DOM are preferentially degraded. DOM with higher percentages of aromatic carbon and carboxyl (COOH) content are less bioavailable.

6. Despite variations related to the source materials of the DOC, bacterial utilization and growth efficiencies can be high (Kaplan and Bott, 1983; Findlay *et al.*, 1986; Edwards and Meyer, 1987).

7. Much of the bacterial respiration of DOM occurs in the hyporheic zone of the sediments or along the surface of the sediments. Community respiration of

TABLE 23-5 Annual Mean Concentrations of Organic Matter in Transport in the Ogeechee River, Georgia^a

	Mean (mg AFDW liter ⁻¹)	Percentage of total organic matter
Dissolved organic matter	25.4	96.32
Particulate organic matter		
Amorphous material (bacteria)	0.301	1.141
Amorphous material (protozoans)	0.039	0.148
Amorphous material (other)	0.521	1.976
Vascular plant detritus	0.028	0.106
Algae (mostly diatoms)	0.060	0.228
Fungi	0.014	0.053
Animals	0.002	0.008
Total particulate organic matter	0.97	3.68
Total organic matter in transport	26.37	100.00

^a Modified from Benke and Meyer (1988). AFDW = ash-free dry weight.

hyporheic sediments can be very high with as much as 60% degradation (McDowell, 1985; Hedin, 1990; Fiebig and Lock, 1991; Findlay and Sobczak, 1996; Pusch, 1996).

8. Up to half of the DOC of stream water can be metabolized by microbes attached to sediment particles from interstitial water flowing through the hyporheic zones of porous sediments of streams (e.g., Crocker and Meyer, 1987; Findlay *et al.*, 1993).

9. Rates of physical and microbial degradation of DOM, particularly humic substances, can be greatly accelerated by exposure to sunlight (see later discussion). In the absence of light, abiotic removal of DOC is slight (e.g., Kuserk *et al.*, 1984).

10. Large POM is decomposed slowly and has a longer retention time within a particular reach of the stream (Chap. 21).

Total organic carbon turnover length is the average downstream distance traveled by a carbon atom in a

fixed or reduced (organic) form, calculated as the ratio of the downstream transport of organic carbon (per unit stream width) to benthic respiration (per unit area). Therefore, turnover length measures the rate at which organic material is lost from streams relative to the rate at which it is used (Webster *et al.*, 1995). Turnover length increases downstream and therefore with increasing stream order and average discharge. The bioavailability of riverine dissolved organic matter (DOM) appears to be greater under low discharge conditions and decreases with distance downstream. The chemical composition of the DOM tends to become more recalcitrant with greater time in the river (Leff and Meyer, 1991; Sun *et al.*, 1997). Downstream decreases in bioavailability were attributable primarily to selective degradation of aliphatic carbon in the riverine DOM.

Estimations of the rates and importance of autochthonous primary production in streams by the attached benthic algae, lotic phytoplankton, and larger aquatic plants are very difficult (reviewed by Wetzel, 1975b; Minshall, 1978; Bott, 1982; Wetzel and Ward, 1992) (cf. Chaps. 15, 18, and 19). Overwhelming evidence indicates that terrestrial photosynthesis and importation of this organic matter to stream ecosystems are the primary carbon and energy sources of these systems; that is, that streams are largely heterotrophic. Such is indeed the case in heavily canopied woodland and forested streams in which autochthonous primary production is very low or negligible.

In noncanopied streams and in rivers as they increase in size and decrease in velocity of flow, the significance of primary productivity of lotic phytoplanktonic and attached algae and macrophytes increases (Fig. 23-4). Animal consumers within the floodplain habitats of large rivers depend heavily on algal organic matter from both phytoplankton and periphyton for

TABLE 23-6 Estimates of Inputs of Particulate Organic Matter to a 135-km Reach of the New River (North Carolina, Virginia, West Virginia)^a

Source	Input (mT AFDW yr ⁻¹)	Percentage of total input
Allochthonous		
Upstream and tributary	5893	53.8
Within study area	64	0.5
Autochthonous		
Periphyton	3570	32.6
Aquatic macrophytes	1435	13.1
Total particulate organic matter input	10962	

^a From Hill and Webster (1983). AFDW = ash-free dry weight.

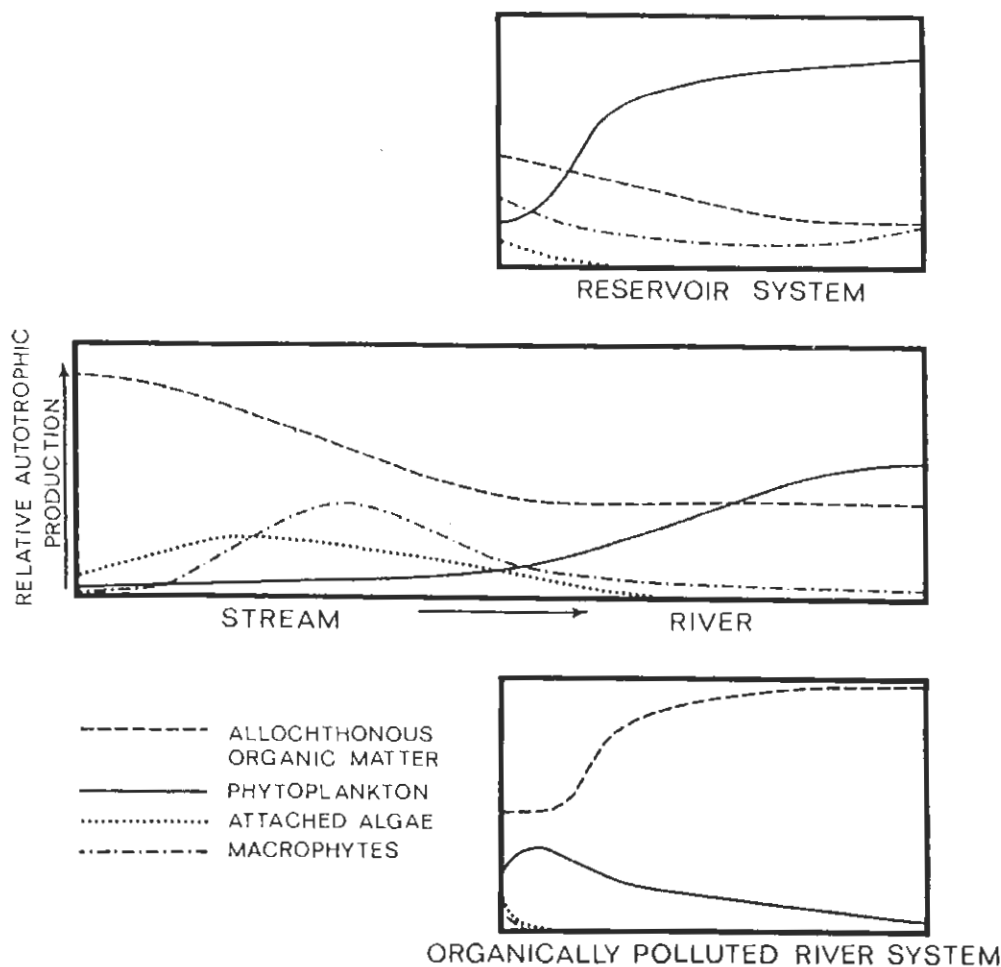


FIGURE 23-4 Generalized scheme of the relative contributions of allochthonous organic matter and autotrophic production by attached algae, phytoplankton, and aquatic macrophytes in the transition of a stream to a river system, if it is impounded where velocity of flow is reduced or practically eliminated or if it is organically polluted. (From Wetzel, R. G.: Primary production. In Whitton, B. (ed.): *River Ecology*. Oxford, Blackwell Sci. Publs., 1975.)

growth (Hamilton and Lewis, 1992; Hamilton *et al.*, 1992). However, the heterotrophic metabolism of these river ecosystems is totally dominated by microbial metabolism. Running waters can clearly vary in their proportion of heterotrophic and autotrophic metabolism. The relative significance of these types of metabolism is dynamic and varies considerably at local levels within a river system and seasonally with shifts in many physicochemical parameters and shifts in loading with allochthonous (natural or artificially by pollution) organic matter. On an annual basis, however, all streams and rivers are net heterotrophic ecosystems (Wetzel, 1995, 2000a).

In many rivers, particularly those of low elevational gradients, flooding events are important for redistribution of both particulate and dissolved organic matter. Inundation of the flood plains of rivers can in-

crease the loading of organic matter from the decaying vegetation of the flood plain. Flooding behavior is very variable in relation to climate, precipitation periodicity and intensity, and extent of water-level regulation by reservoir damming. Examination of the extent and duration of floodplain inundation and flooding periodicity of an unregulated sixth-order river in the southeastern United States over a six-decade period indicated that >50% of the flood plain was inundated 15% of the time (54 day yr⁻¹). During 50% inundation, system width exceeded channel width by 19 times (Benke *et al.*, 2000). Over 50 to 100% of the flood plain was inundated for several months during the winter-spring period of high precipitation. Floods of 50% inundation of the flood plain had a duration of at least 30 days.

The flood pulse for this forested floodplain river was less predictable, and floods tended to be of shorter

duration than those of large tropical rivers. Flooding in this river was correlated primarily with seasonal differences in temperature and plant evapotranspiration. Thus, increases in temperature with decreases in precipitation will lead to large decreases in export of dissolved organic substances (Clair and Ehrman, 1996). Evapotranspiration is linked to precipitation in determining the river discharge because even large increases in precipitation can lead to decreasing discharge when accompanied by higher temperatures. In contrast, in tropical rivers, where annual patterns of flooding are driven by large seasonal variations in precipitation, flood plains can be inundated for four or more months (Junk, 1997a,b; Lewis *et al.*, 2000).

The primary productivity within reservoirs is extremely variable because of individual characteristics of morphometry, seasonal changes in water-retention times, and human manipulations of water level and retention. In general, nutrient loading and trophic state are higher at the river end of reservoirs than at the deeper, dammed end. Although phytoplanktonic productivity per unit volume may be higher at the river end than at the dammed end, increased inorganic turbidity and light reduction at the river end can cause a reduction of the depth of the trophogenic zone and a decrease in total productivity (e.g., Fig. 23-4). The primary productivity per unit area in some reservoirs can be approximately the same over the length of the reservoir. In these cases, the higher trophic state and volumetric productivity at the inflow end of the reservoirs shift to lower epilimnetic trophic states, lower volumetric productivity, but increased depth of the trophogenic zone at the dammed end.

2. General Metabolism of Organic Matter in Streams

Therefore, in summary, much of the dissolved organic matter in streams originates from lignin and cellulose and related structural precursor compounds of higher plants. These substances are abundantly produced in the true lake and river ecosystems—that is, the ecosystem includes the drainage basin and organic matter produced photosynthetically within it. The productivity of terrestrial vegetation and aquatic plants associated with the land–water interface region is manifoldly (usually several orders of magnitude) greater than that of algae. Organic substances from higher plant tissues are abundant, chemically complex, and relatively recalcitrant to rapid biological degradation (Thurman, 1985; Haslam, 1998). During oxidative and anaerobic degradation, these compounds are modified by microbial activities in detrital masses, including standing dead tissues that can remain in an oxidative aerial environment for months or years. Much of the dissolved organic compounds released from partial de-

composition of the plant tissues and from associated microbial degradation products are leached and partially degraded en route toward recipient lakes and streams. That microbial modification continues during partial decomposition in terrestrial soils and hydrosols of wetlands. Once within land–water interface regions, water containing dissolved organic compounds moves, often diffusely, through dense aggregations of living emergent and submersed aquatic plants and massive amounts of particulate, largely plant derived, detritus (extensively reviewed in Wetzel, 1990a). The enormous surface areas of these habitats support large aggregations of rapidly growing microbial communities. During transport through these microbial metabolic sieves associated with wetland and littoral areas, appreciable further selective degradation of more labile dissolved organic constituents occurs before final movement into the receiving lake body or river channel per se.

Although difficult to generalize, a common pattern is that DOM entering rivers is quite different among different sources. For example, in the Amazon ecosystem, heavy storm precipitation events transport relatively labile DOM, whereas DOM from wetlands and ground water tends to be hydrophobic and recalcitrant from selective biological utilization of the more labile components (McClain and Richey, 1996). DOM from litterfall leachates tends to be relatively labile.

As will be emphasized further on, the trophic dynamic structure of aquatic ecosystems depends operationally on a dynamic detrital structure (Wetzel *et al.*, 1972; Wetzel and Rich, 1973; Rich and Wetzel, 1978; Wetzel, 1995). From the standpoint of carbon fluxes, most energy and organic carbon of the systems is dead, of autotrophic origin, and undergoing microbial degradation, the rates of which are variable and serially decrease with increasing recalcitrance of the organic matter. In lakes, reservoirs, and rivers, detrital organic matter is the main supportive metabolic base of carbon and energy. Since most lakes of the world are small to very small, much of the autochthonous production of detrital matter originates from benthic littoral and wetland vegetation, which augments the loadings of dissolved organic matter from terrestrial origins. Similarly, detrital heterotrophic metabolism dominates in streams, where usually the major sources are allochthonously derived terrestrial plant material. Common to both lake and stream ecosystems is the dominance of detrital metabolism, which gives the ecosystems a fundamental metabolic stability. The trophic structure above the producer–decomposer level, with all of its complexities of population fluctuations, metabolism, and behavior, has a relatively small impact on the total carbon flux of the system. The detrital system provides stability to streams; the slower,

relatively consistent degradation of dissolved and particulate detritus by microorganisms underlies the more sporadic autochthonous metabolism that responds rapidly to, and depends to a greater extent on, environmental fluctuations. Autochthonous primary production is often small and variable, but in combination with allochthonous, autotrophically produced detritus, drives the lotic system. The functional operation of lentic and lotic systems converges at this point of similarity in detrital metabolism.

B. Allochthonous Organic Matter Received by Lakes via Streams and Rivers

1. Dissolved Organic Matter

The DOM of surface runoff is composed of relatively recalcitrant organic compounds resistant to rapid microbial degradation. The amounts of DOC and POC reaching a lake and the chemical composition of these organic compounds change seasonally with the volume of flow in relation to duration of retention in the

stream, the growth and decay cycles of the terrestrial and wetland vegetation through which runoff flows, and other factors, especially climatic variations.

An example is seen from quantitative analyses of dynamics of influxes of allochthonous detrital soluble and particulate organic carbon to a small temperate lake over an annual period in relation to their fate within and losses from the lake (Wetzel and Otsuki, 1974; Wetzel, 1989). Detrital organic carbon influxes were determined in water from a primary inlet stream, both before and after its flow had traversed a wetland adjacent to the lake, and from a second inlet stream, both at its headwaters and after the stream water passed through the wetland. Similarly, measurements were made of organic content of ground water where it entered the lake and at the outlet. Concentrations of organic carbon in inflows and outflows were converted to values of total carbon loading and outflow using a detailed annual water budget (Fig. 23-5). The DOC and the dissolved organic nitrogen (DON) increased significantly ($\times 2$) during the active growing season as the inlet water of the streams passed through the

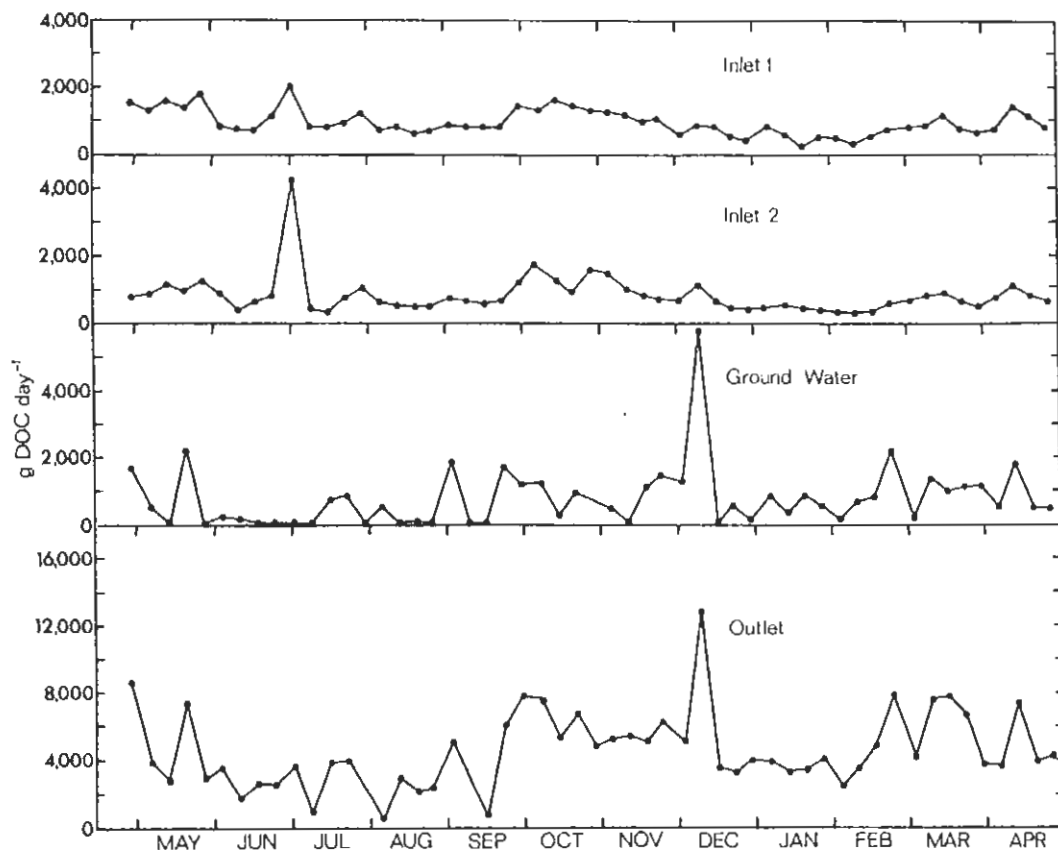


FIGURE 23-5 Dissolved organic carbon entering Lawrence Lake, Michigan, via ground water and the two stream inlets and leaving via the lake outlet. (From Wetzel, R. G., and Otsuki, A.: Allochthonous organic carbon of a marl lake. *Arch. Hydrobiol.* 73:31-56, 1974.)

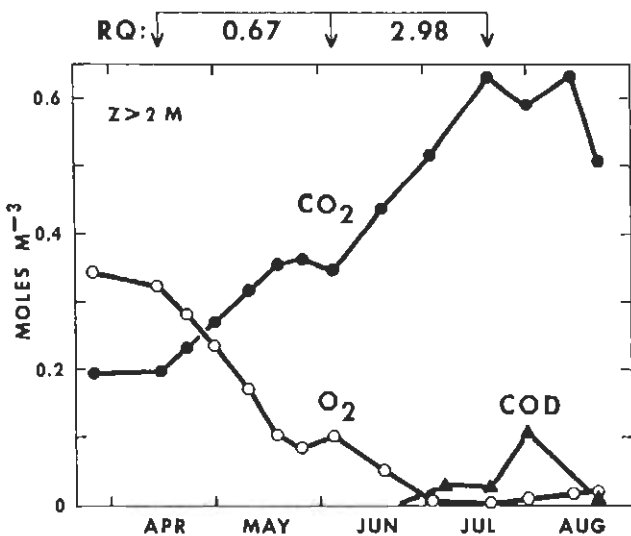


FIGURE 23-15 Changes in the hypolimnetic concentrations of CO₂, O₂, and chemical oxygen demand (COD) and the benthic respiratory quotients, Dunham Pond, Connecticut. (From data of Rich, 1975.)

Lake sediments have an "oxygen debt" that is indicated by low and negative redox potentials and nonbiological chemical uptake of molecular oxygen by reduced substrates that were formed under anaerobic conditions (Rich, 1975). This suggests that microbial metabolism involving glycolysis and reactions in the tricarboxylic acid cycle are continuing, while oxidative reactions using molecular oxygen as the terminal electron acceptor (i.e., the respiratory cytochrome system) are impeded by limited O₂ diffusion (Wetzel *et al.*, 1972). Viewing the RQ concept at the benthic community level, which would include the anaerobic bacteria that utilize electron acceptors other than molecular O₂, the benthic respiratory quotients would be greater than those of organisms undergoing aerobic metabolism. Additionally, the *in situ* RQ values would be expected to vary seasonally with water circulation periods at overturn and changes in redox gradients in response to varying rates of oxygen diffusion. Such was the case in Dunham Pond, Connecticut, in which Rich (1975) found during stratification that respiratory quotients of the hypolimnion varied inversely with the availability of oxygen (Fig. 23-15) from <1 after spring circulation and oxygen renewal. The respiratory quotients increased, however, to nearly 3 under anoxic conditions during the latter portion of summer stratification. Similar results have been found in a number of other lakes (Rich and Devol, 1978; Rich, 1980; Mattson and Likens, 1993). Under anaerobic conditions, high respiratory quotients are the result of the oxidation of

organic carbon to CO₂ during the reduction of alternate electron acceptors, which then appear as oxidizable substrates. Reductions in sediment mass also result from this process, because soluble and gaseous products are formed that increase diffusion of reduced matter out of the sediments. Further, the removal of oxygen (reduction) from permanently sedimented carbon compounds represents the removal of more than half their mass.

To conclude, the alternate role of detrital electron flux suggests that existing lakes can be viewed as temporarily sedimenting energy rather than mass, which permits an extended existence. Simultaneously, benthic detrital electron flux tends to close the carbon and particularly the oxygen cycles of lakes.

V. DETRITUS: ORGANIC MATTER AS A COMPONENT OF THE ECOSYSTEM

Studies that address detrital origins and its metabolism directly, including the nonplanktonic and terrestrial components of the lacustrine ecosystem, are few. The heterogeneity and diversity of lacustrine detritus are reflected in the compound nature of most lake ecosystems. The role of allochthonous inputs in the metabolism and trophic of streams has been emphasized by numerous investigations (Ross, 1963; Hynes, 1963; Darnell, 1964; Cummins, 1973). Similarly, pelagic metabolism can be strongly influenced by edaphic factors and terrestrial metabolism in small lakes with high drainage-area-to-volume ratios. The importance of very high wetland and littoral productivity and extensive loading of organic matter and nutrients from the drainage basin disputes Forbes's (1887) statement that a lake. . . "is an islet of older, lower life in the midst of the higher, more recent life of the surrounding region." Further, it is simply untrue, as Shelford (1918) proposed, that "one could probably remove all the larger plants from a lake and substitute glass structure of the same form and surface texture without greatly affecting the immediate food relations." Most lakes are small with high shoreline-to-surface-area ratios, and pelagic metabolism is modified by littoral metabolic activities and inputs. Moreover, sedimentation of organic matter from both littoral and pelagic sources in the relatively static waters of lakes results in a displacement of much of the lake's metabolism to the sediments. Prerequisite to a study of aquatic ecosystem structure is a complete representation of the productivity inputs of all components. The metabolism of detrital organic matter results in a complex carbon cycle that dominates both the structure and function of lake and river ecosystems.

A. Definitions of Detritus and its Functions

Organic detritus or "biodetritus" was described by Odum and de la Cruz (1963) as dead particulate organic matter inhabited by decomposer microorganisms. The existence and importance of detritus in many habitats have since become the subject of a large and widespread literature. However, the position of detritus in relation to the trophic dynamic concept of Lindeman (Chap. 8) was not clarified until recently. Balogh (1958) demonstrated that detritus, as egested material, can constitute an important fraction of total metabolism in several terrestrial soil and litter communities. On the other hand, Odum (1962, 1963) and others have emphasized that detritus originating as ungrazed primary production supports a "detritus food chain" that is essentially parallel to the conventional "grazer food chain" at succeeding trophic levels.

The importance of the divergence between the concepts of the grazer food chain and the detritus food chain has been emphasized and clarified by Wetzel and co-workers (1972; Rich and Wetzel, 1978; Rich, 1984). Part of the difficulty stems from the concept of ecological efficiencies as it grew out of the original statement of the trophic dynamic model by Lindeman (1942; cf. Kozlovsky, 1968). Lindeman's trophic dynamic concept indeed offers explanations for Eltonian pyramids of numbers and biomass. The postulated trophic levels estimated predation and concluded that energy transmitted by predation influences the amount of biomass at each trophic level. In this way, productivity included biomass and turnover dynamics by respiration, predation, and nonpredatory losses. Lindeman estimated predation or trophic transfers at every trophic level simply by biomass plus respiration at each trophic level. Thus, his corrected productivity was the sum of biomass, respiration, and inferred predation and decomposition. Decomposition was egestion (defecation) by a predator or ingested but unassimilated prey by simple difference (decomposition of trophic level n material was egestion by trophic level $n + 1$). Other nonpredatory losses, such as prey not killed or prey killed or that died but were not eaten, were ignored as trivial, which they are not.

Efficiency is a ratio of product over reactant, or, in the case of an ecological efficiency, the productivity of a predator over predation upon its prey. Lindeman defined trophic efficiency as the ratio between assimilation by one trophic level and the assimilation of the preceding trophic level (i.e., Λ_n/Λ_{n-1}). This formulation recognizes neither the existence of material egested or otherwise lost by trophic level n nor postassimilatory, nonpredatory losses at Λ_{n-1} , which may be lost to

those trophic levels and to the grazer food chain but which are not lost to the ecosystem as a whole. Although later studies on ecological efficiencies have used different formulae (e.g., $\text{Ingestion}_n/\text{Ingestion}_{n-1}$) (Slobodkin, 1960, 1962), discrimination between egestion and other nonpredatory losses from respiration is commonly not done (Burns, 1989; Hairston and Hairston, 1993). Therefore, most empirically derived aquatic ecological efficiencies that do not specify respiration are in reality agricultural or grazer food chain efficiencies and not applicable to complete ecosystems in which detrital organic matter is the significant trophic pathway.

A more realistic system operation is integrated diagrammatically in Figure 23-16. Here autochthonous organic matter represents all carbon fixed by autotrophs living within the lake or river ecosystem, minus their respiratory losses. The actual immediate form of organic matter productivity may be living cellular material (primary POM), which may become detrital secondarily, or dead particulate or dissolved organic carbon, or both.

A three-phase system of organic carbon is operational: dead organic matter, both particulate and dissolved (Fig. 23-16, *left*); living particulate organic material (*right*), which has the potential of entering either the POC or DOC pool upon death and whose metabolism may either create or destroy all three phases; and CO_2 . Nonliving equilibrium forces are also present (e.g., photooxidation and hydrolysis of organic compounds). As is discussed later, these processes potentially represent turnover rates that can equal biological metabolism and certainly can enhance rates of microbial utilization. Therefore, metabolism represents the organizing force in the structure of the organic system, and it is metabolism that determines to a large extent the kinds and magnitudes of transformations that occur between the oxidized and reduced forms of carbon. The top of the diagram represents the zone of reduced carbon inputs, the middle portion the zone of oxidation to CO_2 , and the lower portion represents losses of organic matter from boundaries of the system. The two parallel dynamic pools of organic carbon (dead, *left*; living, *right*) originate photosynthetically and are depleted by oxidation to CO_2 and exports. Although bacteria are shown in association with detritus, they function as biota. Odum's detritus food chain is really a link between the two pools in the direction of the biota. From the standpoint of the ecosystem, however, microbial and photochemical utilization of organic matter is a major utilization of organic matter that totally dwarfs utilization by higher organisms. Moreover, nonpredatory losses are in reality "nonpredatory productivity"—that is, productivity that is available to organisms other than predators, namely bacteria.

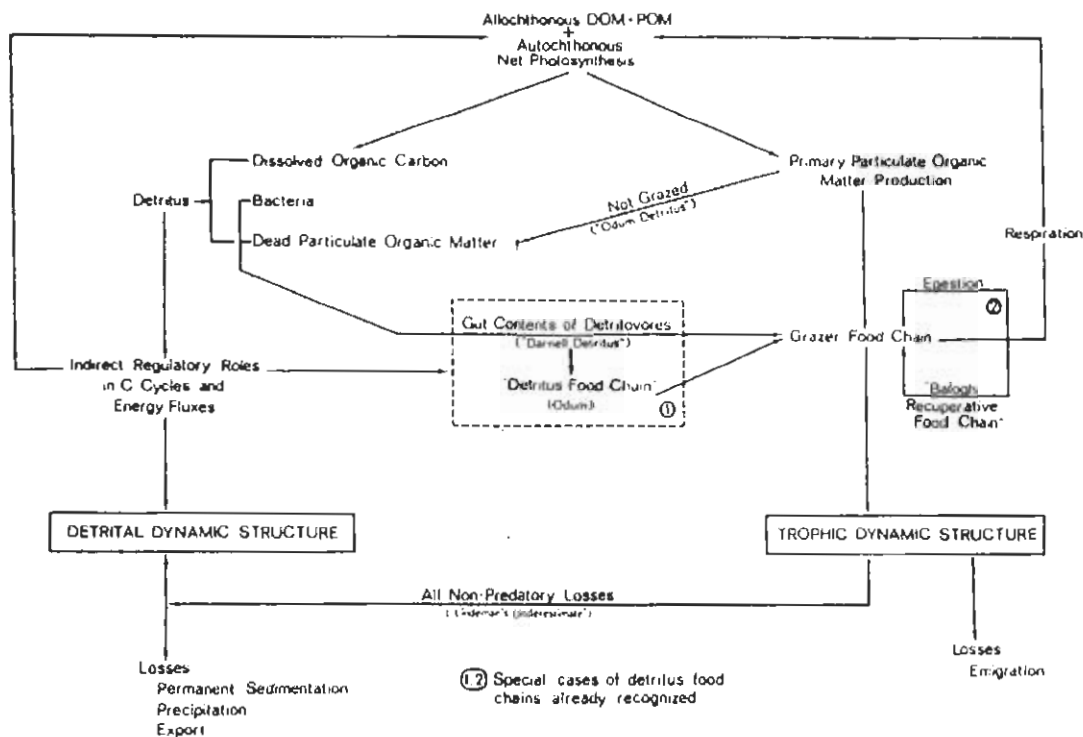


FIGURE 23-16 Generalized integration of the trophic and detrital dynamics of aquatic ecosystems. (From Wetzel *et al.*, 1972.)

A major point to be emphasized is that frequently >90% of the organic matter entering the system from photosynthetic sources is not utilized in the grazer and detrital food chains. Among studies of the trophic dynamic food cycle relationships, lack of appropriate recognition of nonpredatory losses from autotrophs ("Odum's detritus") and nonpredatory losses from heterotrophs ("Lindeman's underestimate"; see Fig. 23-16) represents a major void in contemporary system analyses.³ As noted earlier (Table 16-12), Richman (1958) and Slobodkin (1962) demonstrated that a large amount of ingestion is not assimilated and that egestion can be 80% or more of what is ingested, instead of the 10–20% estimated by Lindeman. Ingestion and the percentage of egestion increase markedly with increasing food availability.

Detritus and associated terms have been redefined (Wetzel *et al.*, 1972; Rich and Wetzel, 1978) in an attempt to make current terminology consistent with the ecosystem concept and to avoid perpetuating the oversight of nonpredatory pathways. The new definitions do not contradict the old, but are defined more broadly

so as to avoid some of the ambiguity inherent in the concepts of the ecosystem and trophic-level efficiencies espoused by earlier investigators and perpetuated by many recent ones.

Detritus consists of organic carbon lost by non-predatory means from any trophic level (includes egestion, excretion, secretion, and so forth) or inputs from sources external to the ecosystem that enter and cycle in the system (allochthonous organic carbon). This definition removes the highly arbitrary "particulate" restriction from existing definitions of detritus. In terms of the ecosystem, there is no energetic difference between DOC lost from a phytoplankter or feces or other exudates lost from an animal. Rates of utilization may differ, but functionally the organic carbon and energy are the same. Detritus is all dead organic carbon, distinguishable from living organic and inorganic carbon.

Second, the bacterial component is not combined with detritus ("biodetritus" = POM plus bacteria of Odum and de la Cruz, 1963) because this interferes with the general applicability of the term to situations in which detritus is not simply ingested. Such cases include the use of detrital energy in the regeneration of nutrients such as CO₂, N, and P; algal heterotrophy; losses by adsorption; flocculation; precipitation with CaCO₃; chelation of elements, and so forth. In some

³Notable exceptions are the theoretical analyses and models of Patten (1985), who has shown the important thermodynamic relationships of detritus and how the ecosystems must operate.

cases, plant and algal materials can pass through the digestive tracts of animals and not be completely killed before being released in feces (e.g., Porter, 1973, 1975; Velimirov, 1991). Growth can continue with these living cells or plant fragments after gut passage and even be enhanced by exposure to concentrated nutrient supplies en route. This material would be excluded from the definition of detritus. Detritus is dead, and therefore living egested material is not detritus.

The *detritus food chain* is any route by which chemical energy contained within detrital organic carbon becomes available to the biota. Detrital food chains must include the cycling of detrital organic carbon, both dissolved and particulate, to the biota by direct heterotrophy of DOC, chemoorganotrophy, or absorption and ingestion. The definition of "detritus food chain" emphasizes the actual trophic linkage between the non-living detritus and living organisms and recognizes the metabolic activities of bacteria attached to detrital substrates as a trophic transfer. The special case of a detrital food chain in which detrital energy is subsequently transferred by noncarbon substrates in an anaerobic environment has been termed *detrital electron flux*. As discussed in the previous section, such energy may reenter the biota (chemosynthesis) or mediate chemical or physical phenomena, or both, such as increasing the availability of inorganic nutrients in an anaerobic hypolimnion or in the sediments. The term *flux* specifies the flow of electrons, not carbon, to alternate electron acceptors in the absence of molecular oxygen.

Detritus, as a component of the environment, can also affect facets of the chemical and physical milieu without clear, defined energetic transformations of the detritus itself. In this situation, reference is made to effects of detritus that do not involve oxidation-reduction reactions. Examples include several indirect effects by which detrital organic carbon can influence and regulate the total energy and carbon flux of an aquatic system. Adsorption onto the surfaces of and coprecipitation of dissolved organic compounds with inorganic particulate matter (clays, CaCO_3 , and others), and complexing of inorganic nutrients by dissolved organic substances (e.g., humic compounds) are examples of this interaction.

Physical processes, such as partial or complete photochemical modification of organic macromolecules, can result in major alterations in biological availability of portions of complex, heterogeneous dissolved organic compounds. These processes can affect the decomposition, utilization, and effects of dissolved organic matter in many ways. Examples include:

a. *Alterations of enzymatic accessibility by the macromolecules.* In particular, cross-linking of polypep-

tide chains with polyphenolic humic substances can lead to enzymatic inhibition or reduction of activity (e.g., Wetzel, 1991, 1993; Haslam, 1998; Boavida and Wetzel, 1999).

b. *Partial photolysis of humic macromolecules,* particularly with the generation of volatile fatty acids and related simple compounds that serve as excellent substrates for bacterial degradation (e.g., Stewart and Wetzel, 1981; Wetzel *et al.*, 1995; Moran and Covert, 2001; discussed in detail in Chap. 17). It is important to recognize that of the total photolytic irradiance, about half of the partial photolysis of organic substrates results from UV-B (285–300 nm) and UV-A (320–400 nm) irradiance. Transmittance and photolytic activity from UV-B and UV-A is restricted largely to the surface waters. In contrast, photosynthetically active radiation (PAR, 400–720 nm), although much weaker energetically than UV, penetrates into water to much greater depths. Although photolysis of organic compounds is appreciably less than that induced by UV at surface waters, the photolytic generation of simple substrates is appreciable by PAR as well as by UV (Fig. 23-17). Results of such studies are indicating that over half of labile organic substrates are generated by PAR irradiance of dissolved humic substances.

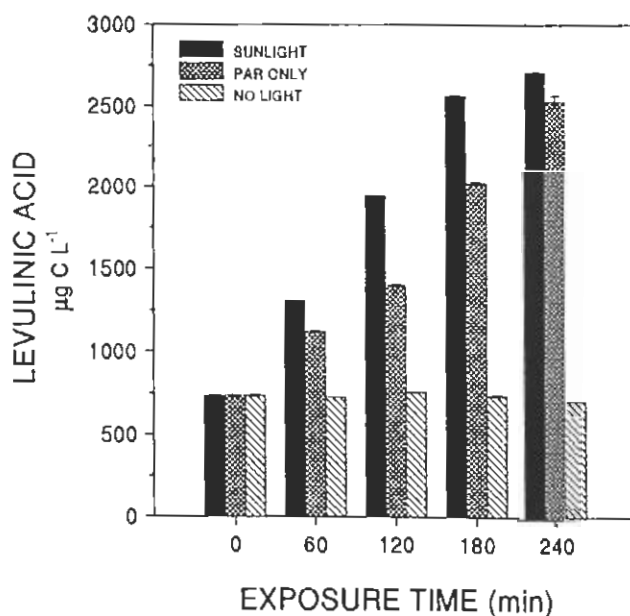


FIGURE 23-17 Net generation of levulinic acid from the partial photolysis of sterile whole leachate (0.2- μm pore-size filtrate) of the emergent macrophyte *Juncus effusus* (10 mg DOC liter⁻¹) after four weeks of microbial decomposition at 20°C in the dark. Exposed to full natural sunlight of UV-B, UV-A, and photosynthetically active radiation (PAR) (13.05 mol m⁻² over the 4-h period), to PAR only, and incubated simultaneously in the dark. Error bars = SD, $n = 3$. (Modified from Wetzel, 2000d.)

If the photodegradation continues to the point that most of the chromophoric humic compounds are photolysed and utilized biologically or converted to CO_2 , the residual nonchromophoric DOC appears to be fairly resistant to appreciable biological degradation. For example, in very shallow wetland pools and saline lakes, chromophoric DOC can be reduced appreciably (Tranvik and Kokalj, 1998; Arts *et al.*, 2000). In many shallow saline lakes, the nonchromophoric DOC concentrations can be very high (to $30 \text{ mg C liter}^{-1}$ or more). The specific nature of the recalcitrance of nonchromophoric DOC to bacterial degradation is unclear. Exposure of dissolved humic substances to strong UV-C (254 nm) reduced subsequent growth of bacteria (Lund and Hongve, 1994). These authors suggested that radicals induced by radiation mediated the negative growth effects. However, most of the identified nonabsorbing photodegradation products are good substrates for bacteria (e.g., Wetzel *et al.*, 1995).

c. *Partial photodegradation of dissolved organic nitrogen and phosphorus compounds* to release inorganic nutrient compounds such as nitrate, ammonia, and phosphate (e.g., Manny *et al.*, 1971; review of Moran and Zepp, 1997).

d. *Complete photolysis of humic substances to CO and CO_2* , with some dissociation to dissolved inorganic bicarbonate as well as evasion of some CO_2 to the atmosphere. Photochemical oxidation by sunlight of natural dissolved organic carbon compounds to both carbon monoxide (CO) and dissolved inorganic carbon (DIC) has been known for some time (e.g., Miller and Zepp, 1995). Depending on the dissociation conditions, some excess CO_2 will evade to the atmosphere. Early studies on the photolytic degradation of dissolved organic matter suggested that the dominant component of solar irradiance was UV-B and UV-A and that PAR above 400 nm was of little consequence. Many of these studies, however, were not performed under sterile conditions, and as a result findings were confounded by nearly instantaneous microbial utilization of the organic compounds generated with rapid degradation and generation of CO_2 . Moreover, many of the DOM sources of these studies had been exposed to natural sunlight for long (e.g., weeks) and noncomparable periods of light. Contemporary research is indicating that although UV-B and UV-A are significant and can contribute to more than half of photochemical mineralization, photosynthetically active radiation (PAR, 400–720 nm) is also a major photolytic agent (Vähätalo *et al.*, 2000; Wetzel, 2000c,d). For example, from nearly 200 separate photolytic experiments on DOM from different waters and plant sources under different conditions of decomposition, the UV-B portion of the spectrum was always most effective in complete photodegradation to CO_2 , but

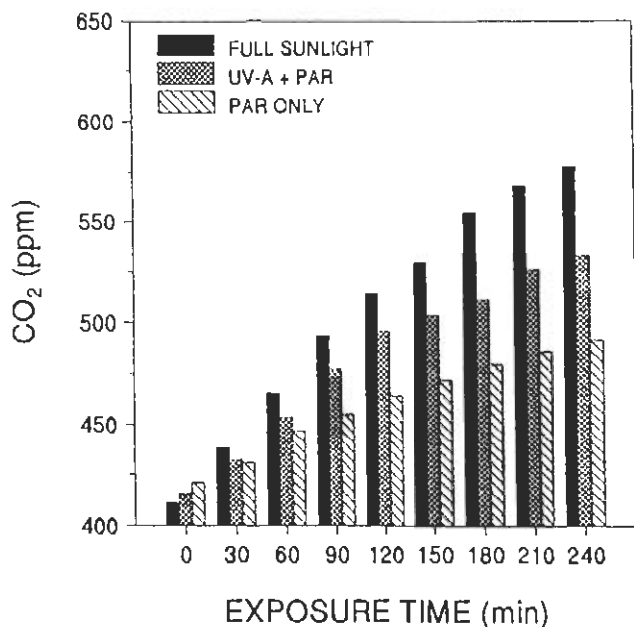


FIGURE 23-18 Photolytic degradation of sterile dissolved organic matter (leachate from *Juncus effusus*, $0.2\text{-}\mu\text{m}$ pore-size filtrate) to CO_2 under replicated, aseptic conditions exposed to full sunlight (UV-B, UV-A, and PAR) of 15.53 mol m^{-2} over the 4-h period, to UV-A + PAR, and PAR only. (From Wetzel, 2000a.)

UV-A was also highly effective, with small differences from the photolytic capacities of UV-B (Fig. 23-18). PAR is also highly effective in photolytic degradation of DOM to CO_2 , and about one-quarter (23.4%) of the collective photolysis can be attributed to the largely blue portion of the PAR spectrum (400–700 nm) and ca. 68% to UV-A (320–400 nm) (Fig. 23-19).

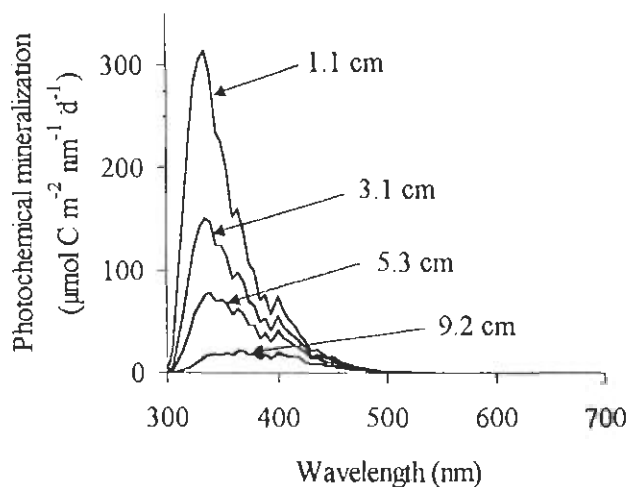


FIGURE 23-19 Photochemical mineralization of chromophoric dissolved organic matter at different depths in humic lake Valkea-Kotinen, Finland, 26 July 1994, indicating the increasing proportion of mineralization with greater depth resulting from irradiance in the visible range. (Modified from Vähätalo *et al.*, 2000.)

Approximately half of the collective photolysis was induced by natural light of a wavelength >360 nm. The relative importance of PAR as a mineralizer to that proportion increases with greater depths.

Both partial photolysis to the generation of volatile fatty acids and other simple organic substrates, as well as complete photolysis with the generation of large quantities of CO_2 by PAR, are important findings because of the much lower extinction rates of PAR in water in comparison to those of ultraviolet irradiance. Photolytic processes, so important to nutrient cycling, are therefore not restricted to the uppermost strata of a few centimeters of aquatic ecosystems, but rather can affect much of the variable volume of the photic zone.

Furthermore, the photolytic responses are very rapid. For example, when natural sunlight was attenuated very rapidly, as by a severe thunderstorm (Fig. 23-20, middle), the rate of photolytic degradation of DOC to CO_2 declined precipitously, but the photolytic capacities of PAR declined more rapidly than did the effects of UV-B (Fig. 23-20, lower). The precise chemi-

cal degradation processes involved in photolysis of dissolved macromolecules, particularly the helical humic substances, represent a major void in our understanding. Interdisciplinary collaboration among chemists and biologists is essential to progress effectively in our understanding of biological implications of organic molecular structure.

Less direct but important biogeochemical interactions of dissolved organic matter in aquatic systems are also important but poorly studied at the ecosystem level. Natural dissolved organic substances, particularly humic compounds, in aquatic ecosystems can interact with other important metabolic components. For example, dissolved organic compounds can:

a. *Interact with inorganic compounds*, particularly in complexation reactions such as chelation, as discussed earlier (Chap. 14; see also Perdue, 1998). Depending on the concentration ratios of the complexing DOM to inorganic elements, the mode of organic complexation, biological availability, and, in some cases, elemental toxicity can be increased or decreased.

b. *Interact with other organic compounds*, such as peptidization, and alter biological susceptibility to enzymatic hydrolysis. Bonding of proteins, glycoproteins, and carbohydrates to polyphenolic humic macromolecules is a common process and results in macromolecules of considerable size (1500–90,000 D) (Münster, 1985). Membrane properties, such as lipid hydrophobicity, can be altered by such interactions with humic substances and in turn affect enzyme hydrolysis rates and nutrient transport mechanisms (e.g., Lemke *et al.*, 1995, 1998). In a most interesting interaction, humic substances can complex with proteins, particularly enzymes both freely soluble and membrane-bound, with noncompetitive inhibition (Wetzel, 1992, 1993; Münster and De Haan, 1998). Enzymes can be stored for long periods (days or weeks) in this complexed, inactive state, be redistributed in the ecosystem with water parcel movements, and be reactivated by partial photolytic cleavage by ultraviolet irradiance (Fig. 23-21) (Wetzel, 1991, 1995, 2000c; Boavida and Wetzel, 1999).

In addition, dissolved humic substances can sorb hydrophobic organic chemicals and thereby reduce their bioconcentration and toxicity (Kukkonen, 1999; Steinberg *et al.*, 2000). The binding capacity is linearly related to the hydrophobicity of the contaminant. The detoxifying capacity of humic substances is directly correlated with the quotient between aromatic and aliphatic carbons in the humic substances.

c. *Alter chemical properties such as redox and pH*; for example, exposure of natural dissolved organic matter to UV of sunlight can result in a photochemical

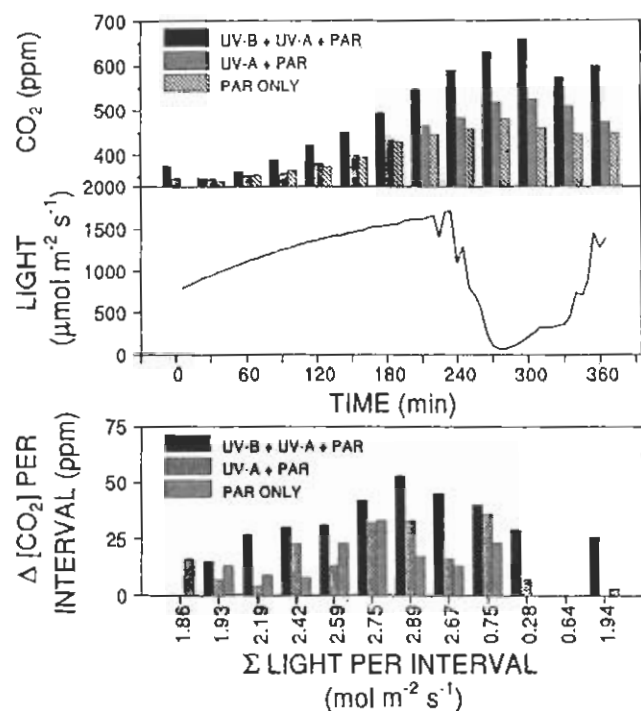


FIGURE 23-20 Photolytic degradation of sterile dissolved organic matter (aquatic plant leachate, *Juncus effusus*, 0.2- μm pore-size filtrate after 20 weeks of microbial decomposition) to CO_2 under replicated, aseptic conditions exposed to full sunlight (UV-B + UV-A + PAR), UV-A + PAR only, and PAR only (upper). A heavy rainstorm occurred during the incubations, which reduced light severely for an hour (middle). The net change in CO_2 production per amount of light received per interval under these conditions (lower). (From Wetzel, 2000a.)

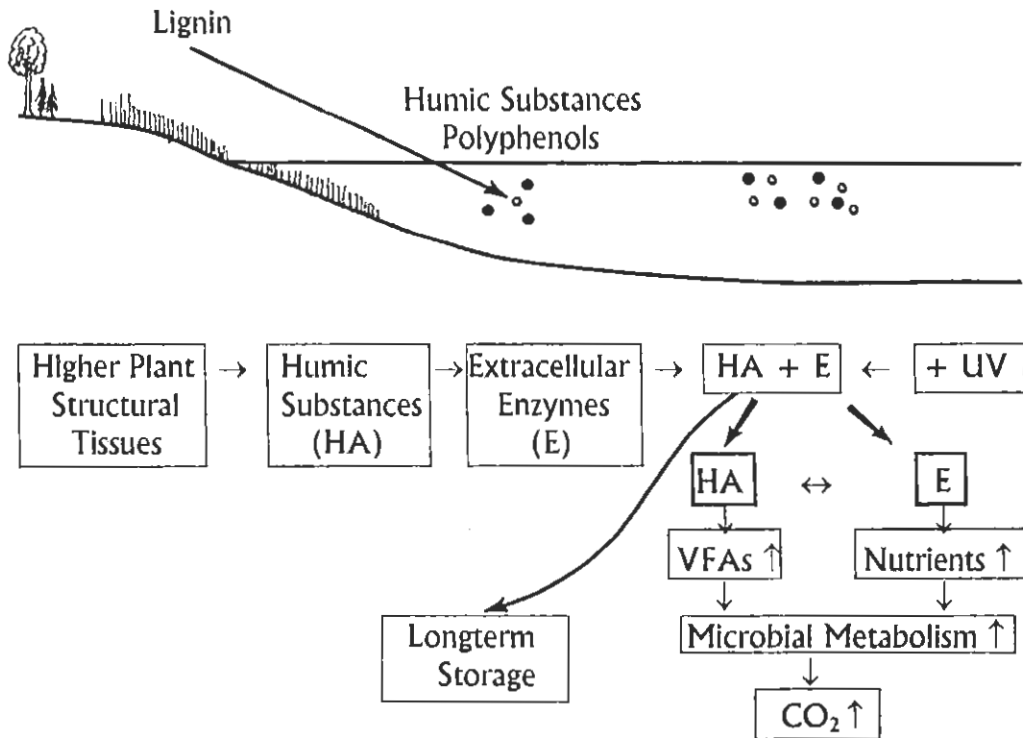


FIGURE 23-21 Potential interactive pathways and processes of humic substances emanating from decomposition products of higher plant tissues with extracellular and surface-bound enzymes and photolytic reactions, particularly with UV irradiance. Humic acid-enzyme complexes can be stable for long periods (weeks or months) and subsequently reactivated upon exposure to weak UV light. Further photolysis can cleave simple compounds from the macromolecules for subsequent utilization. (From Wezel, 2000a.)

formation of reduced oxygen species, particularly hydrogen peroxide (H_2O_2) (Cooper *et al.*, 1988; Scully *et al.*, 1994). H_2O_2 , with a half-life of several hours in natural waters, can radically alter redox cycling of metals (Moffet and Zika, 1987).

Humic substances may buffer against acidification but may also add natural acidity to surface waters when in very high concentrations in waters of low ionic strength. Organic carboxylic and phenolic acids provide a pH buffer when the pH is between 4 and 5 and the carbonate buffering capacity is absent (Kullberg *et al.*, 1993; Lydersen, 1998). Organic acids can modify the acidity of surface waters and depress water from 0.5 to 2.5 pH units when the acid-neutralizing capacity is in the range of $0-50 \mu\text{eq liter}^{-1}$. Thus, a predominance of humic acids can result in an organic acidity that can influence, and at times exceed, inorganically derived acidity from natural or anthropogenic sources (cf. Chap. 11). However, usually organic anions represent $<10\%$ of the total anions and contribute little to acidity except in waters of extremely low ionic strength (Henriksen *et al.*, 1988; Urban *et al.*, 1988; Driscoll *et al.*, 1989; David *et al.*, 1992). Strong acids, particularly H_2SO_4 , can exceed the buffering capacities of or-

ganic acids and shift surface water acidification by organic acids to total dominance by strong acids. High production of organic acids in peat wetlands and similar environments are often neutralized within the fens and bogs.

d. *Microbially reduced humic substances can*, upon entering less-reduced zones of sediments, serve as electron donors for the microbial reduction of several environmentally significant electron acceptors (Lovley *et al.*, 1999). Once microbially reduced, humic substances can transfer electrons to various Fe(III) or Mn(IV) oxide forms abiotically and recycle the humic compounds to the oxidized form, which can then accept more electrons from the humic compound-reducing microorganisms.

e. *Altered physical properties* such as selective modifications of light penetration. The well-known selective attenuation of light by chromophoric dissolved organic matter (cf. Chap. 5) can further modify biogeochemical cycling in numerous ways. Increasing light extinction can result in increased temperatures of surface strata with steep thermal discontinuities in the metalimnion and strong isolation of the colder hypolimnetic waters. The mixed layer depth decreases, which results

in reduced total heat content of the lake or reservoir (Hocking and Sraškraha, 1999). Modifications of the spectral penetration of light from dissolved organic matter can alter rates of photosynthesis, hormonal activities, and migratory distribution and reproductive behaviors (see Chaps. 15 and 16). Absorption of ultraviolet irradiance by humic substances can protect organisms from genetic damage as well as modify macromolecules and enhance bioavailability of organic substrates.

B. Detrital Dynamic Structure of Carbon in Lakes and Reservoirs

There have been very few attempts to examine the dynamics of detrital organic carbon on a functional basis. Such studies require measurements of all nonpredatory losses of organic carbon from any trophic level within the ecosystem as well as inputs from sources external to the ecosystem that enter and cycle in the system. Obviously, a number of simultaneously interacting components are operational. It is clear, nonetheless, that most of the organic metabolism of lake systems involves the detrital dynamic structure and that an understanding of this functional system is a prerequisite for meaningful evaluation of control mechanisms of the whole ecosystem. Stated another way, we must understand carbon flux rates among all components at the same time that we seek an understanding of parameters or human disturbances important in regulating metabolism.

Quantitative analyses of the major organic carbon transformations in lake systems have shown the following general characteristics: (1) The central pool of organic carbon is in the dissolved form; (2) Three major sources of particulate organic carbon occur: allochthonous, and two distinct major zones of autochthonous carbon flux, the littoral and the pelagic of lakes or the channel water of rivers; (3) Allochthonous inputs from the drainage basin and exports from the lake or river occur largely as dissolved organic carbon and represent a major flow of carbon through the metabolism of the system; and (4) Detrital metabolism occurs principally in the benthic region, where a majority of POC is decomposed in many lakes and rivers, and the pelagic area during sedimentation in lakes. Secondary metabolism thus is displaced from sites of production and input, by sedimentation in the case of POC and by aggregation and coprecipitation with inorganic matter in the case of DOC.

Examples in support of these generalizations can be obtained from analyses of an arctic tundra pond and of the pelagic zone of a eutrophic temperate lake for a single day, of a large reservoir over a 30-day period of the summer, and of a softwater and a hardwater tem-

perate lake over an annual period. Because of the complexity of these studies and the insights they offer into the central questions on metabolism, these analyses warrant closer scrutiny than has been given to other examples in this discussion.

The instantaneous carbon mass of the major components and transfer rates of carbon between them were evaluated for a typical midsummer day in a small arctic tundra pond by Hobbie *et al.* (1972, as modified and corrected in Hobbie 1980). These small ponds cover the northern tundra by the thousands, lying in depressions between low ridges formed above ice wedges; beneath them lies permafrost, which prevents any outflow. Most of the ponds are very shallow (<40 cm) and are frozen solid for nine months of the year. The tundra vegetation surrounding the ponds is dominated by two sedges (*Carex aquatilis* and *Eriophorum angustifolium*) and a grass (*Dupontia fischeri*). The dominant herbivore of the area is the brown lemming, which clips this vegetation close to the ground. Litter from these clippings and lemming feces form a significant source of particulate and dissolved matter reaching the ponds.

The DOC pool represented most of the total carbon present in the aqueous portion of the system because the inorganic carbon content was quite low (Fig. 23-22). Although the primary productivity on an annual basis was very low, 50% of the total was contributed by the macrophytes, 47% by the benthic algae, and 3% by the phytoplankton. The most active transfer path was the movement of detrital organic carbon from the aquatic plants to the sediments, where decomposition resulted in major respiratory loss as CO₂. The flux rates were much smaller in the water than in the sediments, and the transfer of organic carbon between POC and the zooplanktonic crustacea was small but significant. The photooxidation of dissolved organic compounds to CO₂, although small, is significant in this shallow habitat, as has been indicated for certain streams and lakes (cf. Gjessing, 1970; Gjessing and Gjerdahl, 1970; Stewart and Wetzel, 1981a; Wetzel, 2000a).

The organic carbon cycle of a shallow (1.5 m) tundra lake of the Northwest Territories of Canada was analyzed for five weeks of the open-water period by examination of CO₂ fluxes through benthic respiration and anaerobic decomposition, photosynthesis of benthic and phytoplankton communities, and gas exchange at the air-water interface (Ramlal *et al.*, 1994). The annual carbon budget estimate for the lake indicated that 50% of the carbon was produced by the benthic community, 20% by phytoplankton, and 30% by allochthonous organic matter. Benthic respiration dominated heterotrophic utilization of the organic matter.