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Concentrations and fluxes of organic carbon substrates in the aquatic environment

Dedicated to Prof. Drs. J. Overbeck on the occasion of his 70th birthday

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Abstract

Data concerning concentrations and fluxes of dissolved organic compounds (DOC) from marine and lacustrine environments are reviewed and discussed. Dissolved free amino acids and carbohydrates comprised the main fraction in the labile organic carbon pool. Dissolved free amino acids in marine waters varied between 3–1400 nM and those of freshwaters between 2.6–4124 nM. Dissolved free carbohydrates varied between 0.4–5000 nM in marine systems and between 14–1111 nM in freshwaters. The turnover times of both substrate pools varied in marine waters between 1.4 hours and 948 days and in freshwaters between 2 hours and 51 days. Measurements of stable $^{12/13}$C-ratio and ^{14}C-isotope dating in ocean deep water samples revealed DOC turnover times between 2000–6000 years. Studies on carbon flows within the aquatic food webs revealed that about 50% of photosynthetically fixed carbon was channelled via DOC to the bacterioplankton. Excreted organic carbon varied between 1–70% of photosynthetically fixed carbon in marine waters and between 1–99% in freshwaters. The labile organic carbon pool represented only 10–30% of the DOC. The majority (70–90%) of the DOC was recalcitrant to microbial assimilation. Only 10–20% of the DOC could be easily chemically identified. Most of the large bulk material represented dissolved humic matter and neither the chemical structure nor the ecological function of the DOC is as yet clearly understood.

Abbreviations: ATP: Adenosine Tri-Phosphate; AMS: Accelerated Mass Spectrometry; BSA: Bovine Serum Albumin; βGlAse: βGlucosidAse activity; DAA: Dissolved Amino Acids; DCAA: Dissolved Combined Amino Acids; DFAA: Dissolved Free Amino Acids; DTAA: Dissolved Total Amino Acids; DCHO: Dissolved Carbohydrates; DCCHO: Dissolved Combined Carbohydrates; DFCHO: Dissolved Free Carbohydrates; DTCHO: Dissolved Total Carbohydrates; DLCFaAc: Dissolved Long Chain Fatty Acids; DSCFaAc: Dissolved Short Chain Fatty Acids; DOC: Dissolved Organic Carbon; DOM: Dissolved Organic Matter; DHM: Dissolved Humic Matter; DTPhOH: Dissolved Total Phenolic compounds; DCPhOH: Dissolved Combined Phenolic compounds; DFPhOH: Dissolved Free Phenolic compounds; EOC: Excreted Organic Carbon; HS: Humic Substances; HPLC: High Performance Liquid Chromatography; HTCO:

High-Temperature Catalytic Oxidation; ($K_t + S_n$): Transport Constant + Natural Substrate from Michaelis Menten Kinetics; LOCP: Labile Organic Carbon Pool; OM: Organic Matter; MEE: Microbial Extracellular Enzymes; PER: Percent of Extracellular Release; PhDOC: Photosynthetically derived Dissolved Organic Carbon; POC: Particulate Organic Carbon; ROCP: Recalcitrant Organic Carbon Pool; T_t: Turnover time; UDOC: Utilizable Dissolved Organic Carbon; V_{max}: Maximum Uptake Velocity; WCO: Wet Chemical Oxidation

Introduction

Studies on the role of dissolved organic matter (DOM) in aquatic environments are relatively new compared to research on planktonic organisms (Brandt 1899; Fischer 1894; Korinek 1928; Reinheimer 1986). Emphasis has been placed on studies of the role of DOM and its interaction with aquatic microorganisms (Birge & Juday 1934; Ohle 1934; 1937; Krogh & Lange 1932; Waksman 1936). Based on carbon measurements on DOC in aquatic environments by wet chemical oxidation two fractions were defined by using 0.2μm–0.45μm pore size filtration: dissolved organic carbon (DOC) and particulate organic carbon (POC). The carbon concentrations of both fractions varied over a wide range. The ratio of DOC to POC covered mostly a range between 10:1 to 100:1 in different aquatic environments (Williams 1971, 1986; Romankevich 1984; Thurman 1985; Wetzel 1983). However, recent data have shown that small particles and colloids can also pass through 0.2–0.45 μm pore size filters (Moran & Buesseler 1992; Druffel & Williams 1990). The definitions of DOC and POC are therefore still more or less operational rather than absolute and of little help to characterize their ecological function. Both DOC and POC are important substrates for osmotrophic heterotrophs. DOC is the larger and dominant carbon pool in both small water bodies (e.g. lakes, ponds, rivers) and large water bodies (e.g. large lakes, estuaries, oceans). This fact has a fundamental influence on carbon cycling of global carbon pools (Hedges 1992; Woodwell et al. 1978).

The input of DOC and POC into aquatic environments occurs via many different routes (Wetzel 1990; Schindler et al. 1992; Faust & Hunter 1971; Münster & Chróst 1990; Hedges 1992). Odum & de la Cruz (1963), Odum (1963) and Wetzel (1984) defined DOC and POC as detritus having a definite function in aquatic ecosystems (Rich 1984; Rich & Wetzel 1978). Detritus can be either of autochthonous or allochthonous origin (Wetzel 1983). Both sources differ in their chemical composition and structure and this is essential in understanding the function of detritus (Gagosian & Lee 1981; Thurman 1985; Steinberg & Münster 1985) as a carbon, nutrient and energy source for microorganisms (Allen 1976, 1977; Rich 1984; Wetzel 1972, 1979, 1990).

The extent of detritus input into aquatic environments depends on productivity and non-predatory losses of organic matter (OM) (Wetzel 1972, 1979; Rich & Wetzel 1978). On the global scale detritus from rivers, lakes and oceans comprise a large carbon pool as shown in Table 1 and this carbon pool is of considerable importance for global carbon balances (Dixon 1992). Living biomass and detritus in oceans constitute one of the largest carbon pools and may exceed that of terrestrial biomass (Table 1). The organic carbon pools of lacustrine environments are quantitatively of minor importance. They act functionally equally at similar trophic levels in freshwater ecosystems as in oceans. These large carbon pools of OM are finally oxidized to CO_2 (Dixon 1992; Hedges 1992). Especially with respect to CO_2-fluxes and global climate changes more information about sources and sinks of these carbon pools are needed (Ducklow et al. 1986; Farrington 1992; Post et al. 1992). The detritus pools are primarily exploited by heterotrophic microorganisms. Osmotrophic microorganisms (e.g. bacteria) are the most efficient utilizers of DOM and they can even solubilize some POM for nutrient, energy and carbon requirements (Azam & Cho 1987; Azam & Ammerman 1984; Smith et al. 1992). Both, detritus and bacteria bridge the carbon, nutrient and energy flow between primary producers and the classical grazing food chain via the 'microbial loop' (Pome-

roy 1974; Sorokin 1977; Williams 1881; Azam et al. 1983; Azam 1986).

Assessment of the role of DOC and carbon fluxes in ecological studies

There is mutual agreement among aquatic microbiologists that bacteria play a major role in the cycling of organic carbon in aquatic environments (Williams 1981; Azam et al. 1983; Pomeroy & Wiebe 1988; Hobbie 1992). However, substrate utilization, growth rates and population dynamics of natural bacterioplankton are still not completely understood (Overbeck & Chróst 1990; Hobbie 1992). A crucial question is concerned with the role of organic substrate supply and the effect of grazers on bacterial populations (Wright 1984; Riemann et al. 1986). The role of DOC compounds and their availability for assimilation by bacterioplankton is especially poorly understood (Overbeck 1979; Münster & Chróst 1990; Hobbie 1992). The chemical composition and the complexity of monomeric and polymeric compounds in the DOC pool and the limited methods available to specifiy their structures and function under 'in situ' conditions are some of the most restricting factors in understanding their role (Farrington 1992; Lee & Wakeham 1992). Most studies on the main utilizer of the DOC pool, the bacteria, have been related to their trophic interactions with other plankton organisms and their role as prey for grazing microplankton. Investigations on the role of DOC compounds and their utilization by bacterioplankton have been largely restricted to small organic compounds from the labile organic carbon pool (LOCP), e.g. DFAA or DFCHO and used radiotracer methods. Only a few studies have combined radiotracer methods with chemical substrate analysis (Chróst et al. 1989; Burney 1986a; Burney et al. 1981a; Mopper & Lindroth 1982; Dawson & Gocke 1978; Liebezeit et al. 1980; Gocke et al. 1981; Coffin 1989; Fuhrman 1987; Fuhrman & Ferguson 1986).

Analytical-chemical methods versus radiotracer techniques in DOC studies

Chemical analyses of monomeric LOCP compounds alone do not provide suitable data to measure the actual flux of substrates from the place of synthesis or release to the consumer and utilizer. The values obtained represent more or less the equilibrium or threshold concentrations (Jannasch 1970) between two processes: release and uptake. The real flux of organic carbon can be better measured with an integrated approach, combining chemical analysis of those compounds of interest (monomers and polymers) and radiotracer methods for measurements of release and uptake of spe-

Table 1. Estimates of global organic carbon sources.

Location	Carbon sources in Gt (10^{15} g)		References
	DOC^{+}	POC*	
Terr. biomass (plants)		827	Whittaker & Likens (1973)
Terr. humus		1000–3000	Bohn (1976)
Trop. rain forest		344	Woodwell et al. (1978)
Boreal forest		108	Woodwell et al. (1978)
Oceans	780	24	Williams (1971)$^{\$}$
Oceans	1,800		Martin & Fitzwater (1992)$^{\$\$}$
Freshwater: lakes and rivers	0.02**		Woodwell et al. (1978)

* POC was defined as the organic matter fraction retained by 0.45 µm pore size filters.

** Not specified for DOC; sum of DOC and POC.

$^{+}$ DOC was defined as the organic matter fraction passing 0.45 µm pore size filters.

$^{\$}$ Measured by wet chemical oxidation method (Menzel & Vaccaro 1964).

$^{\$\$}$ Measured by high-temperature catalytic oxidation method (Sugimura & Suzuki 1988).

cific compounds under natural conditions as shown by Jørgensen et al. (1983), Carlucci et al. (1984), Chróst et al. (1989), Coffin (1989), Fuhrman & Ferguson (1986), Fuhrman (1987) and Riemann et al. (1986c).

The role of substrate availability from DOC for microbial starvation and growth

Jannasch (1970) and Sieburth (1979) have argued that labile substrates, such as glucose, are mostly found at threshold concentrations. Chemical analysis has confirmed that DFAA and DFCHO substrate pools are mostly found in nM concentrations and may represent such threshold concentration values. Therefore, it can be assumed that in many aquatic environments bacteria are living under substrate limitation or even under starvation conditions (Morita 1982; 1984; Kirchman 1990).

Only during short substrate pulses with higher DFAA and DFCHO concentrations do bacteria experience luxury conditions concerning sufficient substrate availability. From studies on extracellular products of free living and cultivated algae it has been found that light-dark cycles have a strong influence on the synthesis of intra- and extracellular (excreted) products (reviewed by Fogg 1983; Hellebust 1974). Carbohydrates are predominantly synthesized during the light period (Moris & Skea 1978; Hama & Handa 1987; 1992; Eppley & Sharp 1975), whereas during the dark period algae synthesize more proteinaceous organic substances (Cuhel et al. 1984; Lancelot & Mathot 1985; Hama & Handa 1987). Part of these photosynthetic products are released into the surrounding environment and can serve as excellent substrates for bacteria (Aaronson 1971, 1978; Anderson & Zeutschel 1970; Bell 1983). There are only few experimental data sets available where the effects of DOC substrate pulses on natural bacterioplankton activities and populations have been described and discussed. In addition to the direct metabolic coupling between e.g. phytoplankton and bacteria on the basis of released monomeric substrates, it has been shown that polymeric organic substrates from DOC play an important role in the nutrition and growth of microbial heterotrophs (Billén 1984, 1991). However, these substrates are partially recalcitrant to degradation (Benner et al. 1986; Cunningham et al. 1989; Stabel & Steinberg 1976; Stabel 1977; Steinberg 1977; Geller 1985a, 1985b, 1986; De Haan 1974; Haider 1988; Moran & Hodson 1990; Stabel et al. 1979; Zeikus 1981). Their assimilation requires an extracellular hydrolysis or degradation step (Priest 1984; Wood 1985; Wood & McCrea 1979) and their degradation may also be associated with photo-chemical reactions (Kieber & Mopper 1987, 1990; Mopper et al. 1990, 1991; Geller 1985a; Salonen & Tulonen 1990). The significance of such depolymerization processes in aquatic environments is now well recognised (Billén 1991; Hoppe 1991; Chróst 1989, 1991; Wetzel 1991, 1992). However, the amount of data is limited and examples of their use for total carbon flux calculations and modelling are still rare. Limitation of growth because of restricted substrate availability is the situation that pertains in natural aquatic environments. Microorganisms have efficiently adapted to such habitats to enable growth and substrate uptake (Matin 1979; Harder & Dijkhuizen 1982). One fitness criterium for growth in highly diluted environments is the efficiency of the established transport systems into the cell (Button 1985). The kinetic properties of these enzyme systems determine the organisms ability to bind the capture sub-

Table 2a. Chemical speciation of dissolved organic matter in the Pacific Ocean.[1]

Identified compounds	DOC ($\mu gC*1^{-1}$)	
	0–300 m depth	300–3000 m depth
Total organic carbon:	1000	500
Amino acids (DFAA and DCAA)	25	25
Sugars (DFCHO)	10	10
Fatty acids (free and combined)	40	10
Urea (free)	20	2
Aromatics (substituted phenols)	1	–
Vitamins (B^{12}, B^{1}, biotin)	0.01	0.01
Total	~ 100	~ 50
% Identified of total:	~ 10	~ 10

[1] Modified from Williams (1971).

strates at the cell surface and translocate them into the cell (Matin 1979; Button 1986). The mechanisms and regulation of these transporters under natural conditions are still poorly understood.

Autochthonous and allochthonous DOC in aquatic environments: the role of labile organic carbon and recalcitrant organic carbon pools

Autochthonously produced DOC differs significantly from allochthonous with respect to its chemical structure (Hedges et al. 1988a). Stepwise degradation of the DOC by bacteria, fungi and protozoa

Table 2b. Chemical speciation of dissolved organic matter in lake Plußsee.[$]

Identified compounds[aa]	DOC ($mgC*1^{-1}$)			
	0–1 m*	3–5 m**	5–8 m***	20–25 m****
Total organic carbon[+]:	4.28	4.13	3.21	3.56
Aromatic compounds (substituted phenols):				
DTPhOH[a$]	1.89 (44.2)[f]	1.93	1.26	1.10
DFPhOH[b$]	0.44 (10.3)[f]	0.41	0.34	0.22
DCPhOH[c$]	1.45 (33.9)[f]	1.70	0.92	0.75
Dissolved amino acids:				
DTAA	0.61 (14.3)[df]	–	–	–
DFAA[$$]	0.005 (0.1)[f]	0.006	0.005	0.003
DFAA[xxx]	0.004 (0.09)[f]	–	–	–
Peptide-AA[$$]	0.24–0.96 (5.6–22.4)[f]	–	–	–
Peptide-AA[xxx]	0.23 (5.4)[f]	–	–	–
Dissolved carbohydrates:				
DTCHO[a$]	0.94 (21.9)[f]	0.83	0.44	0.36
DFCHO[b$]	0.12 (2.8)[f]	0.10	0.05	0.05
DCCHO[c$]	0.82 (19.2)[f]	0.73	0.39	0.31
Fatty acids[x]	0.05 (1.2)[ef]	–	–	–
Organic acids[xx]	0.001–0.23 (0.02–5.4)[f]	–	–	–
% of identified organic carbon in DOC:	84	67	53	41

[a] Dissolved Total (DT–).
[b] Dissolved Free (DF–).
[c] Dissolved Combined (DC–).
[d] Mean value from DFAA and Peptide-AA.
[e] Mainly from particulate organic matter.
[f] % Organic carbon from DOC in Epilimnion.
[aa] Samples were taken weekly from spring to winter and presented data are mean values from all samples.
[*] Epilimnion.
[**] Interface Epi-/Metalimnion.
[***] Interface Meta/Hypolimnion.
[****] Interface Hypolimnion/Sediment.
[+] Measured by WCO-method.
[$] From Münster (1985).
[$$] From Brehm (1974).
[x] From Poltz (1973).
[xx] From Münster (1991, and unpubl. results).

and selective utilization and assimilation then results in a mixture of organic compounds with different molecular weights and chemical properties (Stabel & Steinberg 1976; Geller 1985b; McKnight et al. 1991; Benner et al. 1986). This bulk material may be a precursor in the formation of dissolved humic matter (DHM), a highly complex geopolymer (Harvey et al. 1983). In lacustrine environments DHM comprises the majority of DOC (Gjessing 1976; Thurman 1985; Steinberg & Münster 1985). However, microbial utilization of this bulk material has been less well studied and is consequently poorly understood (Benner et al. 1986; Hessen 1985, 1992; Salonen 1981; Salonen et al. 1992; Tranvik 1988, 1989a, 1989b, 1990; Moran & Hodson 1990). In order to more exactly calculate and model global carbon balances more precise knowledge about the composition, carbon content, microbial utilization and fluxes under *in situ* conditions of DHM is required (Ducklow 1991; Farrington 1992; Hedges 1992).

In the following sections examples are given about composition, distribution, utilization and turnover of some organic carbon substrates. Besides data from the literature I have included some own experimental results about DOC composition and utilization from eutrophic and humic lakes.

Dissolved organic carbon: the basis for microbial heterotrophy

The analytical-chemical approach

When the characterization of DOC is based on its utilization by heterotrophic microorganisms as substrates and carbon sources, it can be divided into two fractions: One carbon pool is rapidly, within minutes to hours, utilized as carbon substrate and is therefore called the Labile Organic Carbon Pool (LOCP), whereas, the second carbon pool is slowly within days-years utilized and therefore called the Recalcitrant Organic Carbon Pool (ROCP). However, both substrate pools have a distinct function as carbon and energy sources for microbial processes in aquatic ecosystems (Wetzel 1990). On the basis of these definitions their composition, variation and dynamics will be characterized and discussed in the following sections.

Composition, distribution and chemical characterization of DOC

The DOC pool in lacustrine and marine environments is a mixture of thousands of different organic compounds (Faust & Hunter 1971; Williams 1971; Farrington 1992) with different structures, sizes and changing concentrations. Among them, dissolved amino acids (DAA), carbohydrates (DCHO), short chain fatty acids (DSCFaAc) and long chain fatty acids (DLCFaAc) are the most frequent and studied ones. Other compounds (e.g. pigments, hydrocarbons, steroids, vitamins), are present in very low concentrations. Some of these compounds have biomarker functions (e.g. DLCFaAc, pigments, hydrocarbons, steroids) for tracing and reconstruction of paleo-ecological processes (Farrington 1992). DAA and DCHO are regarded as the main energy and carbon sources for microbial metabolism and growth (Azam & Ammerman 1984; Azam & Cho 1987; Azam 1986; Hobbie & Rublee 1977; Wright 1984). They act also as precursors and subunits for synthesis of biopolymers and energy sources and participate in many pathways of microbial cell metabolism (Kirchman et al. 1985; Kirchman & Hodson 1986; Amano et al. 1982; Burnison & Morita 1974; Carlucci et al. 1984; Gocke 1975; Gardner et al. 1989; Gardner & Lee 1975; Crawford et al. 1984; Chin-Leo & Kirchman 1988; Simon & Azam 1989; Cowie & Hedges 1992). Knowledge about their concentration and dynamics is therefore essential for a better understanding of microbial life in natural aquatic environments. However, only a small part (10–30%) of this total DOC has been chemically identified (Table 2a, b).

According to Williams (1971, 1986) roughly 10–15% of marine organic carbon may be easily chemically identified. Among those fractions are DAA, DCHO, DLCFaAc, DSCFaAc, some vitamins, hydrocarbons, aromatics and urea. The bulk material, mostly classified as 'Gelbstoff' (Kalle 1966; Sieburth & Jensen 1968), or 'Humic Substances' (HS) has still not been completely identified. Their chemical structure is still a matter of research and discussion (reviewed by Aiken et al. 1985; Christ-

man & Gjessing 1983). Much more uncertain than their chemical composition and structure is their ecological function (Perdue & Gjessing 1990; Steinberg & Münster 1985). According to studies on DOC from lake Plußsee (Table 2b) about 10–20% of DOC was found to be in the LOCP fraction and consisted of DCHO, DAA and traces of DLCFaAc and DSCFaAc (Münster 1984, 1985, 1991; Münster

Table 3a. DFAA* in marine and freshwaters.

Location	DFAA (nM)	References
Marine waters:		
Chesapeake Bay, USA	6.5–23	Fuhrman (1990)
New York Bay, USA	4.2–14.5	Fuhrman & Ferguson^{++} (1986)
English-Channel	30–160	Martin-Jezequel et al.$^{+}$ (1992)
Delaware Estuary, USA	50–1,400	Coffin (1989)
Celtic Sea, GB	10–722	Williams & Poulet$^{\#}$ (1986)
Scripps-Pier, USA	20–230	Anderson et al.$^{\#\#}$ (1985)
Sargasso-Sea, USA	3–56	Suttle et al. (1991)
German Bight, FRG	10–1,200	Hammer & Brockmann*** (1983)
Atlantic Ocean	8–62	Mopper & Zika (1987)
Black Sea	5–120	Mopper & Kieber (1992)
Sargasso Sea	10–300	Vaughan & Mopper (1987)
Marine Rain	1,7000–15170	Mopper & Zika (1987)
South. Californ. Bay	14–66	Carlucci et al. (1984)
Pacific Coast, USA	42–123	Carlucci et al$^{\$}$ (1986)
Freshwater:		
L.-Bodensee, FRG (1978)	< 25– > 100	Feierabend**
L.-Bodensee, FRG	2.6–43.9	Simon$^{+\#\#}$ (1985)
L.-Mossø, Denmark	400–600	Jøorgensen et al. (1983)
L.-Kalgaard, Denmark	155	Jørgensen & Søndergaard (1984)
L.-Knudsø, Denmark	720	Jørgensen & Søndergaard (1984)
L.-Skanderborg, Denmark	296	Jørgensen & Søndergaard (1984)
L.-Esrom, Denmark	600–1,400	Riemann et al.$^{\#}$ (1986)
L.-Esrom, Denmark	700–1,850	Jørgensen (1986)
L.ørn, Denmark	700–2,400	Jøorgensen (1986)
L.-Hylke, Denmark	190–1,963	Jørgensen (1987)
L.-Slotsø, Denmark	78–377	Jørgensen (1987)
L.-Almind, Denmark	54–912	Jørgensen & Bosselman^{+++} (1988)
L.-Hylke, Denmark	189–4,124	Jørgensen & Bosselman^{+++} (1988)
L.Plußsee, FRG	10–2,401	Münster^{+++} (1991)
L.-Mekkojärvi, Finland	1.7–1,990	Münster et al.$^{++++}$ (1992a)
L.-Skjervatjern, Norway	120–650	Münster^{+} (1992b)

* DFAA: Dissolved Free Amino Acids.
** If not otherwise specified all data were obtained by HPLC method according to Lindroth & Mopper (1979).
*** DFAA were analyzed by ion-exchange chromatography technique and ninhydrin post-column reaction.
$^{+}$ From daily studies.
$^{++}$ From comparisons of HPLC and radiotracer method.
$^{+++}$ From diurnal studies.
$^{++++}$ From annual studies.
$^{\#}$ From effect of zooplankton grazing on DFAA concentrations.
$^{\#\#}$ From effect of flagellate grazing on DFAA concentrations.
$^{\#\#\#}$ From labelled DFAA uptake kinetics (Kt + Sn) in μgC^{*-1}.
$^{\$}$ From biofilms in marine waters.

& Chróst 1990; Brehm 1967; Poltz 1972; Weinmann 1970). The remaining part of the DOC was classified as ROCP and consisted of polyphenols and DHM (Table 2b, Fig. 4).

The labile organic carbon pool: a 'light fuel' for aquatic bacteria

DAA and DCHO are important carbon and nitrogen sources for bacterioplankton (Billén 1984; Gocke 1970; Simon & Azam 1989; Chin-Leo & Kirchman 1988; Zehr et al. 1985; Gardner & Lee 1975; Gardner et al. 1986, 1989; Bengtsson 1988).

Table 3b. DFCHO[a] in aquatic environments.

Location	DFCHO	References
Marine waters:		
Open waters:		
Black Sea[+]	0.03–0.29 $\mu gC*l^{-1}$	Mopper et al. (1980)[$*]
North Sea[+]	0.14–0.56 $\mu gC*l^{-1}$	Mopper et al. (1980)[$*]
Baltic Sea[+]	0.05–0.56 $\mu gC*l^{-1}$	Mopper et al. (1980)[$*]
Sargasso Sea[+]	0.19–0.29 $\mu gC*l^{-1}$	Mopper et al. (1980)[$*]
Pacific Ocean[+]	0.41 $\mu gC*l^{-1}$	Mopper et al. (1980)[$*]
Sargasso Sea[+]	20–120 $\mu gC*l^{-1}$	Liebezeit et al. (1980)[$*]
North Pacific[++]	1.68–40 $\mu gC*l^{-1}$	Sakugawa & Handa (1985)[$#]
New York Bight	20–360 $\mu gC*l^{-1}$	Harvey (1983)[$##]
Western Sargasso Sea[+++]	40–100 $\mu gC*l^{-1}$	Burney et al. (1981a)[##]
Eastern Gulf Stream[+++]	40–80 $\mu gC*l^{-1}$	Burney et al. (1981a)[##]
Coastal water and salt marshes:		
Narragansett Bay, USA	90–307 $\mu gC*l^{-1}$	Burney et al. (1981b)[##]
Carribean Sea[+++]	80–120 $\mu gC*l^{-1}$	Burney et al. (1981)[##]
Coastal water:		
Florida, Bermuda and Oahu, USA	50–110 $\mu gC*l^{-1}$	Burney (1986a + b)[##]
North Sea	5.6–72 $\mu gC*l^{-1}$	Ittekot et al. (1981)[$*]
Fresh waters:		
Lake Nakanuma[+]	5.6–364 $\mu gC*l^{-1}$	Ochiai & Hanya (1980)[$$]
Lake Plußsee[+]	240–320 $\mu gC*l^{-1}$	Münster (1984)[$$$b]
Lake Plußsee[+]	< 0.5–320 $\mu gC*l^{-1}$	Münster (1985)[$$$c]
Lake Mekkojärvi	1–50 $\mu gC*l^{-1}$	Münster et al. (1992)[$$$]
Lake Plußsee[+]	15–800 $\mu gC*l^{-1}$	Münster (1991)[$$$d]

[a] DFCHO: Dissolved Free Carbohydrates.
[b] From diurnal studies.
[c] From annual studies.
[d] From seasonal studies.
[$] The original data were multiplied by the conversion factor 0.4 to have unique carbon units, assuming that the majority of DFCHO was composed of hexoses.
[*] DFCHO were measured by HPLC and anion-exchange chromatography according to Mopper et al. (1980).
[#] DFCHO were measured as alditol acetates by GC, GC-MS according to Sakugawa & Handa (1983).
[##] DFCHO were measured with spectrophotometer according to Johnson & Sieburth (1977).
[$$] DFCHO were measured as alditol acetates by GC.
[$$$] DFCHO were measured as trimethylsilyl ether according to Poole (1978).
[+] From vertical profiles.
[++] From surface and deep water samples.
[+++] From integrated water samples.

However, only a small fraction (1–10%) has been found in the dissolved free form which can be directly assimilated by bacteria. The majority of DAA and DCHO are polymeric in nature and cannot be directly assimilated. However, the DFAA and DFCHO pools are regarded as important intermediate substrate pools in the turnover of the DOC (Fuhrman 1987, 1990; Fuhrman & Ferguson 1986; Jørgensen 1986, 1987; Gocke 1970, 1975, 1977; Simon 1985). Measurements of composition and dynamics of DFAA and polymeric pool sizes may give a good estimate of substrate turnover and utilization by bacterioplankton under natural conditions (Dawson & Gocke 1978; Jørgensen et al. 1983; Jørgensen & Søndergaard 1984).

Dissolved free amino acids and dissolved free carbohydrates in DOC of marine and freshwater

DFAA and DFCHO are one of the most studied and well known natural substrates in aquatic environments. This is because of the progress that has been made in advanced analytical techniques (Lindroth & Mopper 1979; Mopper et al. 1980) for DFAA and DFCHO measurements in aquatic environments. The natural concentrations of DFAA and DFCHO in aquatic environments are generally low and differ between marine and lacustrine ecosystems (Table 3a, b).

Measurements of DFAA in marine waters varied from 3–1400 nMol depending on the trophy of the sampled water bodies (Table 3a). Low concentrations were found more frequently in oligotrophic water samples from the Pacific and Atlantic Ocean (Mopper & Zika 1987a, Fuhrman 1990; Fuhrman & Ferguson 1986). Higher values were reported for coastal marine water samples like the English Channel, North Sea etc. (Hammer & Brockmann 1983; Martin-Jézéquel et al. 1992; Coffin 1989; Williams & Poulet 1986). These higher DFAA values from more productive marine environments are similar to those found in eutrophic and mesotrophic freshwater samples (Brehm 1967; Jørgensen et al. 1983; Jørgensen & Søndergaard 1984; Jørgensen 1982, 1986, 1987; Münster 1991; Münster et al. 1992). In general, DFAA values in freshwaters (Table 3a) are 5–10 times higher compared to marine samples. These higher DFAA concentrations can be mostly correlated with higher nutrient contents, primary production, biomass and allochthonous input of DOC (Jørgensen et al. 1983; Riemann et al. 1986; Münster & Chróst 1990; Münster 1991). Surprisingly high DFAA values (1.7–15.2μM) were found by Mopper & Zika (1987a) in marine rain, which may significantly contribute to the local input of nitrogen and carbon in marine surface waters.

Similar to DFAA, dissolved free carbohydrates are important exogenous organic carbon substrates for heterotrophic microorganisms and have received a lot of attention in aquatic microbial ecology research. A survey of DFCHO concentrations in marine and freshwater is given in Table 3b. From these data it became obvious, that the methods for analysis of DFCO in aquatic environments were more variable compared to DFAA measurements. Comparisons of the results are therefore more difficult. The concentration of DFCHO in natural waters (marine and lacustrine systems) varied between 0.03–800 $\mu g\ C \times l^{-1}$. Similar to those results found for the DFAA pool, the concentrations of DFCHO in marine samples were 5–10 times lower compared to freshwater samples. Lowest values were found again in oligotrophic ocean samples (Mopper et al. 1980) where they varied between 0.03–0.41 $\mu gC \times l^{-1}$. Coastal marine water samples contained more DFCHO and varied between 20–360 $\mu gC \times l^{-1}$ (Harvey 1983; Burney et al. 1981a, 1981b; Burney 1986a, 1986b; Ittekot et al. 1981). The concentration of DFCHO in these coastal marine water samples was in a similar range to that in eutrophic and mesotrophic lake water samples which was reported to range between 0.5–800 $\mu gC \times l^{-1}$ (Ochiai & Hanya 1980; Münster 1984, 1985, 1991; Münster et al. 1992). In earlier studies on DCHO using paper and gas-chromatography techniques DFCHO could not be precisley enough detected even after high enrichment (Weinmann 1970; Stabel 1977). Modern more sensitive chromatographic techniques with even smaller enrichment factors (5–10 fold) have been more successful (Münster 1985; Mopper et al. 1980; Wicks et al. 1991).

Seasonal variation of DFAA and DFCHO in Lake Plußsee. LOCP compounds may vary with time and sampling depth. As an example the DFAA pool size

during a spring bloom development in the eutrophic lake Plußsee (North Germany) varied between 0.15–1.85 µM with three maxima of 0.7 µMol, 1.8 µMol and 0.8 µMol (mean 0.6 µMol). The first small peak appeared in early spring (April 14th), the second and largest one, in late spring (May 12th) and a third small one in early summer (June 19th). The organic carbon contribution of the DFAA to the total DOC varied between 0.1–1.2% (mean 0.3%). The carbon content of the DFAA pool of lake Plußsee is in a similar range as has been found by Jørgensen et al. (1983) in eutrophic Danish lakes and other meso- or eutrophic water bodies (Table 3a). DFCHO concentrations varied in lake Plußsee between 0.5–616.3 µM (mean 246.5 µM). Higher values were found in spring, late summer and in autumn. DFCHO carbon contributed 0.21–6.4% (mean 2.6%) of organic carbon to DOC.

Diurnal variation of DFAA and DFCHO of the Plußsee. Early studies showed that low molecular weight compounds in the LOCP pool varied only slightly on a seasonal or annual scale but more intensely on a diurnal and diel scale (Münster 1984, 1985; Münster & Chróst 1990; Jørgensen et al. 1983; Carlucci et al. 1984). Labile organic substrates like DFAA or DFCHO are usually rapidly taken up and have short turnover times (see also Table 5a, b). Most studies have measured the EOC and its utilization by bacterioplankton only using diurnal or diel scales (see also Table 4). Less studies have followed the variation of specific compounds like

Table 4. Survey of EOC in aquatic environments.

Location	Range of EOC[$] (%)	References
Marine waters:		
Coastal N.-Pacific	7 –17	Anderson & Zeutschel (1970)
Chesapeake Bay, USA	4 –68	Chróst & Faust (1983)
North Sea	11 –62	Lancelot (1979)
Coast of Bahamas	< 1 –23	Williams & Yentsch (1976)
N.-Atlantic	4 –16	Hellebust (1965)
Baltic Sea	8	Larsson & Hagström (1979)
Gulf of Maine, USA	1 –28	Mague et al. (1980)
N.-Atlantic	13 –70	Choi (1972)
Baltic Sea	1 –13	Lignell (1990)
Freshwater:		
Lake Mendota	0.8–74.5	Brock & Clyne (1984)
ELA lakes, Canada	10 –45	Nalewajko & Schindler (1976)
Lake Nakanuma, Japan	8 –54	Watanabe (1980)
Danish Lakes	18 –71	Jensen & Søndergaard (1985)
Polisch Lakes	< 1 –44.5	Chróst (1983)
Schöhsee, FRG	1 –54	Rai (1984)
Plußsee, FRG	30.5–99.9	Sell & Overbeck (1992)
Lawrence Lake, USA	18	Wetzel et al. (1972)
Frains lake, USA	2 –58	Storch & Saunders (1978)
Lake Tahoe, USA	5 –17	Tilzer & Horne (1979)
Lake Almind, Denmark	18 –37	Søndergaard & Jensen (1986)
Lake Erken, Sweden	13 –49	Bell & Kuparinen (1984)
Lake Constance, FRG	10 –60	Kato & Stabel (1984)
Lake Windermere, UK	3 –50	Fogg et al. (1965)
Lake Suwa, Japan	1.5–15	Hama & Handa (1987)
Eutroph. and oligotr. waters	5 –40	Fogg (1983)
Sörmogen, Sweden	38 –60	Sundh (1989)
Bysjön, Jähasjön, Sweden	1.3– 6.8	Coveney (1982)

[$] EOC represents percentage of excretion of photosynthetically fixed radiocarbon from phytoplankton.

DFAA or DFCHO, and their release and uptake under natural conditions (Jørgensen et al. 1983; Carlucci et al. 1991; Burney et al. 1981a, 1981b; Burney et al. 1982; Burney 1986a, 1986b; Mopper & Lindroth 1982; Hama & Handa 1987, 1992; Münster 1984, 1985; Münster & Chróst 1990). However, such studies are very useful to better understand the dynamics of LOCP compounds and their close coupling to their producers (phytoplankton, macrophytes, grazers) and consumers (bacteria). One example of diurnal variation and dynamics of LOCP compounds (DFAA and DFCHO) is given in Fig. 1a, b. The DFAA varied in the euphotic zone (0–5 m) between 0.004–2.3 µM (mean 0.26–0.78 µM) with a significant diurnal cycle. Maxima in surface water were found from 10–14h during the light phase and minima during the dark phase from 22–2 h (Fig. 1a). This distribution pattern changed how-

Table 5a. Survey of turnover times of organic substrates in marine waters.

Location	Substrate	T_t (h) range	References
McMurdo Sound	Glucose	52–24,242	Hodson et al. (1981)
McMurdo Sound	Leucine	24–2,075	Hodson et al. (1981)
McMurdo Sound	ATP	3.9–82	Hodson et al. (1981)
North Sea	Glucose	11–69	Hoppe (1978)
North Sea	Leucine	3–166	Hoppe (1978)
Baltic Sea			
Kiel Fjord, FRG	Glucose	2.1–2.3	Gocke (1977)[#]
Kiel Fjord, FRG	Glucosamin	15.1–15.8	Gocke (1977)[#]
Kiel Fjord, FRG	Acetate	2.7–2,8	Gocke (1977)[#]
Kiel Fjord, FRG	Aspartic acid	3.8–4.1	Gocke (1977)[#]
Kiel Fjord, FRG	Leucine	1.4–1.7	Gocke (1977)[#]
Kiel Fjord, FRG	Lysine	1.5–1.8	Gocke (1977)[#]
Gotland deep	Glucose	60.2–344	Gocke (1977)[#]
Kiel Fjord, FRG	Glucose	2.9–45.8	Gocke et al. (1981)[#]
Kiel Bight, FRG	Glucose	5.39	Gocke et al. (1981)[#]
Sargasso Sea	DFAA	3.6–182	Suttle et al. (1991)[###]
Black Sea[$]	DFAA	88–4,142	Mopper & Kieber (1992)*
Black Sea[$]	Acetate	242	Mopper & Kieber (1992)*
Black Sea[$]	Glucose	2.4	Mopper & Kieber (1992)*
Black Sea[$]	Pyruvate	367.2	Mopper & Kieber (1992)*
Black Sea[$]	DFAA	11,690–22,759	Mopper & Kieber (1992)*
Black Sea[$]	Acetate	244.8	Mopper & Kieber (1992)*
Black Sea[$]	Glucose	8,297	Mopper & Kieber (1992)*
Chesapeake Bay, USA	DOC	72–2,688	Malone et al. (1991)[#]
North Atlantic	DOC	1.2–8.64	Kirchman et al. (1991)[##]
North-Central Pacific	DOC	~ 6,000 years	Bauer et al. (1992)[$$$]
Pacific Ocean	DOC	> 6,000 years	Williams (1971)[$$$]
Southern California Bight	DFAA	11–36	Carlucci et al. (1984)*
Gulf Stream, US-coast	Leucine	0.11	Kirchman et al. (1985)[#]
Coast of Florida	Leucine	0.35	Kirchman et al. (1985)[#]
Sapelo Island, USA	Leucine	0.17	Kirchman et al. (1985)[#]

* From radiotracer methods and HPLC measurements of natural substrate pools.

$ Samples from 30 m depth.

$$ Samples from 200 m depth.

$$$ Measured by wet chemical oxidation (WCO), high temperature catalytic oxidation (HTCO) methods combined with 14C/12C-accelerator mass spectrometry (AMS).

From radiotracer methods.

From DOC measurements and DOC degradation studies in batch experiments.

From DFAA measurements.

ever in deeper water layers (4–5 m), where maxima appeared now in the dark phase (22–4 h) and smaller DFAA peaks during the light phase (6–14 h). The reason for these differences is not clear, but the light-dark synchronicity in the upper layers may change with depths according to a decrease of photosynthetic available light and a change in the microbial community structure. Similar diurnal variations of DFAA have been found by Jørgensen et al. (1983) in two Danish lakes and by Carlucci et al. (1984) in the bight of Southern California.

The DFCHO pool varied at the same time between 0.4–9.7 µM (mean 2.8–5.3 µM) with a maximum of 9.7 µM in the upper 0.2–1.0 m depth (Fig. 1b). Below this depth, the concentration maxima decreased down to 7.1–9.3 µM. In the upper two me-

Table 5b. Survey of turnover times of organic substrates in freshwaters.

Location	Substrate	T_t (h) range	References
German lakes:			
Plußsee	Acetate	7.8 – 29.7	Moaledj & Overbeck (1980)$*$
Plußsee	Glucose	3.4 – 15.2	Moaledj & Overbeck (1980)$*$
Plußsee	Glucose	6.9 – 201.8	Overbeck (1975)*
Plußsee	Glucose	126 – 263	Chróst (1984)*
Plußsee	Acetate	150 – 290	Chróst (1984)*
Plußsee	PhDOC[a]	40 – 120	Chróst (1984)*
Kellersee	Glucose	96 – 216^{+}	Overbeck (1979)*
Kellersee	Glucose	70 – 149^{++}	Overbeck (1979)*
Gr. Plöner See	Glucose	84 – 129^{+}	Overbeck (1979)*
Gr. Plöner See	Glucose	97 – 186^{++}	
Schöhsee	Glucose	318 – 414^{+}	Overbeck (1979)*
Schöhsee	Glucose	166 – 340^{++}	Overbeck (1979)*
Schöhsee	Glucose	20 –1230^{+++}	Rai (1984)*
Schöhsee	Glucose	2 – 28^{++++}	Rai (1984)*
Stocksee	Glucose	10.8	Gocke (1977)$^{\#}$
River Schwentine	Glucose	5.39	Gocke (1977)$^{\#}$
Bodensee	DFAA[b]	27 – 386	Simon (1985)*
Swedish lakes:			
Erken	PhDOC[a#]	9.2 – 99.4	Sundh (1992)*
Vallentunasjøn	PhDOC[a#]	14.6 – 141	Sundh (1992)*
Siggeforasjøn	PhDOC[a#]	16.5 – 68.9	Sundh (1992)*
Danish lakes:			
Mossø	DFAA	15 – 57$^{\#\#\#}$	Jørgensen et al. (1983)$^{\#}$
Mossø	Glutamic acid	21.1 – 23.3	Jørgensen et al. (1983)$^{\#}$
Mossø	Serine	41.1 – 43.1	Jørgensen et al. (1983)$^{\#}$
Slotsø	DFAA	2.5 – 11$^{\#\#\#}$	Jørgensen et al. (1983)$^{\#}$
Others:			
Jacks Lake, Canada	ATP	0.17– 0.28	Bentzen & Taylor (1991)*
L.-Kinneret, Israel	DFAA	20 – 152	Berman & Gerber (1980)*
L.-Kinneret, Israel	Glucose	20 – 168	Berman & Gerber (1980)*

$^{\$}$ From two isolated oligocarbophilic bacteria strains.
^{a} PhDOC means photosynthetically derived DOC.
^{b} DFAA from protein hydrolysate.
^{z} Samples from 1 m depth.
$^{++}$ Samples from 5 m depth.
$^{\#}$ From radiotracer and kinetic methods and HPLC analysis.
$^{\#\#}$ From DOC measurements and DOC degradation studies in batch experiments.
$^{\#\#\#}$ From DFAA measurements by HPLC.
* From radiotracer and kinetic methods.

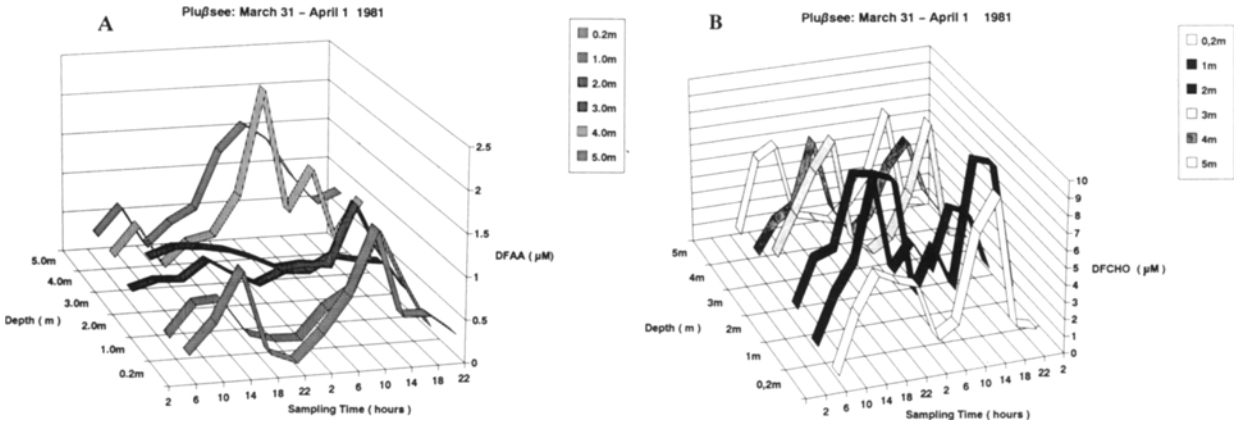

Fig. 1a, b. Diurnal variation of dissolved free- (DFAA) and dissolved free carbohydrates (DFCHO) in the trophogenic zone of lake Plußsee, 1981 (modified from Münster 1991).

ters a significant diurnal light-dark cycle could be measured. This light-dark cycle was also detectable in deeper water layers. Maxima of DFCHO followed 2–4 h after the photosynthesis maxima. The measured DFCHO concentrations were higher compared to former DFCHO results (Münster 1985) and this is assumed to be due to the predominance of a diatom bloom, which had just reached its biomass maximum and decreased rapidly within the next 2–5 days (Hickel 1978). The diurnal DFCHO values differed more than when weekly sampling periods or even longer intervals were used (Münster 1985).

Dissolved short chain and long chain fatty acids in DOC

Dissolved short chain fatty acids and long chain fatty acids are very common organic acids in nature. They participate in many different cellular and metabolic processes (Parrish 1988). However, their abundance, variation and function have not been as intensively studied in aquatic environments compared with DFAA or DFCHO. Particularly little information is available concerning DLCFaAc in aquatic environments. Because of their lipohilic character they are mostly attached or combined to POC (reviewed by Parrish 1988). DSCFaAc have been studied more often under special environmental conditions such as in sediments with aerobic/anaerobic interfaces (Thompson & Nedwell 1985) or with respect to the specific physiological status of phototrophs and their excretion products (e.g. glycolic acid, reviewed by Fogg 1983). More recently, as a result of increasing UV-radiation, photochemical reactions in the DOC have become more relevant for substrate modification, cleavage and microbial degradation (Mopper et al. 1991). DSCFaAc like pyruvate or glyoxylate are significant intermediate compounds in such photochemical reactions in surface waters (Mopper et al. 1991; Kieber & Mopper 1987, 1990). Although their production rate is low (e.g. 0.8–2.3 nmoles $\times l^{-1} \times h^{-1}$ for glyoxylate), it may have some relevance to global carbon cycling (Mopper et al. 1991).

From biologically derived DSCFaAc, glycolic acid may function as a biomarker for the release of DOC or EOC by phytoplankton (Fogg 1966, 1983; Wright & Shah 1975). Glycolate production is a result of the competition of O_2 with CO_2 as a substrate in the ribulosebisphosphate carboxylase reaction (Tolbert 1974). Glycolic acid produced in this reaction can be excreted or metabolized via glyoxylate to serine or glycine (Tolbert 1974; Tolbert & Zill 1956). In natural waters, glycolic acid concentrations were found to be relatively high compared to other low molecular weight organic compounds (Shah & Wright 1974; Shah & Fogg 1973; Al-Hasan et al. 1975). It is not surprising that it has been found that bacteria from upper layers of lake water can assimilate glycolic acid and may also use this carbon source for energy requirements (Wright & Shah 1975; Wright 1970, 1975).

During a diurnal experiment on the release of photosynthetically fixed carbon (PhDOC) by phy-

toplankton glycolic acid was studied as an indicator compound for phytoplankton EOC (Münster & Chróst 1990; Münster 1991). Results of this study are shown in Fig. 2. Glycolic acid showed distinct light-dark variation in water samples of the upper 5 m depths. But this biphasic distribution pattern was expressed more distinctly in the uppermost 2 m and was less pronounced down at a depth of 5 m. Glycolic acid concentrations varied between 1.1–104 $\mu gC \times l^{-1}$ (mean 15.5–36.2 $\mu gC \times l^{-1}$) over the whole water column. Maxima (52–104 $\mu gC \times l^{-1}$) appeared mostly between 10–14 h and most of the produced glycolic acid disappeared during the dark phase (22–4 h). Many bacteria can assimilate glycolic acid, but do not metabolize it for growth or biosynthesis. They preferentially oxidize it to CO_2 and use it as an energy source in the respiration pathway (Berland et al. 1970; Baumann et al. 1971, 1972; Wright 1975). According to Wright & Shah (1975) energy from glycolic acid oxidation may be coupled to active transport of multiple mixed substrates. The key enzyme glycolate oxidase is a membrane bound enzyme and couples the energy to transport systems of other carbon substrates (Lord 1972).

Microbial extracellular enzymes and biopolymer processing in DOC

Large molecules cannot easily pass the cell membrane of bacteria, but have to be hydrolyzed to smaller molecules before their assimilation (Priest 1984). This rate limiting step for DOC utilization has for a long time not been sufficiently considered when studying DOC utilization by bacterioplankton and modelling carbon flow. However, recently these important processes have been recognized in aquatic microbial studies (reviewed by Billén 1984, 1991; Hoppe 1991; Chróst 1990, 1991; Meyer-Reil 1991; Wetzel 1991). Good correlations have been found between bacterial biomass and exo-proteolytic activities (Billén 1991; Hollibaugh & Azam 1983; Hoppe et al. 1988; Meyer-Reil 1986). Turnover rates of monomeric substrates (e.g. leucine) and proteins (BSA) were found to be in a similar range (1–1000 hours) in the Belgian and Dutch coastal water bodies (Billén et al. 1990). It has been further found, that the majority of these enzymes are cell surface bound and followed Michaelis-Menten kinetics (Chróst 1989, 1990b, 1991). V_{max} of β-glucosidase and β-galactosidase measured in lake Plußsee increased at the end of a spring phytoplankton bloom development at the same time as the amount of DCCHO increased (Chróst et al. 1989; Münster 1991). Münster (1991, 1992a) found significant correlations between βGlAse activities and the concentration of DC-glucose ($r = 0.8511$, $p < 0.001$, $n = 16$) and between aminopeptidase activity and DC-leucine ($r = 0.9263$; $p < 0.01$, $n = 14$) in the polyhumic lake Mekkojärvi (South of Finland). However, many aspects of the function of these enzymes in humic rich or acid environments are not well understood (Wetzel 1991). In many cases these enzymes may be inhibited or adsorbed onto particles and immobilized and translocated to other water bodies where reactivation may occur (Wetzel 1991).

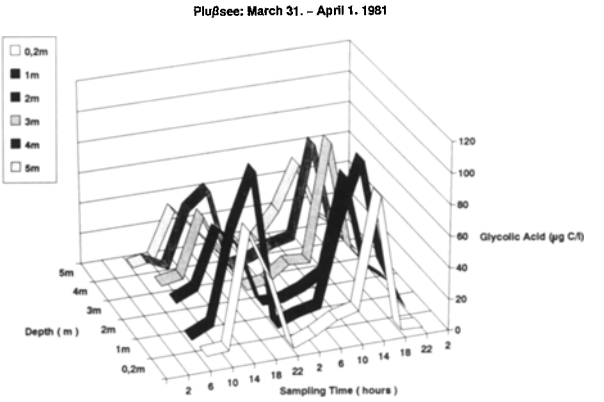

Fig. 2. Diurnal variation of glycolic acid in the trophogenic zone of lake Plußsee, 1981 (modified from Münster 1991).

Seasonal variation of biopolymers in DOC. During seasonal and annual sampling in lake Plußsee DCCHO and DCAA concentrations were 10–50 times higher compared to the DFAA and DFCHO and showed much higher variations (Brehm 1976; Münster 1984, 1985). Maxima of DCCHO were found in spring (May 17th), in the mid and late summer (July 20th, August 8th) and early and late autumn (September 9th, October 19th). DCCHO varied between 250–1755 $\mu gC \times l^{-1}$ (mean 898.1 $\mu gC \times l^{-1}$) and contributed 2.7–44.4% (mean 21.2%) organic carbon to the DOC. Data from phytoplankton biomass (Hickel 1978) correlated with DCCHO ($r = 0.675$–0.8975, $p < 0.001$, $n = 35$) and suggested that autochthonously produced DOC was a major con-

tributor to the DCCHO pool size (Münster 1985). Recent results about DFCHO, DCCHO, ^{14}C-glucose uptake and βGlAse activity measurements support the former data from lake Plußsee, that DCCHO are important substrates for bacterioplankton in this lake (Chróst et al. 1989; Münster 1991).

Diurnal variation of biopolymers in DOC. Studies on short term variation of DCAA and DCCHO pool sizes in aquatic environments are rather scarce but these pools are important for LOCP compounds (DFAA and DFCHO) when hydrolyzed by MEE. Results from a diurnal study in lake Plußsee the variation of DCAA and DCCHO are shown in Fig. 3a, b. In the euphotic zone DCAA was significantly stratified on a vertical and temporal scale. Highest concentrations were found during the light phase (6–10 h) and lowest during the dark phase (18–2 h). DCAA concentrations decreased rapidly in the upper two meters and varied between 3.2–54.6 µM (mean 8.9–16.5 µM) and in the lower 3–5 m between 3.3–16.3 µM (mean 6.04–8.86 µM). Highest concentrations were found in surface water (0.2 m) after sunrise (6–10 h) on both days. In the vertical profile there was a sharp decrease in the DCAA concentration between 1–2 m depth. This decline in DCAA was not found to occur with the DFAA pool. DCCHO varied in the same water samples between 7.3–115.8 µM (mean 51.9–67.6 µM). Highest values (74–115 µM) were found during late afternoon (14–18 h) and lowest values (42.2–73 µM) during the dark period (22–2 h). DCCHO concentrations were two to three times higher than those of DCAA values (Fig. 3b). Both polymeric substrate pools displayed a similar diurnal variation as the monomeric (DFAA and DFCHO) compounds (Fig. 1a, b) and may be also efficiently utilized by bacterioplankton after hydrolysis by MEE.

The recalcitrant organic carbon pool: a 'heavy fuel' for aquatic bacteria

About 10–30% of the DOC in aquatic environments have been chemically identified (Table 2a, b, Fig. 1a, b, Fig. 3a, b). Knowledge about their trophic functions and interactions with the aquatic community has substantially improved during the last 10–20 years. However, the remaining 70–90% of the DOC is still a 'black box'. The trophic role of this ROCP in energy and food web processes is still poorly understood (Wetzel 1992; Schindler 1992; Hobbie 1992). Physical-chemical methods have characterized part of this ROCP suggesting turnover times of about 2000–6000 years (Bauer et al. 1992; Williams 1971; Druffel & Williams 1990). However, microbiological experiments found much lower turnover times (about 1–10 h) for such DOC-bulk material (Kirchman et al. 1991). These discrepancies certainly reflect our poor knowledge about the trophic role of refractory or recalcitrant organic carbon pools (Geller 1985a, 1985b, 1986; Gagosian & Lee 1981; De Haan 1974; Haider 1988; Hedges 1992; Hedges et al. 1988a, 1988b; Horvath 1972; Jannasch et al. 1971; McKnight et al. 1991; Mar-

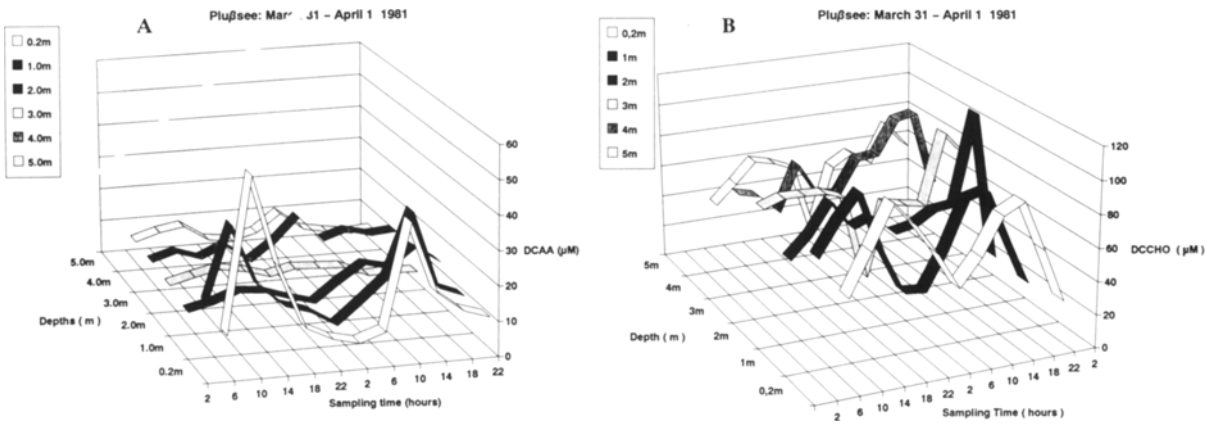

Fig. 3a, b. Diurnal variation of dissolved combined amino acids (DCAA) and dissolved combined carbohydrates (DCCHO) in the trophogenic zone (0–5 m) of lake Plußsee, 1981 (modified from Münster 1991).

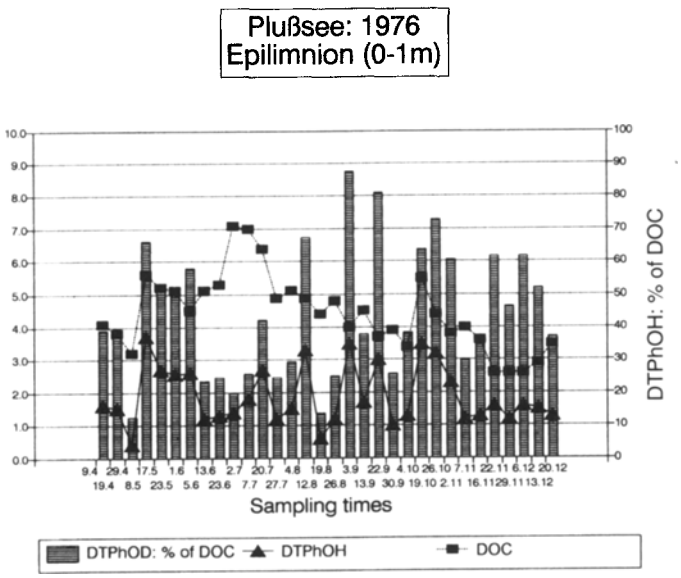

Fig. 4. Annual variation of dissolved organic carbon (DOC), dissolved total polyphenols (DTPhOH) and their contribution to the DOC (DTPhOH: % of DOC) in the epilimnion of lake Plußsee, 1976 (modified from Münster 1991).

tin & Fitzwater 1992; Stabel et al. 1979; Stabel & Steinberg 1976).

Humic matter, polyphenols, lignins, lignocellulose: a continual carbon source for microbial heterotrophs
An attempt was made to characterize a part of the ROCP fraction with a chemical method by analyzing and identifying dissolved polyphenolic compounds present in the DOC pool by capillary gas-chromatography during weekly sampling from spring to winter in the water column of lake Plußsee (Münster 1985). Some results are shown in Fig. 4. The dissolved total polyphenolic fraction (DTPhOH) varied in lake Plußsee surface water between 0.36–3.66 mg $C \times l^{-1}$ (mean 1.89 mg $C \times l^{-1}$) and contributed 11.6–87.4% (mean 44.5%) organic carbon to the DOC pool. 80–90% of these polyphenols were bound to higher molecular weight fractions (> 1,000 Daltons), and only 2.5–20.1% (mean 10.8%) of the DOC was found in dissolved free monomeric polyphenolic compounds (DFPhOH). When this data is included in the DOC characterization, about 50–80% of the DOC could be identified on the basis of only chemical measurements (Table 2b). This fraction was much higher than that fraction, which was formerly characterized by only biological approaches when studying the trophic role of DOC and interactions with the microorganisms in this lake (Overbeck 1979). In summary, 0.5–10% of DOC in lake Plußsee could be characterized by chemical analysis as LOCP. The total sum of monomeric compounds comprised about 10–30% of DOC in lake Plußsee. Seventy–ninety percent of the DOC was found in biopolymers of partially completely unknown chemical structures and ecological functions.

DOC composition in polyhumic environments
Brown water lakes are classified by limnologists as dystrophic lakes (Thienemann 1925). This means that they are less productive because of low nutrient contents compared to eutrophic or mesotrophic lakes. Results from recent studies have corrected this definition (Salonen 1981; Salonen et al. 1983, 1992; Hessen 1985, 1992; Tranvik 1988, 1989, 1990, 1992; Tranvik & Höfle 1987). Chlorophyll values and bacterioplankton biomass (e.g. acridine orange direct counts) can be as high in humic lakes as in meso- and eutrophic lakes (Arvola 1986; Bergström et al. 1986). Moreover, heterotrophic processes are more dominant compared to autotrophic activities (Salonen & Hammar 1986; Salonen et al. 1992). Humic waters contain 2–10 times higher DOC (Arvola 1986). Therefore, the basic question arises, which substrates in DOC support higher heterotrophy in humic waters (Münster 1991; Münster et al. 1992).

The analytical-chemical approach to studies of DOC compounds in humic lakes revealed that in polyhumic lake Mekkojärvi (South Finland) DFCHO varied on a seasonal scale between 7.8–465.5 nM (mean 141.7 nM) and contributed 0.13–9.86% (mean 2.2%) organic carbon to the LOCP pool and 0.01–0.16% (mean 0.04%) to the DOC pool. Thus, DFCHO in lake Mekkojärvi represented a lower LOCP pool fraction in the DOC than in the eutrophic lake Plußsee. The DFAA concentrations in the polyhumic lake Mekkojärvi varied between 1.7–1990 nM (mean 470 nM) and contributed only 0.02–0.54% (mean 0.12%) of DFAA organic carbon to the DOC. The LOCP pool from lake Mekkojärvi, calculated from DFAA and DFCHO

contributed 0.03–0.64% (mean 0.18%) organic carbon to the DOC.

DCAA in lake Mekkojärvi varied between 1.91–15.45 µM (mean 7.78 µM) and contributed 0.44–23.3% (mean 1.89%) of organic carbon to the DOC. This is also lower than the values found in the eutrophic lake Plußsee (Münster 1991). In contrast, DCAA in lake Mekkojärvi contributed 70.3–97.7% (mean 85.2%) to the LOCP pool. The DCCHO pool varied between 0.053–0.95 µM (mean 0.47 µM) and showed maxima in mid and late summer (July 16th, 28th, and August 18th). DCCHO contributed 0.6–22.2% (mean 7.5%) organic carbon to the LOCP pool and only 0.02–0.37% organic carbon (mean 0.18%) to the DOC pool. Both LOCP substrate pools were found in relatively low concentrations in this polyhumic lake compared to the eutrophic lake Plußsee. However, this LOCP pool supported an equivalent bacteria biomass as found in eutrophic waters (Münster 1991; Münster et al. 1992; Salonen et al. 1992). High turnover rates of the LOCP compounds or additional external carbon sources may support such high biomass (Salonen et al. 1992; Tranvik 1992; Hessen 1992).

The microbial-biochemical approach

In pelagic water bodies two paradigms have been established to describe the trophic interactions between autotrophic and heterotrophic processes on the basis of carbon flow: The first paradigm claims that bacterial growth depends largely on low molecular weight organic carbon substrates (EOC) from phytoplankton exudates (Andersson et al. 1985; Bell 1980, 1983; Bjørnsen & Riemann 1988; Cole et al. 1982; Fogg 1983; Lancelot 1979, 1984; Larsson & Hagström 1979, 1982; Herbst 1984; Herbst & Overbeck 1978; Nalewajko 1977; Riemann & Søndergaard 1984; Sell & Overbeck 1992; Søndergaard & Schierup 1982; Storch & Saunders 1978; Sundh 1992; Williams & Yentsch 1976; Williams 1990). The second paradigm argues that lysis of aging phytoplankton cells release, in addition to monomeric, higher molecular weight organic carbon substrates which can also be utilized and assimilated after microbial extracellular enzymatic hydrolysis (Lancelot & Mathot 1985; Lancelot & Billén 1984; Billén 1984; Billén et al. 1990; Billén 1991; Chróst & Faust 1983; Chróst et al. 1989; Chróst 1990, 1991; Wetzel 1992). Certainly, both paradigms effectively describe two extreme situations, but both have a fundamental experimental and eco-physiological background and are still under discussion in the literature. Recent results from studies on marine aggregates ('marine snow'), viruses and bacteriophages in aquatic environments may provide greater support to the last scenario (Bradtbak et al. 1992; Proctor & Fuhrman 1990, 1992; Smith et al. 1992). Viruses and bacteriophages may accelerate the cycling of polymeric organic carbon and particles via the 'viral loop' (Bratbak et al. 1992). In this loop more polymeric carbon (Koike et al. 1990; Longhurst et al. 1992; Smith et al. 1992) participates in carbon fluxes than when considering phytoplankton exudation only.

The significance of excreted organic carbon in DOC

On a daily and a seasonal scale, transient variations in the concentration of specific compounds of the DOC pool have been observed. The source of this DOC input is mainly from the release of organic carbon compounds by photosynthesizing phytoplankton (reviewed by Fogg 1983), as a result of lysis and 'sloppy feeding' by macrozooplankton (Poulet et al. 1986; Lampert 1978; Riemann et al. 1986c, Williams & Poulet 1986; Anderson et al. 1985; Gardner & Warren 1980; Gardner & Miller 1981) and from phagotrophic micrograzers (Nagata & Kirchman 1991). Bacteria are regarded more as sinks for organic carbon and less directly as contributors to the total DOC input (Ducklow et al. 1986; Ducklow 1991).

There has been a long scientific discussion in the literature about the relevance and significance of phytoplankton EOC with respect to trophic interactions in aquatic ecosystems (Sharp 1977; Mague et al. 1980; Fogg 1966, 1983; Aaronson 1971, 1978; Bjørnsen 1988). Many measurements and published results have contributed substantially to the present paradigm, that phytoplankton and macrophytes EOC are one of the main routes by which DOC and energy are channeled via bacteria to higher trophic levels. Most of these results have supported directly or indirectly the final formula-

tion of the concept of energy flow and the 'microbial loop' (Pomeroy 1974; Pomeroy & Wiebe 1988; Azam et al. 1983; Azam 1986; Hagström et al. 1988; Sorokin 1977; Williams 1981). Central to this paradigm is the assumption that more than 50% of photosynthetically fixed carbon is channelled via bacteria to higher trophic levels (Pomeroy & Wiebe 1988; Azam et al. 1983). This means that DOC and energy from the lowest trophic level is stepwise dissipated over a longer number of cascading trophic levels compared to the traditional grazing food chains (Pomeroy 1974; Pomeroy & Wiebe 1987; Williams 1981; Azam 1986). This scenario of trophic and food web interactions has substantially improved our picture and knowledge concerning aquatic ecosystem function.

EOC from phototrophs (algae, macrophytes)
The measured percentages of excreted or released photosynthetically fixed radiocarbon from phytoplankton from diverse aquatic environments are summarized in Table 4. There is principally no large difference between EOC values from marine or freshwater environments. In all water bodies the fraction of EOC was highly variable with slightly higher values found in freshwater samples compared to marine samples. The fraction of EOC in marine samples varied between 1–70% with slightly lower values in oligotrophic water bodies. In freshwater the fraction of EOC varied between 0.8–99.9%. Higher values were observed in eutrophic lakes (Sell & Overbeck 1992) and lower values in oligotrophic lakes (Tilzer & Horne 1979). Chemical analysis of EOC compounds from eutrophic lake Plußsee (Fig. 2) revealed that labile compounds like glycolate, DF-Glucose and DF-Glycine can contribute to the EOC pool (Fig. 5) and may explain the rapid uptake and close metabolic coupling between phytoplankton and bacteria (Fig. 2, 5).

EOC from heterotrophs: macrozooplankton, ciliates, flagellates, other micrograzers
The impact of grazing activities on DOC concentrations is a well known phenomenon (Webb & Johannes 1967; Lampert 1978; Jacobson & Azam 1985; Nagata & Kirchman 1991). However, less understood are the mechanisms and variations of these grazing activities and their influence on the composition and structure of DOC pools (Koike et al. 1990; Longhurst et al. 1992).

Macrozooplankton. There is increasing evidence that macrozooplankton, ciliates and phagotrophic nanoflagellates may contribute to the carbon input of DOC (Webb & Johannes 1967; Lampert 1978; Eppley et al. 1981; Jacobson & Azam 1985; Olsen et al. 1986). 10–45% of ingested organic carbon from macrozooplankton can be lost by 'sloppy feeding' effects and more than 10% of ingested organic carbon can be found in the DOC fraction (Lampert 1978). This dissolved fraction consists mainly of low molecular weight compounds ($< 10^3$ daltons) and may comprise DAA, DCHO, FAA and other complex compounds (Olsen et al. 1986). Similar effects on DOC may be also contributed to by ciliates and other mesozooplankton species.

Phagotrophs. It is now generally accepted that phagotrophic protists (ciliates and flagellates) can control the standing stock of bacterioplankton and are the major cause of baterial mortality (Sieburth 1979; Fenchel 1986; Sherr et al. 1989). According to Koike et al. (1990) this grazing activity on bacteria was closely related to the abundance of high molecular weight organic particles (0.36–1 µm in diameter). Nagata and Kirchman (1991) found that heterotrophic nanoflagellates released a certain

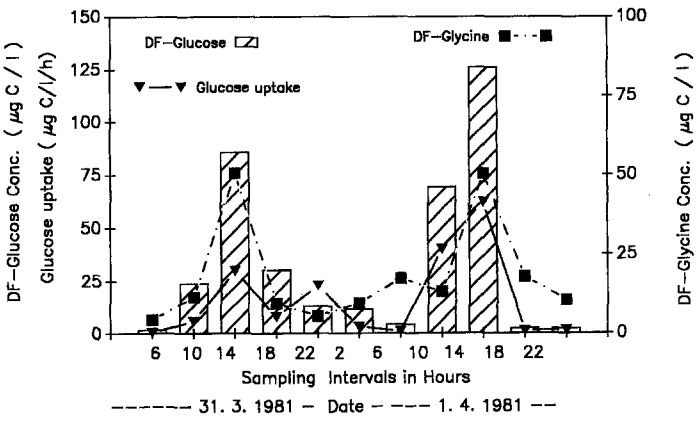

Fig. 5. Diurnal variation of dissolved free glucose (DF-Glucose), dissolved free glycine (DF-Glycine) and ^{14}C-glucose uptake in the trophogenic zone of lake Plußsee, 1981 (modified from Münster 1991).

amount of DFAA and DCAA into the DOC pool. This result was recently confirmed by Nagata & Kirchman (1992) who found that heterotrophic marine flagellates also released high molecular weight dissolved organic matter, which contained in one fraction significant acid phosphatase activity. The presence of this phosphatase activity may better explain the positive effect of phagotrophic grazing on the recycling and mobility of phosphorus (Jürgens & Güde 1991). The data reported by Nagata & Kirchman (1991, 1992) can also explain the higher amount of dissolved free acid phosphatase activity recently reported for polyhumic lakes (Münster (1991, 1992a, 1992b; Münster et al. 1989; 1992). These results also raise new questions about the sources and sinks of DOC in aquatic environments (Sherr 1988; Sherr et al. 1982, 1989; Taylor et al. 1985; Wright 1988a, 1988b).

Bacteria and their interaction with DOC

Dissolved organic carbon occupies the lowest trophic level in the trophic dynamic concept (Stephens 1981; Mann 1988; Rich 1984; Rich & Wetzel 1978; Wetzel 1992). Bacteria, as the main utilizer of DOC, act more as a sink for organic carbon than as a source (Ducklow et al. 1986; Cho & Azam 1988). Bacteria are known to develop efficient physiological and biochemical mechanisms to respond to changing environmental conditions which may favor or limit the uptake and conversion of inorganic and organic compounds into energy and biomass (Harder & Dijkhuizen 1982; Matin 1979). One limiting step in the bacterial response to changing environments is the communication with exogenous events (e.g. oxygen, nutrient, substrate supply). This communication takes place at the cell surface where receptors and enzyme systems can communicate with the cell's changing environment (Aaronson 1981; Priest 1984; Francko & Wetzel 1981). One example of such a communication system is based on the synthesis and regulation of extracellular enzymes and their contribution to substrate processing and final substrate capture and uptake (Button 1986; Wood 1985; Chróst 1990). For such processes bacteria may release certain amounts of extracellular enzymes to initiate biopolymer hydrolysis with subsequent uptake of mono- or small oligomers (Priest 1984; Wood & McCrea 1979). The existence of such export of organic compounds is well known from bacterial cultures but less studied in natural waters (Button 1986).

Uptake, utilization and turnover of DOC compounds

Metabolic interactions between detritus and heterotrophic microorganisms is a process of general interest in aquatic environments, but still not completely understood (Button 1986; Hobbie 1988, 1992). The largest progress in DOC-microbe interactions has been made with radiotracer methods by tracing the flow of organic carbon through the food web (Hobbie & Rublee 1977; Sorokin 1977; Williams 1981; Hobbie & Williams 1984; Pomeroy & Wiebe 1988; Overbeck & Chróst 1990). However, only 10–50% of the traced carbon could be characterized and quantified from the place of synthesis to the end point of consumption and final metabolic oxidation to CO_2 (Saunders 1977; Bjørnsen & Riemann 1988; Søndergaard et al. 1988; Riemann et al. 1982). With radiotracer and kinetic approaches, turnover time of DOC compounds could be measured and large variations were found. Turnover times of specific organic compounds (Table 5) varied over a range from 10–20 minutes (Kirchman et al. 1985) up to 1.4–2.6 years (Hodson et al. 1981; Mopper & Kieber 1992). Largest differences were observed between open ocean oligotrophic waters and coastal eutrophic waters (Table 5a). Turnover times from freshwater (Table 5b) did not differ significantly from marine samples and varied between 0.2–320 hours. Methods using physical-chemical techniques measured turnover times of the DOC pool in deep ocean water samples between 2000–6000 years (Williams 1971; Bauer et al. 1992). These data reflect the large discrepancy and the poor knowledge about mechanisms and regulation of short and long term DOC-microbe interactions for marine and freshwater ecosystems.

Microbial response to single substrate additions

Since the introduction of the radiotracer approach for heterotrophic activity measurements by Parsons & Strickland (1962) for marine waters and the modification of this approach by Wright & Hobbie

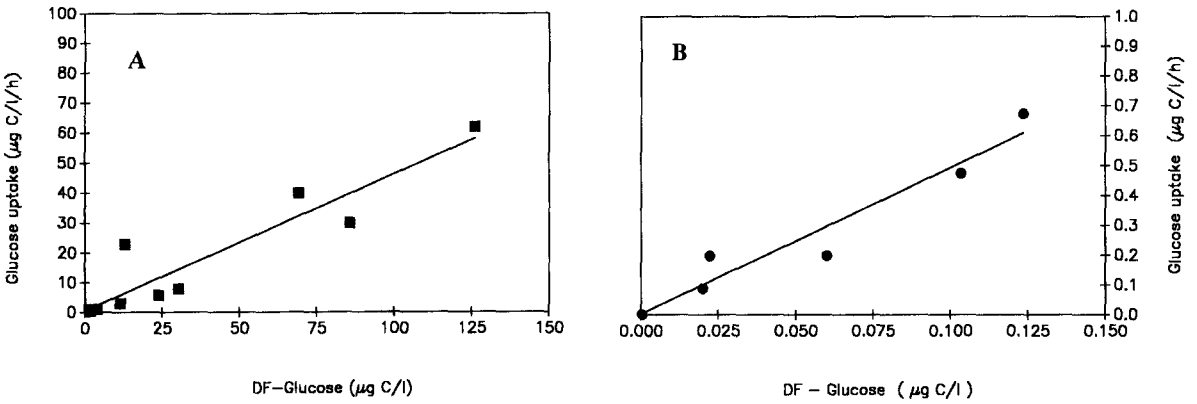

Fig. 6. Relation between dissolved free glucose concentration (DF-glucose) and ^{14}C-glucose uptake in the trophogenic zone of lake Plußsee during a diurnal (A) and a spring bloom (B) experiment (modified from Münster 1991).

(1965, 1966) for freshwater, the number of studies on the uptake of labile monomeric organic compounds by bacteria have increased rapidly. Two methods have been used: the 'tracer level' method (addition of only one concentration of radiolabelled substrate) and the 'kinetic' method (addition of multiple concentrations of radiolabelled substrate up to saturation of the transport/uptake system, reviewed by Hobbie & Rublee 1977; Hoppe 1978). In nearly all cases the added radiolabelled organic tracer molecule was taken up by the heterotrophs and metabolized (Table 5). No special preference for any kind of added substrate was observed (Hobbie 1992). This indicates that natural aquatic bacteria have a broad metabolic potential for assimilation and metabolism of different DOC compounds. Maximum uptake velocities (V_{max}) of added radiolabelled monomeric substrates (e.g. glucose, acetate, leucine) varied between 0.5–0.6 $\mu gC \times l^{-1} \times h^{-1}$ in oligotrophic waters and 7–10 $\mu gC \times l^{-1} \times h^{-1}$ in eutrophic waters. Kinetic approaches revealed further, that aquatic bacteria displayed partially multiphasic uptake kinetics, an indication of flexible assimilation and transport systems for changing environmental conditions and substrate supply (Azam & Hodson 1981; Overbeck 1975, 1979, 1990; Nissen et al. 1984; Wright 1984; Button 1986).

Metabolic response of microbial heterotrophs to substrate pulses

In previous sections it has been shown that LOCP compounds can vary within short time scales (Fig. 1a, b). The question arises how natural bacteria may respond to such substrate pulses. Another, less recognized problem in DOC studies is the dilution effect of added 'hot' radiolabelled substrates by 'cold' natural substrates. Such 'isotope dilution effects' should be considered when uptake experiments are applied. As an example: when ^{14}C-glucose uptake was corrected for the dilution effect during a spring bloom and a diurnal cycle in lake Plußsee, both parameters – DF-glucose concentration and ^{14}C-glucose uptake – correlated well (Fig. 6a, b). Simple linear regressions between DF-glucose concentrations and ^{14}C-glucose uptake gave a positive correlation ($r = 0.9643$, $p < 0.01$, $n = 6$ for the spring bloom, Fig. 6a) and for the diurnal cycle in surface water (0–1 m) correlation varied between $r = 0.8641$–0.9876, $p < 0.001$, $n = 10$, Fig. 6b). The DF-glucose concentrations varied in spring bloom experiments between 0.004–0.11 $\mu g\ C \times l^{-1}$ (Fig. 6b) and between 0.1–130 $\mu g\ C \times l^{-1}$ in the diurnal experiment (Fig. 6a). ^{14}C-glucose uptake ranged in the same experiments between 0.001–0.67 $\mu g\ C \times l^{-1} \times h^{-1}$ (mean 0.27 $\mu g\ C \times l^{-1} \times h^{-1}$) during the spring bloom (Fig. 6b) and between of < 0.1–65 $\mu g\ C \times l^{-1} \times h^{-1}$ during the diurnal cycle (Fig. 6a). From the average cell number one can calculate that for an individual bacterial cell the uptake rate varied during the diurnal experiment (Fig. 6a) between < 0.1–7.5 $fg\ C \times l^{-1} \times h^{-1} \times cell^{-1}$. DF-glucose values were 10–100 times lower in early spring studies than during diurnal studies. This lower natural DF-glucose availability was also encountered in the glucose uptake

experiments. This substrate-uptake relationship covers a large range of natural observed DF-glucose concentrations and may show how aquatic bacteria can respond metabolically to low and high pulses of different amounts of labile organic substrates. However, without correction for 'isotope dilution' no correlation was obtained in any of the experiments.

Microbial response to mixed substrates uptake

Single substrate uptake experiments are very common in aquatic microbiology ecology (Overbeck 1990; Hobbie 1992; Wright 1984). Whereas mixed substrate uptake experiments are more exceptional in natural environments (Simon & Azam 1989; Coffin 1989). Chemostat experiments have shown that mixed substrates displayed different transport and uptake kinetics in bacteria than single substrates (Harder & Dijkhuizen 1982; Egli & Mason 1991). Under limiting growth conditions mixed substrates were utilized at even lower substrate concentrations than in single substrate conditions (Egli & Mason 1991; Egli et al., this issue).

During a spring bloom in lake Plußsee a mixed ^{14}C-DFAA substrate was added and the uptake by bacterioplankton was studied simultaneously with HPLC measurements of natural DFAA concentrations (Münster, unpublished results). The DFAA-uptake (corrected for dilution of added 'hot'-DFAA by natural 'cold'-DFAA) varied between 0.12–2.01 $\mu g\ C \times l^{-1} \times h^{-1}$ (mean 0.67 $\mu g\ C \times l^{-1} \times h^{-1}$) and the specific uptake per bacterial cell varied from 47.7–1,047 $fg\ C \times l^{-1} \times h^{-1} \times cell^{-1}$ (mean 216 $fg\ C \times l^{-1} \times h^{-1} \times cell^{-1}$). Two ^{14}C-DFAA-uptake maxima appeared and covaried with 'cold'-DFAA maxima on May 12th and June 19th, where the highest DFAA concentration was measured. Linear correlation ($r = 0.8446$, $p < 0.01$, $n = 10$) was obtained between the DFAA and the ^{14}C-DFAA uptake. DFAA varied during this experiment between 18.8–135.2 $\mu g\ C \times l^{-1}$ (mean 51 $\mu g\ C \times l^{-1}$).

In former studies discrepancies have been observed between the amount or concentration of chemically analysed DFAA and DFCHO compared to those concentrations calculated from kinetic approaches with radiotracer methods (Gocke 1977; Gocke et al. 1981; Dawson & Gocke 1978; Kirchman et al. 1991). Some improvements have been made for the DFAA pool size by using HPLC and isotope dilution techniques with radiolabelled compounds (Fuhrman 1987; Fuhrman & Ferguson 1986; Chróst 1990a). But, for the bulk material of the DOC, there is still a lack of knowledge as to how this carbon pool affects the uptake of labelled substrates by heterotrophs. A final chemical characterization and speciation of all organic constituents of the DOC is still missing. Such knowledge would help to understand better the microbial utilization of labelled and natural DOC compounds.

Fluxes of organic carbon

Since the introduction of ^{3}H-thymidine incorporation measurements of bacterial production methods by Fuhrman & Azam (1980) and Riemann & Søndergaard (1986b) many approaches have been made to measure and quantify the carbon flow within aquatic ecosystems. In most cases it has been shown that bacteria play a major role in the carbon flux in marine (Azam 1986; Cho & Azam 1988; Azam et al. 1983; Sorokin 1977; Williams 1981) and in freshwater environments (Overbeck 1979; Riemann et al. 1982; Riemann & Søndergaard 1986a; Billén et al. 1990). A summary of such flux studies is shown in Table 6. The main problem with the data is that the techniques used for measuring flux differed in many cases and in most instances not all compartments of the food web system were analyzed. Therefore, where possible, in this table the sources and sinks for carbon are specified by indices. In most of the results the carbon flux from phyto- to bacterioplankton was studied. In the Baltic Sea, Dawson & Gocke (1978) measured the carbon flux from DOC to bacteria and found flux ranges between 4.6–150 $\mu gC \times l^{-1} \times h^{-1}$. Similar values were found by Vadstein et al. (1984) in Norwegian freshwater with values between 35–92 $\mu g\ C \times l^{-1} \times h^{-1}$. Flux rates in Danish lakes varied between 10–88 $\mu gC \times l^{-1} \times h^{-1}$ (Jørgensen et al. 1983). Riemann et al. (1982) have measured the carbon flux within the different carbon compartments of lake Mossø, Denmark, during a spring bloom development. They found an organic carbon flow of 0.37–3.51 $\mu gC \times l^{-1} \times h^{-1}$ as EOC to the bacteria and 0.03–0.13 $\mu g\ C \times l^{-1} \times h^{-1}$ flows from the DOC to the bacteria as glucose

Table 6. Survey of carbon flux in aquatic environments.

Location	Fluxes	References
Marine waters:		
Bornholm Basin	4.6–47.8 $\mu gC*l^{-1}*d^{-1}$	Dawson & Gocke (1978)[+]
Gotland Deep	4.8–7.6 $\mu gC*l^{-1}*d^{-1}$	Dawson & Gocke (1978)[+]
Danzig Deep	5.4–150.5 $\mu gC*l^{-1}*d^{-1}$	Dawson & Gocke (1978)[+]
Tvärminne, Finland	16 µgC*l–1*h–1**	Tamminen et al. (1984)[#]
Kelø Vig, Norway	4.7 µgC*l–1*d–1**	(Bratbak et al. 1992)
Kelø Vig, Norway	3.0 $\mu gC*l^{-1}*d^{-1}$***	(Bratbak et al. 1992)
Kelø Vig, Norway	2.9 $\mu gC*l^{-1}*d^{-1}$****	(Bratbak et al. 1992)
Kelø Vig, Norway	9.2 $\mu gC*l^{-1}*d^{-1}$	(Bratbak et al. 1992)
Freshwaters:		
Nesjøvatn, Norway	92 µgC*l^{-1}*d*	Vadstein et al. (1989)[#]
Nesjøvatn, Norway	36 µgC*l^{-1}*d**	Vadstein et al. (1989)[#]
Nesjøvatn, Norway	36 µgC*l^{-1}*d***	Vadstein et al. (1989)[#]
Nesjøvatn, Norway	35 µgC*l^{-1}*d****	Vadstein et al. (1989)[#]
Kjelsåsputten, Norway	3.8 $\mu gC*l^{-1}*d^{\#\#\#}$	Hessen (1992)
Kjelsåsputten, Norway	2.6 $\mu gC*l^{-1}*d^{\#\#\#\#}$	Hessen (1992)
Kjelsåsputten, Norway	50 $\mu gC*l^{-1}*d^{\#\#\#\#\#}$	Hessen (1992)
Bysjön, Hälsjasjön, Sweden	1.44–2.92 $\mu gC*l^{-1}*m2$***	Coveney (1982)[#]
Plußsee, FGR	0.2–1.5 $\mu gC*l^{-1}*h^{-1}$	Overbeck (1989)[#]
Plußsee, FRG	0.3–3 $\mu gC*l^{-1}*h^{-1}$***	Chróst (1984)[#]
Plußsee, FRG	0.55–5.3 $\mu gC*l^{-1}*h^{-1}$	Chróst (1984)[#]
Plußsee, FRG	0.65–8.1 $\mu gC*l^{-1}*h^{-1}$	Chróst (1984)[#]
L.-Erken, Sweden	66 $\mu gC*l^{-1}*h^{-1}$**	Tamminen et al. (1984)[#]
L.-Mossø, Denmark	73 $\mu gC*l^{-1}*24h^{-1}$**	Jørgensen et al. (1983)[##]
L.-Mossø, Denmark	53 $\mu gC*l^{-1}*24h^{-1}$***	Jørgensen et al. (1983)[##]
L.-Mossø, Denmark	16 $\mu gC*l^{-1}*24h^{-1}$[++]	Jørgensen et al. (1983)[##]
L.-Mossø, Denmark	88 $\mu gC*l^{-1}*24h^{-1}$[$]	Jørgensen et al. (1983)[##]
L.-Slotsø, Denmark	81 $\mu gC*l^{-1}*24h^{-1}$**	Jørgensen et al. (1983)[##]
L.-Slotsø, Denmark	10 $\mu gC*l^{-1}*24h^{-1}$***	Jørgensen et al. (1983)[##]
L-Slotsø, Denmark	12 $\mu gC*l^{-1}*24h^{-1}$[++]	Jørgensen et al. (1983)[##]
L.-Slotsø, Denmark	107 $\mu gC*l^{-1}*24h^{-1}$[$]	Jørgensen et al. (1983)[##]

[$] Based on DOC measurements.
[+] Based on DFAA measurements by HPLC and 14C-labelled AA uptake measurements according to Gocke (1977).
[++] Based on radiotracer methods according to Jørgensen et al. (1983).
[#] Based on radiotracer methods.
[##] Based on radiotracer methods combined with HPLC analysis of DFAA.
[###] Carbon flux from phytoplankton EOC to bacteria.
[####] Carbon flux from zooplankton EOC to bacteria.
[#####] Carbon flux from Humus-DOC to bacteria.
* Carbon flux from phyto- to zooplankton (grazing!).
** Carbon flux from phytoplankton to ECO (excretion!).
*** Carbon flux from EOC to bacteria (metabolic coupling!).
**** Carbon flux from DOC to bacteria (UDOC uptake).
**** Carbon flux from bacteria to flagellates (micrograzing!).
***** Carbon flux from bacteria to DOC ('viral loop').

carbon. However, the majority, 2.7–4.6 $\mu gC \times l^{-1} \times h^{-1}$, was measured by CO_2-dark fixation ('anaplerotic carbon shuttle'). It was this fraction which they could not clearly identify or characterize as carbon source (Riemann et al. 1982). Such examples additionally show that there is still little known about the contribution of the major carbon pool to bacterial metabolism. Studies on the carbon flux may be one of the main tasks for the future.

The viral loop

Recent studies on the occurrence and distribution of viruses and bacteriophages in aquatic environments have indicated that DOC may cycle at an earlier and lower trophic level in the aquatic food web, by-passing the 'traditional grazing food chain' and the 'microbial loop' (Bradtbak et al. 1992). The number of viruses and bacteriophages can be high and varied e.g. in the Chesapeake Bay between 2.6×10^6–1.4×10^8 viruses $\times$ ml^{-1} (mean 2.5×10^7 viruses $\times$ ml^{-1}) from spring to autumn (Wommack et al. 1992). The virus to bacteria ratio varied from 12.6–25.6:1 (Wommack et al. 1992) with the largest contribution by bacteriophages. Similar high frequencies of viruses and bacteriophages have been found by Bergh et al. (1989). High frequencies of viruses and bacteriophages could result in high mortality rates of bacteria (Proctor & Fuhrman 1990, 1992; Heldal & Bradtbak 1991). From infection and burst rates Bradtbak et al. (1992) calculated that about 100 phages were produced per one lysed bacterial cell. This accounts for roughly 70% of bacterial removal by lysis and was higher than that by grazing activities (Bratbak et al. 1992). Converted to carbon units, Bratbak et al. (1992) calculated as a result of bacterial lysis a carbon flux of 110 $\mu g\ C \times l^{-1} \times d^{-1}$ which was returned directly to the DOC pool. This carbon loss was calculated to be 6.1 times higher than the thymidine based measured bacterial production (18 $\mu g\ C \times l^{-1} \times d^{-1}$). Such imbalances in the carbon flux within the microbial loop raise many new questions about the role and dynamics of bacteria, viruses or bacteriophages and the DOC pool sizes and processing.

Final remarks

A large fraction of detritus still represents an unknown source of carbon and energy in aquatic food webs. There is principally no large difference in the level of understanding of the chemistry of the DOC and the DOC-microbe interactions in marine and freshwater. Only the absolute carbon values are higher in lacustrine systems compared to marine waters. 70–90% of the DOC is not labile but recalcitrant or refractory for microbial assimilation. The minor labile carbon pool size (10–20%) is rapidly taken up and shows a high diurnal variation and cycling. Seasonally, the metabolism of this labile organic carbon pool may be superimposed on the refractory organic carbon pool and can temporarily stimulate the degradation of the refractory pool. Release of organic carbon by phytoplankton and the rapid uptake by bacteria are closely coupled and display the highly dynamic character of this labile substrate pool. Short term substrate pulses may be more a luxury income for aquatic bacteria than an average income. In most cases bacteria are living under carbon and nutrient limitations and have to develop survival strategies even in carbon rich environments like polyhumic waters. Bottom up processes are of much greater importance for bacterial nutrition with energy and carbon substrates than reported in the literature. Top down processes may control bacterial mortality and link the carbon flux to higher trophic levels. Viruses and bacteriophages can significantly modify and shorten the energy and carbon flux from the primary producers via DOC back to the bacteria, by-passing the carbon flux of the grazing food chain and the microbial loop. This 'viral loop' will raise for the future many new questions on the understanding of the whole energy and carbon flux in aquatic environments.

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References

Aaronson S (1971) The synthesis of extracellular micromolecules and membranes by a population of the phytoflagellate *Ochromonas danica*. Oceanogr. 16: 1–9

— (1978) Excretion of organic matter by phytoplankton *in vitro*. Limnol. Oceanogr. 23: 838

— (1981) Chemical communication at the microbial level, Vol 1. CRC Press, Boca Raton

Aiken GR, McKnight DM, Wershaw RL & MacCarthy R (1985) Humic substances in soil, sediment and water. Geochemistry, isolation, and characterization. Wiley & Sons, NY

Al-Hasan RH, Coughlan SJ, Aditipant A & Fogg GE (1975) Seasonal variations in phytoplankton and glycollate concentrations in the Menai Straits, Anglesey. J. Mar. Biol. Assoc. 55: 557–565

Allen HL (1976) Dissolved organic matter in lakewater: characteristics of molecular weight size-fractions and ecological implications. Oikos 27: 64–70

— (1977) Experimental studies of dissolved organic matter in a soft-water lake. In: Cairns J (Ed) Aquatic Microbial Communities (pp 440–476) Garland Publishing Inc., New York

Amano M, Hara S & Taga N (1982) Utilization of dissolved amino acids in seawater by marine bacteria. Mar. Biol. 68: 31–36

Anderson GC & Zeutschel RD (1970) Release of dissolved organic matter by marine phytoplankton in coastal and offshore areas of the northeast Pacific Ocean. Limnol. Oceanogr. 16: 402–407

Andersson A, Lee C, Azam F & Hagström A (1985) Release of amino acids and nutrients by heterotrophic marine microflagellates. Mar. Ecol. Prog. Ser. 23: 99–106

Arvola L (1986) Spring phytoplankton of 54 small lakes in Southern Finland. Hydrobiologia 137: 125–134

Azam F (1986) Nutrient cycling and food web dynamics in southern California bight: the microbial food web. In: Eppley RW (Ed) Plankton Dynamics of the Southern California Bight. Lecture Notes on Coastal and Estuarine Studies, Vol 15 (pp 274–288) Springer Verlag, Berlin

Azam F & Ammerman JW (1984) Mechanisms of organic matter utilization by marine bacterioplankton. In: Holm-Hansen O, Bolis L & Gilles R (Eds) Lecture Notes on Coastal and Estuarine Studies, Vol 8 (pp 45–54) Springer Verlag, Berlin

Azam F & Cho BC (1987) Bacterial utilization of organic matter in the sea. In: Fletcher M, Gray TRG & Jones JG (Eds) Ecology of Microbial Communities (pp 261–281) Cambridge University Press

Azam F & Hodson RE (1981) Multiphasic kinetics for D-glucose uptake by assemblages of natural marine bacteria. Mar. Ecol. Prog. Ser. 6: 213–222

Azam F, Fenchel T, Field JG, Gray JS, Meyer-Reil LA & Thingstad F (1983) The ecological role of water column microbes in the sea. Mar. Ecol. Prog. Ser. 10: 257–263

Baumann P, Baumann L & Mandel M (1971) Taxonomy of marine bacteria: the genus *Beneckea*. J. Bacteriol. 107: 268–294

Baumann L, Baumann P, Mandel M & Allen RD (1972) Taxonomy of aerobic marine eubacteria. J. Bacteriol. 110: 402–429

Bauer JE, Williams PM & Druffel ERM (1992) ^{14}C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea. Nature 357: 667–670

Bell RT & Kuparinen J (1984) Assessing phytoplankton and bacterioplankton production during early spring in lake Erken, Sweden. Appl. Environ. Microbiol. 48: 1221–1230

Bell WH (1980) Microbial ecology of algal extracellular products. The specificity of algal-bacterial interactions. Biol. Bull. 159: 456–487

— (1983) Bacterial utilization and algal extracellular products. 3. Specificy of algal-bacteria interactions. Limnol. Oceanogr. 28: 1131–1143

Bengtsson G (1988) The impact of dissolved amino acids on protein and cellulose degradation in stream waters. Hydrobiologia 164: 97–102

Benner R, Moran MA & Hodson RE (1986) Biogeochemical cycling of lignocellulosic carbon in marine and freshwater ecosystems: relative contributions of procaryotes and eucaryotes. Limnol. Oceanogr. 31: 89–100

Bentzen E & Taylor WD (1991) Estimating organic P utilization by freshwater plankton using [^{32}P]ATP. J. Plankt. Res. 13: 1223–1231

Bergh O, Børsheim KY, Bradtbak G & Heldal M (1989) High abundance of viruses found in aquatic environments. Nature 340: 467–468

Bergström I, Heinänen A & Salonen K (1986) Comparison of acridine orange, acriflavine, and bisbenzimide stains for enumeration of bacteria in clear and humic waters. Appl. Environ. Microbiol. 51: 664–667

Berman T & Gerber C (1980) Differential filtration studies of carbon flux from living algae to microheterotrophs, microplankton size distribution and respiration in Lake Kinneret. Microb. Ecol. 6: 1869–198

Berland BR, Bonin DJ & Maestrini SY (1970) Study of bacteria associated with marine algae in culture. III. Organic substrates supporting growth. Mar. Biol. 5: 68–76

Billén G (1984) Heterotrophic utilization and regeneration of nitrogen. In: Hobbie JE & Williams LeB PJ (Eds) Hetrotrophic Activity in the Sea (pp 313–355) NATO SAD, Plenum Press

— (1991) Protein degradation in aquatic environments. In:

Chróst RJ (Ed) Microbial Enzymes in Aquatic Environments (pp 123–143) Brock/Springer Series in Contemporary Bioscience, Springer Verlag, Berlin

Billén G, Servais P & Becquevort S (1990) Dynamics of bacterioplankton in oligotrophic and eutrophic aquatic environments: bottom-up or top-down control. Hydrobiologia 207: 37–42

Birge EA & Juday C (1934) Particulate and dissolved organic matter in inland lakes. Ecol. Oceanogr. 4: 440–474

Bjørnsen PK (1988) Phytoplankton release of organic matter: Why healthy cells do it? Limnol. Oceanogr. 33: 151–159

Bjørnsen PK & Riemann B (1988) Towards a quantitative stage in the study of microbial processes in pelagic carbon flows. Arch. Hydrobiol. Ergebn. Limnol. 31: 185–193

Bohn HL (1976) Estimates of organic carbon in world soils. Soil Sci. Soc. Am. J. 40: 468–470

Bradtbak G, Heldal M, Thingstad TF, Riemann B & Haslund OH (1992) Incorporation of viruses into the budget of microbial C-transfer. A first approach. Mar. Ecol. Prog. Ser. 83: 273–280

Brandt K (1899) Über den Stoffwechsel im Meere. Wiss. Meeresunters. Abt. Kiel 4: 213–221

Brehm J (1967) Untersuchungen über den Aminosäure-Haushalt holsteinischer Gewässer, insbesondere des Plußsees. Arch. Hydrobiol. Suppl. 32: 313–435

Brock TD & Clyne J (1984) Significance of algal excretory products for growth of epilimnetic bacteria. Appl. Environ. Microbiol. 47: 731–734

Burney CM, Davis PG, Johnson KM & Sieburth JMcN (1981a) Dependence of dissolved carbohydrate concentrations upon the populations of nanoplankton and bacterioplankton in the western Sargasso Sea. Mar. Biol. 65: 175–187

Burney CM, Johnson KM & Sieburth JMcN (1981b) Diel flux of dissolved carbohydrate in a salt marsh and simulated estuarine ecosystem. Mar. Biol. 63: 175–187

Burney CM, Davis PG, Johnson KM & Sieburth JMcN (1982) Diel relationships of microbial trophic groups and *in situ* dissolved carbohydrate dynamics in the Carribean Sea. Mar. Biol. 67: 311–322

Burney CM (1986a) Bacterial utilization of total *in situ* dissolved carbohydrate in offshore waters. Limnol. Oceanogr. 31: 427–431

— (1986b) Diel dissolved carbohydrate accumulation in coastal water of South Florida, Bermuda and Oahu. Estuarine, Coastal and Shelf Sci. 23: 197–203

Burnison BK & Morita RY (1974) Heterotrophic potential for amino acid uptake in a naturally eutrophic lake. Appl. Microbiol. 27: 488–495

Button DK (1985) Kinetics of nutrient-limited transport and microbial growth. Microbiol. Rev. 49: 270–297

— (1986) Affinity of organisms for substrate. Limnol. Oceanogr. 31: 453–456

Carlucci AF, Craven DB & Henrichs SM (1984) Diel production and microheterotrophic utilization of dissolved free amino acids in waters off Southern California. Appl. Environ. Microbiol. 48: 165–170

Carlucci AF, Craven DB, Wolgast (1991) Microbial populations in surface films and subsurface waters: amino acid metabolism and growth. Mar. Biol. 108: 329–339

Chin-Leo G & Kirchman DL (1988) Estimating bacterial production in marine waters from the simultaneous incorporation of thymidine and leucine. Appl. Environ. Microbiol. 54: 1934–1939

Cho BC & Azam F (1988) Major role of bacteria in biogeochemical fluxes in the ocean's interior. Nature 332: 441–443

Choi CI (1972) Primary production and release of dissolved organic carbon from phytoplankton in the western north Atlantic Ocean. Deep Sea Res. 19: 731–735

Christman RF & Gjessing ET (1983) Aquatic and terrestrial humic materials (p 538). Ann Arbor Sci. Publ., Ann Arbor, Mi

Chróst RJ (1984) Use of [^{14}C]-dissolved organic carbon (RDOC) released by algae as a realistic tracer for heterotrophic activity measurements for aquatic bacteria. Arch. Hydrobiol. Ergebn. Limnol. 19: 207–214

— (1989) Characterization and significance of β-glucosidase activity in lake water. Limnol. Oceanogr. 34: 660–672

— (1990a) Application of the isotope dilution principle to the determination of substrate incorporation by aquatic bacteria. Arch. Hydrobiol. Ergebn. Limnol. 34: 111–117

— (1990b) Ectoenzymes in aquatic environments: origin, activity and ecological significance. In: Overbeck J & Chróst RJ (Eds) Advanced Biochemical and Molecular Approaches to Aquatic Microbial Ecology (pp 47–78) Brock/Springer Series in Contemporary Bioscience, Springer Verlag, Berlin

— (1991) Environmental control of the synthesis and activity of aquatic microbial ectoenzymes. In: Chróst RJ (Ed) Microbial Enzymes in Aquatic Environments (pp 29–59) Brock/Springer Series in Contemporary Bioscience, Springer Verlag, Berlin

Chróst RJ & Faust MA (1983) Organic carbon release by phytoplankton: its composition and utilization by bacterioplankton. J Plankt. Res. 5: 477–493

Chróst RJ, Münster U, Rai H, Albrecht D, Witzel KP & Overbeck J (1989) Photosynthetic production and exoenzymatic degradation of organic matter in euphotic zone of an eutrophic lake. J. Plankt. Res. 11: 223–242

Coffin RB (1989) Bacterial uptake of dissolved free and combined amino acids in estuarine waters. Limnol. Oceanogr. 34: 531–542

Cole JJ, Likens GE & Strayer DL (1982) Photosynthetically produced dissolved organic carbon: an important carbon source for planktonic bacteria. Limnol. Oceanogr. 27: 1080–1090

Coveney MF (1982) Bacterial uptake of photosynthetic carbon from freshwater phytoplankton. Oikos 38: 8–20

Cowie GL & Hedges JI (1992) Sources and reactivities of amino acids in a coastal marine environment. Limnol. Oceanogr. 37: 703–724

Crawford CC, Hobbie JE & Webb KL (1974) The utilization of dissolved free amino acids by estuarine microorganisms. Ecology 55: 551–563

Cuhel RL, Ortner PB & Lean RS (1984) Night synthesis of protein by algae. Limnol. Oceanogr. 29: 731–744

Cunningham HW & Wetzel RG (1989) Kinetic analysis of pro-

tein degradation by freshwater wetland sediment community. Appl. Environ. Microbiol. 55: 1963–1967

Dawson R & Gocke K (1978) Heterotrophic activity in comparison to the free amino acid concentrations in the Baltic Sea samples. Oceanol. Acta 1: 45–54

Dixon RK (1992) Global carbon cycle and climatic change. ACS Symp. Ser. 483: 375–378

Ducklow HW (1991) The passage of carbon through microbial foodwebs: results from flow network models. Mar. Microb. Food Webs 5: 129–144

Ducklow HW, Purdie DA, Williams LeB PJ & Davis JM (1986) Bacterioplankton: a sink for carbon in a coastal marine plankton community. Science 332: 865–867

Druffel ERM & Williams PM (1990) Identification of a deep marine source of particulate organic carbon using bomb ^{14}C. Nature 347: 172–174

Egli Th & Mason CA (1991) Mixed substrates and mixed cultures. In: Goldberg I & Rokem JS (Eds) Biology of Methylotrophs (pp 173–201) Butterworth-Heinemann, Boston

Eppley RW & Sharp JH (1975) Photosynthetic measurements in the Central North Pacific: the dark loss of carbon in 24-h incubation. Limnol. and Oceanogr. 20: 981–987

Farrington JW (1992) Marine organic geochemistry: review and challenges for the future. Mar. Chem. 39: 1–241

Faust SJ & Hunter JV (1971) Organic compounds in aquatic environments (p 638). Marcel Dekker, New York

Fogg GE (1966) The extracellular products of algae. Oceanogr. Mar. Biol. Ann. Rev. 4: 195–205

— (1983) The ecological significance of extracellular products of phytoplankton photosynthesis. Bot. Mar. 26: 3–14

Fenchel T (1986) The ecology of heterotrophic microflagellates. Adv. Microb. Ecol. 9: 57–97

Fischer B (1984) Die Bakterien des Meeres nach den Untersuchungen der Plankton-Expedition unter gleichzeitiger Berücksichtigung einiger älterer und neuerer Untersuchungen. Centalbl. Bakteriol. 15: 657–666

Fuhrman JA (1987) Close coupling between release and uptake of dissolved free amino acids in seawater studied by an isotope dilution approach. Mar. Ecol. Progr. Ser. 37: 45–52

— (1990) Dissolved free amino acid cycling in an estuarine outflow plume. Mar. Ecol. Prog. Ser. 66: 197–203

Fuhrman J & Azam F (1980) Bacterioplankton secondary production estimates for coastal waters of British Columbia, Antarctica, and California. Appl. Environ. Microbiol. 39: 1085–1095

Fuhrman JA & Ferguson RL (1986) Nanomolar concentrations and rapid turnover of dissolved free amino acids in seawater: agreement between chemical and microbiological measurements. Mar. Ecol. Prog. Ser. 33: 237–242

Francko DA & Wetzel RG (1981) Dynamics of cellular and extracellular cAMP in *Anabaena flos-aquae* (Cyanophyta): correlation with metabolic variables. J. Phycol. 17: 129–134

Gagosian RB & Lee C (1981) Processes controlling the distribution of biogenic organic compounds in seawater. In: Duursma EK & Dawson R (Eds) Marine Organic Chemistry. Evolution, Composition, Interactions and Chemistry of Organic Matter in Seawater (pp 91–123) Elsevier, Amsterdam

Gardner W & Lee GF (1975) The role of amino acids in the nitrogen cycle in Lake Mendota. Limnol. Oceanogr. 20: 379–388

Gardner W, Chandler JF, Laird GA & Scavia D (1986) Microbial response to amino acid additions in Lake Michigan: grazer control and substrate limitation of bacterial populations. J. Great Lakes Res. 12: 161–174

Gardner WS & Warren HM (1980) Intracellular composition and net release rates of free amino acids in *Daphnia magna.* Can. J. Fish. Aquat. Sci. 38: 157–162

Gardner WS & Miller WH (1981) Intracellular and net release rates of free amino acids in *Daphnia magna.* Can. J. Fish. Aquat. Sci. 38: 157–162

Gardner WS, Chandler JF & Laird GA (1989) Organic nitrogen mineralization and substrate limitation of bacteria in lake Michigan. Limnol. Oceanogr. 34: 478–485

Geller A (1985a) Light-induced conversion of refractory, high molecular weight lake water constituents. Schweiz. Z. Hydrol. 47: 21–26

— (1985b) Degradation and formation of refractory DOM by bacteria during simultaneous growth on labile substrates and persistent lake water constituents. Schweiz. Z. Hydrol. 47: 27–34

— (1986) Comparison of mechanisms enhancing biodegradability of refractory lake waters constituents. Limnol. Oceanogr. 31: 755–764

Gjessing ET (1976) Physical and chemical characteristics of aquatic humics. Ann Arbor Science, Ann Arbor, Mi

Gocke K (1970) Untersuchungen über Abgabe und Aufnahme von Aminosäuren und Polypeptiden durch Planktonorganismen. Arch. Hydrobiol 67: 285–367

— (1975) Studies on short-term variations of heterotrophic activity in the Kiel Fjord. Mar. Biol. 33: 49–55

— (1977) Comparisons of methods for determining the turnover times of dissolved organic compounds. Mar. Biol. 42: 131–141

Gocke K, Dawson R & Liebezeit G (1981) Availability of dissolved free glucose to heterotrophic microorganisms. Mar. Biol. 62: 209–216

Haan H de (1974) Effect of a fulvic acid fraction on the growth of a *Pseudomonas sp.* from Tjeukemeer (The Netherlands). Freshw. Biol. 4: 301–310

Hagström A, Azam F, Andersson A, Wikner J & Rassoulzadegan F (1988) Microbial loop in an oligotrophic pelagic marine ecosystem: possible roles of cyanobacteria and nanoflagellates in the organic fluxes. Mar. Ecol. Prog. Ser. 49: 171–178

Hagström A, Ammerman JW, Henrichs S & Azam F (1984) Bacterioplankton growth in seawater: II. Organic matter utilization during steady-state growth in seawater cultures. Mar. Ecol. Prog. Ser. 18: 31–39

Haider K (1988) The microbial degradation of lignin and its role in the carbon cycle. Forum Mikrobiol. 11: 477–489

Hama J & Handa N (1987) Pattern of organic matter production of natural phytoplankton population in a eutrophic lake. 1. Intracellular products. Arch. Hydrobiol. 109: 107–120

— (1992) Diel photosynthetic production of cellular organic

matter in natural phytoplankton populations, measured with ^{13}C and gas chromatography/mass spectrometry. Mar. Biol. 112: 175–181

Hammer KD & Brockmann UH (1983) Rhythmic release of dissolved free amino acids from partly synchronized *Thalassiosira rotula* under nearly natural conditions. Mar. Biol. 74: 305–312

Harder W & Dijkhuizen L (1982) Strategies of mixed substrate utilization in microorganisms. Philos. Trans. R. Soc. London 297: 459–479

Harvey GR (1983) Dissolved carbohydrates in the New York bight and the variability of marine organic matter. Mar. Chem. 12: 333–339

Harvey GR, Boran DA, Chosal LA & Tokar JM (1983) The structure of marine fulvic and humic acids. Mar. Chem. 12: 119–132

Hedges JI (1992) Global biogeochemical cycles: progress and problems. Mar. Chem. 39: 67–93

Hedges JI, Clark WA, Conoric GL (1988a) Organic matter sources to the water column and surfical sediments of marine bay. Limnol. Oceanogr. 33: 1116–1136

— (1988b) Fluxes and reactivities of organic matter in a coastal marine bay. Limnol. Oceanogr. 33: 1137–1152

Heldal M & Bradtbak G (1991) Production and decay of viruses in aquatic environments. Mar. Ecol. Prog. Ser. 72: 205–212

Hellebust JA (1974) Extracellular products. In: Stewart WDP (Ed) Algal Physiology and Biochemistry, Vol 10 (pp 838–863) Blackwell Sci. Publ., Oxford

Herbst V (1984) Physiologische Untersuchungen zur Kopplung der Stoffwechsel von *Oscillatoria redekei van Goor* und Begleitbakterien. Arch. Hydrobiol. Suppl. 69: 525–594

Herbst V & Overbeck J (1978) Metabolic coupling between the algae *Oscillatoria redekei* and accompanying bacteria. Naturwiss. 65: 598–599

Hessen DO (1985) The relation between bacterial carbon and dissolved humic compounds in oligotrophic lakes. FEMS Microb. Ecol. 31: 215–223

— (1992) Dissolved organic carbon in a small humic lake: effects on bacterial production and respiration. In: Salonen K, Kairesalo T & Jones RI (Eds) Dissolved Organic Matter in Lacustrine Ecosystems: Energy Source and System Regulator. Hydrobiologia 229: 115–123

Hickel B (1978) Phytoplankton population dynamics in Plußsee (East-Holstein, Germany). Verh. Ges. Ökol. Kiel 1977 (pp 119–126)

Hobbie JE (1992) Microbial control of dissolved organic carbon in lakes: research for the future. In: Salonen K, Kairesalo T & Jones RI (Eds) Dissolved Organic Matter in Lacustrine Ecosystems: Energy Source and System Regulator. Hydrobiologia 229: 115–123

Hobbie JE & Rublee P (1977) Radioisotope studies of heterotrophic bacteria in aquatic ecosystems. In: Cairns J (Ed) Aquatic Microbial Communities (pp 440–476) Garland Publ., New York

Hodson RE, Azam F, Carlucci AF, Furhman JA, Karl DM & Holm-Hansen O (1981) Microbial uptake of dissolved organic matter in McMurdo Sound, Antarctica. Mar. Biol. 61: 89–94

Hollibaugh JT & Azam F (1983) Microbial degradation of dissolved proteins in seawater. Limnol. Oceanogr. 28: 1104–1116

Hoppe HG (1978) Relationships between active bacteria and heterotrophic potential in the sea. Netherlands J. Sea Res. 12: 78–98

— (1983) Significance of exoenzymatic activities in the ecology of brackish water: measurements by means of methylumbelliferyl-substrates. Mar. Ecol. Prog. Ser. 11: 299–308

— (1991) Microbial extracellular enzyme activity: a new key parameter in aquatic ecology. In: Chróst RJ (Ed) Microbial Enzymes in Aquatic Environments (pp 60–83) Brock/Springer Series in Contemporary Bioscience, Springer Verlag

Hoppe HG, Kim SJ & Gocke K (1988) Microbial decomposition in aquatic environments: combined processes of extracellular enzyme activity and substrate uptake. Appl. Environ. Microbiol. 54: 784–790

Horvath RS (1972) Microbial co-metabolism and the degradation of organic compounds in nature. Bact. Rev. 36: 146–155

Ittekot V, Brockmann U, Michael W & Degens ET (1981) Dissolved free and combined carbohydrates during a phytoplankton bloom in the North Sea. Mar. Ecol. Prog. Ser. 4: 299–305

Jannasch HW (1970) Threshold concentration of carbon sources limiting bacterial growth in seawater. In: Hood DW (Ed) Symposium on Organic Matter in Natural Waters (pp 321–330) Univ. Alaska Mar. Sci. Occ. Publ. No. 1

Jannasch HW, Eimhjellen K, Wirsen CO & Farmanfarmian A (1971) Microbial degradation of organic matter in the deep sea. Science 171: 672–675

Jacobsen TR & Azam F (1985) Role of bacteria in copepod fecal pellet decomposition: Colonization, growth rates and mineralization. Bull. Mar. Sci. 35: 495–502

Jensen LM (1985) ^{14}C-labelling patterns of phytoplankton: specific activity of different product pools. J. Plankt. Res. 7: 643–652

Jensen LM & Søondergaard M (1985) Comparison of two methods to measure algal release of dissolved organic carbon and the subsequent uptake by bacteria. J. Plankt. Res. 7: 44–56

Johnson KM & Sieburth JMcN (1977) Dissolved carbohydrates in seawater. I. A precise spectrophotometric analysis for monosaccharides. Mar. Chem. 5: 1–13

Jørgensen NOG (1982) Heterotrophic assimilation and occurrence of dissolved free amino acids in a shallow estuary. Mar. Ecol. Prog. Ser. 8: 145–159

— (1986) Fluxes of free amino acids in three Danish lakes. Freshw. Biol. 16: 255–268

— (1987) Free amino acids in lakes: Concentrations and assimilation rates in relation to phytoplankton and bacterial production. Limnol. Oceanogr. 32: 97–111

Jørgensen NOG, Søndergaard M, Hansen HJ, Bosselman S & Riemann B (1983) Diel variation in concentration, assimilation and respiration of dissolved free amino acids in relation to planktonic primary and secondary production in two eutrophic lakes. Hydrobiologia 107: 107–122

Jørgensen NOG & Sondergaard M (1984) Are dissolved free amino acids free? Microb. Ecol. 10: 301–316

Jørgensen NOG & Bosselman S (1988) Concentrations of free amino acids and their bacterial assimilation rates in vertical profiles of two Danish lakes: Relations to diel changes in zooplankton grazing activity. Arch. Hydrobiol. Ergebn. Limnol. 31: 289–300

Jürgens K & Güde H (1990) Incorporation and release of phosphorus by planktonic bacteria and phagotrophic flagellates. Mar. Ecol. Prog. Ser. 59: 271–284

Kalle K (1966) The problem of the Gelbstoffe in the Sea. Oceanogr. Mar. Biol. Ann. Rev. 4: 91–104

Kato K & Stabel HH (1984) Studies on the carbon flux from phyto- to bacterioplankton communities in Lake Constance. Arch. Hydrobiol. 102: 177–192

Kieber DJ & Mopper K (1987) Photochemical formation of glyoxylic and pyruvic acids in seawater. Mar. Chem. 21: 135–149

— (1990) Determination of picomolar concentrations of carbonyl compounds in natural waters, including seawater, by liquid chromatography. Environ. Sci. Tech. 24: 1477–1481

Kirchman DL (1990) Limitation of bacterial growth by dissolved organic matter in the subarctic Pacific. Mar. Ecol. Progr. Ser. 62: 47–54

Kirchman DL & Hodson R (1984) Inhibition by peptides of amino acid uptake by bacterial populations in natural waters: Implications for the regulation of amino acid transport and incorporation. Appl. Environ. Microbiol. 47: 624–631

— (1986) Metabolic regulation of amino acid uptake in marine waters. Limnol. Oceanogr. 31: 339–350

Kirchman DL, K'ees E & Hodson R (1985) Leucine incorporation and its potential as a measure of protein synthesis by bacteria in natural aquatic systems. Appl. Environ. Microbiol. 49: 599–607

Kirchman DL, Suzuki Y, Gadide C & Ducklow HW (1991) High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. Nature 352: 612–614

Koike I, Hara S, Terauchi K & Kogure K (1990) Role of submicrometer particles in the ocean. Nature 345: 242–244

Korinek J (1928) Über die Zersetzungsprozesse der organischen Substanz im Meere. Biochem. Z. 192: 230

Kreutzberg GW, Reddington M & Zimmermann H (1986) Cellular biology of ectoenzymes. Springer Verlag, Berlin

Krogh AA & Lange E (1932) Quantitative Untersuchungen über Plankton, Kolloide und gelöste organische und anorganische Substanzen in dem Furesee. Int. Rev. Ges. Hydrobiol. 26: 20–53

Lampert W (1978) Release of dissolved organic carbon by grazing zooplankton. Limnol. Oceanogr. 23: 831–834

Lancelot C (1979) Gross excretion rates of natural marine phytoplankton and heterotrophic uptake of excreted products in the Southern North Sea, as determined by short-term kinetics. Mar. Ecol. Prog. Ser. 1: 179–186

— (1984) Extracellular release of small and large molecules by phytoplankton in the southern bight of the North Sea. Estuarine and Coastal Shelf Sciences 18: 65–77

Lancelot C & Billén G (1984) Activity of heterotrophic bacteria and its coupling to primary production during the spring phytoplankton bloom in the southern bight of the North Sea. Limnol. Oceanogr. 29: 721–730

Lancelot C & Mathot S (1985) Biochemical fractionation of primary production by phytoplankton in Belgian coastal water during short- and long-term incubations with [^{14}C]-bicarbonate. I. Mixed diatom population. Mar. Biol. 86: 219–226

Larsson U & Hagström A (1979) Phytoplankton exudate release as energy source for the growth of pelagic bacteria. Mar. Biol. 52: 199–206

— (1982) Fractionated phytoplankton primary production, exudate release, and bacterial production in a Baltic eutrophication gradient. Mar. Biol. 67: 57–70

Lee C & Wakeham SG (1992) Organic matter in the water column: future research challenges. Mar. Chem. 39: 95–118

Liebezeit G, Bölter M, Brown IF & Dawson R (1980) Dissolved free amino acids and carbohydrates at the pycnocline boundaries in the Sargasso Sea and related microbial activity. Oceanol. Acta 3: 357–362

Lignell R (1990) Excretion of organic carbon by phytoplankton: its relation to algal biomass, primary production and secondary productivity in the Baltic Sea. Mar. Ecol. Prog. Ser. 68: 85–99

Lindroth P & Mopper K (1979) High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivatization with ophthaldehyde. Anal. Chem. 51: 1667–1674

Lord JM (1972) Glycolate oxidoreductase in Escherichia coli. Biochim. Biophys. Acta 267: 227–237

Longhurst AR, Koike I, Li WKW, Rodriguez J, Dickie P, Kepay P, Partensky F, Bautista B, Ruiz J, Wells M & Bird DF (1992) Sub-micron particles in northwest Atlantic shelf water. Deep Sea Res. 39: 1–7

Mague TH, Friberg E, Highes DJ & Morris I (1980) Extracellular release of carbon by marine phytoplankton: a physiological approach. Limnol. Oceanogr. 23: 262–279

Malone TC, Ducklow HW, Peele ER & Pike SE (1991) Picoplankton carbon flux in Chesapeake Bay. Mar. Ecol. Prog. Ser. 78: 11–22

Mann KH (1988) Production and use of detritus in various freshwater, estuarine, and coastal marine ecosystems. Limnol. Oceanogr. 33: 910–930

Mantoura RFC & Riley JP (1975) The analytical concentration of humic substances from natural waters. Anal. Chim. Acta 76: 97–106

Matin A (1979) Microbial regulatory mechanisms at low nutrient concentrations as studied in chemostat. In: Shilo M (Ed) Strategies of Microbial Life in Extreme Environments (pp 323–339) Verlag Chemie, Weinheim

Martin JH & Fitzwater SE (1992) Dissolved organic carbon in the Atlantic, Southern and Pacific Oceans. Nature 356: 699–700

Martin-Jézéquel V, Sournia A & Birrien JL (1992) A daily study of the diatom spring bloom at Roscoff (France) in 1985. III.

Free amino acids composition studied by HPLC analysis. J. Plankt. Res. 14: 409–421

McKnight DM, Aiken GR & Smith RL (1991) Aquatic fulvic acids in microbially based ecosystem: Results from two desert lakes in Antarctica. Limnol. Oceanogr. 36: 998–1006

Menzel DW & Vaccaro RF (1964) The measurement of dissolved organic and particulate carbon in seawater. Limnol. Oceanogr. 9: 138

Meyer-Reil LA (1986) Measurements of hydrolytic activity and incorporation of dissolved organic substrates by microorganisms in marine sediments. Mar. Ecol. Progr. Ser. 31: 143–149

— (1991) Ecological aspects of enzymatic activity in marine sediments. In: Chróst RJ (Ed) Microbial Enzymes in Aquatic Environments (pp 84–95) Brock/Springer Series in Contemporary Bioscience. Springer Verlag, New York

Moaledj K & Overbeck J (1980) Studies on uptake kinetics of oligocarbophilic bacteria. Arch. Hydrobiol. 89: 303–312

Mopper K & Lindroth P (1982) Diel and depth variations in dissolved free amino acids and ammonium in the Baltic Sea determined by shipboard HPLC analysis. Limnol. Oceanogr. 27: 336–347

Mopper K & Zika RG (1987a) Free amino acids in marine rains: evidence for oxidation and potential role in nitrogen cycling. Nature 325: 246–249

Mopper K, Ittekot V, Dawson R & Liebezeit G (1980) The monosaccharide spectra of natural waters. Mar. Chem. 10: 55–66

Mopper K, Zika RG & Fischer A (1990) Photochemistry and photophysics of marine humic substances. In: MacCarthy P, Gjessing ET, Mantoura RFC & Seki E (Eds) Humic Substances (pp 123–132) Vol 4

Mopper K, Xianliang Z, Kieber RJ, Kieber DJ, Sikorski RJ & Jones RG (1991) Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. Nature 353: 60–62

Mopper K & Kieber DJ (1992) Distribution and biological turnover of dissolved organic compounds in the water column of the Black Sea. Deep Sea Res. Suppl. 39: S1021–S1047

Moran MA & Hodson RE (1990) Bacterial production on humic and nonhumic components of dissolved organic carbon. Limnol. Oceanogr. 35: 1744–1756

Moran BS & Buesseler KO (1992) Short residence time of colloids in the upper ocean estimated from ^{238}U-^{234}Th disequilibria. Nature 359: 221–223

Morris I & Skea W (1978) Products of photosynthesis in natural populations of marine phytoplankton from the Gulf of Maine. Mar. Biol. 47: 303–312

Morita RY (1982) Starvation survival of heterotrophs in the marine environment. In: Marshall KC (Ed) Adv. Microb. Ecol. 6: 171–198

— (1984) Substrate capture by marine heterotrophic bacteria in low nutrient waters. In: Hobbie JE & Williams LeB PJ (Eds) Heterotrophic Activity in the Sea (pp 83–100) Plenum Press, New York

Münster U (1984) Distribution, dynamic and structure of free dissolved carbohydrates in the Plußsee, a North German eutrophic lake. Verh. Internat. Verein. Limnol. 22: 929–935

— (1985) Investigations about structure, distribution and dynamics of different organic substrates in the DOM of lake Plußsee. Arch. Hydrobiol. Suppl. 70: 429–480

— (1991) Extracellular enzyme activity in eutrophic and polyhumic lakes. In: Chróst RJ (Ed) Microbial Enzymes in Aquatic Environments (pp 96–122) Brock/Springer Series in Contemporary Bioscience, Springer Verlag, New York

— (1992a) Microbial extracellular enzyme activities and biopolymer processing in two polyhumic lakes. Arch. Hydrobiol. Ergebn. Limnol. 37: 21–32

— (1992b) Microbial extracellular enzyme activities in HUMEX lake Skjervatjern. Environ. Internat. 18: 637–647

Münster U, Einiö P & Nurminen J (1989) Evaluation of the measurements of extracellular enzyme activities in a polyhumic lake by means of studies with 4-methylumbelliferyl-substrates. Arch. Hydrobiol. 115: 321–337

Münster U & Chróst RJ (1990) Dissolved organic matter (DOM) in aquatic environments: origin, distribution, composition and microbial utilization. In: Overbeck J & Chróst RJ (Eds) Advanced Biochemical and Molecular Approaches to Aquatic Microbial Ecology (pp 8–46) Brock/Springer Series in Contemporary Bioscience, Springer Verlag, New York

Münster U, Einiö P, Nurminen J & Overbeck J (1992) Extracellular enzymes in a polyhumic lake: important regulators in detritus processing. In: Salonen K, Kairesalo T & Jones RI (Eds) Dissolved Organic Matter in Lacustrine Ecosystems: Energy Source and System Regulator. Hydrobiologia 229: 225–238

Nagata T & Kirchman DL (1991) Release of dissolved free and combined amino acids by bacteriovorous marine flagellates. Limnol. Oceanogr. 36: 433–443

— (1992) Release of macromolecular organic complexes by heterotrophic marine flagellates. Mar. Ecol. Prog. Ser. 83: 233–240

Nalewajko C (1977) Extracellular release in freshwater algae and bacteria: extracellular products of algae as a source of carbon for heterotrophs. In: Cairns J (Ed) Aquatic Microbial Communities (pp 589–626) Garland, New York

Nissen H, Nissen P, Azam F (1984) Multiphasic uptake of D-glucose by an oligotrophic marine bacterium. Mar. Ecol. Prog. Ser. 16: 155–160

Ochiai M & Hanya T (1980) Change in monosaccharide composition in the course of decomposition of dissolved carbohydrates in lake water. Arch. Hydrobiol. 90: 257–264

Odum EP (1963) Primary and secondary energy flow in relation to ecosystem structure. Proc. 16th Intern. Congr. of Zool. 4: 336–338

Odum EP & de la Cruz AA (1963) Detritus as a major component of ecosystems. Bull. Am. Inst. Sci. 13: 39–48

Ohle W (1934) Über organische Stoffe in Binnenseen. Verh. Internat. Verein. Limnol. 6: 249–262

— (1937) Kolloidgele als Nährstoffregulatoren der Gewässer. Naturwiss. 25: 471–474

Olsen Y, Varum KM & Jensen A (1986) Some characteristics of

the carbon compounds released by daphnia. J. Plankt. Res. 8: 505–518

Overbeck J (1975) Distribution pattern of uptake kinetic responses in a stratified eutrophic lake. Verh. Internat. Verein. Limnol. 19: 2600–2615

— (1979) Studies on the heterotrophic function and glucose metabolism of microplankton in Plußsee. Arch. Hydrobiol. Ergebn. Limnol. 13: 56–76

— (1990) Aspects of aquatic microbial carbon metabolism: regulation of phosphoenolpyruvate carboxylase. In: Overbeck J & Chróst RJ (Eds) Aquatic Microbial Ecology: Biochemical and Molecular Approaches (pp 79–95) Springer Verlag, New York

Overbeck J & Chróst RJ (1990) Aquatic microbial ecology: Biochemical and molecular approaches (p 190) Springer Verlag, New York

Parrish CC (1988) Dissolved and particulate mareine lipid classes: a review. Mar. Chem. 23: 17–40

Parsons TR & Strickland JDH (1962) On the production of particulate organic carbon by heterotrophic processes in sea water. Deep Sea Res. 8: 211–222

Pearl H (1991) Ecophysiological and trophic implications of light-stimulated amino acid utilization in marine phytoplankton. Appl. Environ. Microbiol. 57: 473–479

Perdue & Gjessing ET (1990) Organic acids in aquatic ecosystems (p 345) Wiley & Sons, Chichester

Poltz J (1972) Untersuchungen über das Vorkommen und den Abbau von Fettsäuren in Seen. Arch. Hydrobiol. Suppl. 40: 315–399

Pomeroy LR (1974) The ocean's food web, a changing paradigm. Biosci. 24: 499–504

Pomeroy LR & Wiebe WJ (1988) Energetics of microbial food webs. Hydrobiologia 156: 7–18

Poole CF (1978) Recent advances in the silylating of organic compounds for gas chromatography. In: Blau K & King GS (Eds) Handbook of Derivatives for Chromatography (pp 152–200) Heyden, London

Post WM, Chavez F, Mulholland PJ, Pastor J, Peng TH, Prentice K & Webb T (1992) Climatic feedbacks in the global carbon cycle. ACS Symp. Ser. 483: 392–412

Poulet SA, Harris RP, Martin-Jezequel V, Moal J & Samain JS (1986) Free amino acids in copepod faecal pellets. Oceanol. Acta 9: 1991–197

Priest FG (1984) Extracellular enzymes. Aspects of microbiology 9 (p 79) Van Nostrand Reinhold (UK) Co. Ltd.

Proctor LM & Fuhrman JA (1990) Viral mortality of marine bacteria and cyanobacteria. Nature 343: 60–62

— (1992) Mortality of marine bacteria in response to enrichments of the virus size fraction from seawater. Mar. Ecol. Progr. Ser. 87: 283–293

Rai H (1984) Magnitude of heterotrophic metabolism of photosynthetically fixed dissolved organic carbon (PDOC) in Schöhsee, West Germany. Arch Hydrobiol. 102: 91–103

Reinheimer G (1986) One hundred years marine microbiology – history and future development. IFREMER, Actes de Colloques 3: 15–22

Rich PH (1984) Trophic-detrital interactions: vestiges of ecosystem evolution. Amer. Natur. 123: 20–29

Rich PH & Wetzel RG (1978) Detritus in the lake ecosystem. Amer. Natur. 112: 57–71

Riemann B, Søndergaard M, Schierup HH, Bosselmann S, Christensen G, Hansen J & Nielsen B (1982) Carbon metabolism during a spring diatom bloom in the eutrophic lake Mossø. Int. Rev. Ges. Hydrobiol. 67: 145–185

Riemann B & Søndergaard M (1984) Bacterial growth in relation to phytoplankton primary production and extracellular release of organic carbon. In: Hobbie JR & Williams leB PJ (Eds) Heterotrophic Activity of the Sea (pp 233–248) NATO SAD, Plenum Press, New York

— (1986a) Carbon dynamics in eutrophic, temperate lakes (p 290) Elsevier, Amsterdam

— (1986b) Regulation of bacterial secondary production in two eutrophic lakes and in experimental enclosures. J. Plank. Res. 8: 519–536

Riemann B, Jørgensen NOG, Lampert W & Fuhrman JA (1986c) Zooplankton induced changes in dissolved free amino acids and in production rates of freshwater bacteria. Microb. Ecol. 12: 247–258

Riley JP & Segar DA (1970) Seasonal variation of the free and combined dissolved amino acids in the Irish Sea. J. Mar. Biol. Assoc. UK 50: 713–720

Romankevich EA (1984) Geochemistry of organic matter in the ocean (p 334) Springer Verlag, Tokyo

Sakugawa H & Handa N (1985) Chemical studies on dissolved carbohydrates in the water samples collected from North Pacific and Bering Sea. Oceanol. Acta 8: 185–196

Salonen K (1981) The ecosystem of the oligotrophic lake Pääjärvi. 2. Bacterioplankton. Verh. Int. Verein. Limnol. 21: 448–553

Salonen K, Kolonen K & Arvola L (1983) Respiration of plankton in two small, polyhumic lakes. Hydrobiol. 101: 65–70

Salonen K, Kairesalo T & Jones RI (1992) Dissolved organic matter in lacustrine ecosystems: energy source and system regulator. Hydrobiologia 229: 291

Salonen K & Hammar T (1986) On the importance of dissolved organic matter in the nutrition of zooplankton in some lakes waters. Oecologia 68: 246–253

Salonen K & Tulonen T (1990) Photochemical and biological transformation of dissolved humic substances. Verh. Internat. Verein. Limnol. 24: 294

Saunders GW (1977) Carbon flow in the aquatic systems. In: Cairn J Jr (Ed) Aquatic Microbial Communities (pp 417–440) Garland, New York

Schindler DW, Mayley SE, Curtis PJ, Parker BR, Stainton MP & Kelly CA (1992) Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in precambrian shield lakes. In: Salonen K, Kairesalo T & Jones RI (Eds) Dissolved Organic Matter in Lacustrine Ecosystems: Energy Source and System Regulator. Hydrobiologia 229: 1–2

Sell A & Overbeck J (1992) Exudates: phytoplankton-bacterioplankton interactions in Plußsee. J. Plankt. Res. 14: 1199–1215

Shah NM & Fogg GE (1973) The determination of glycolic acid in sea water. J. Mar. Biol. Assoc. UK 53: 321–324

Shah NM & Wright RT (1974) The occurrence of glycolic acid in coastal sea water. Mar. Biol. 24: 121–124

Sharp JH (1977) Excretion of organic matter by marine phytoplankton: Do healthy cells do it? Limnol. Oceanogr. 22: 381–399

Sherr EB (1988) Direct use of high molecular weight polysaccharide by heterotrophic flagellates. Nature 335: 348–351

Sherr BF, Sherr EB & Berman T (1982) Decomposition of organic detritus: a selective role for microflagellate protozoan. Limnol. Oceanogr. 27: 765–769

Sherr BF, Sherr EB & Hopkinson CS (1989) Trophic interactions within pelagic microbial communities: Indications of feedback regulation of carbon flow. Hydrobiologia 159: 19–26

Sieburth JMcN (1979) Sea microbes (p 654) Oxford Univ. Press, New York

Sieburth JMcN & Jensen A (1968) Studies on algal substances in the Sea. J. Exp. Mar. Biol. Ecol. 2: 174–189

Sugimura Y & Suzuki Y (1988) A high temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample. Mar. Chem. 24: 105–131

Simon M (1985) Specific uptake rates of amino acids by attached and free-living bacteria in a mesotrophic lake. Appl. Environ. Microbiol. 49: 1254–1259

Simon M & Azam F (1988) Protein content and protein synthesis rates of planktonic marine bacteria. Mar. Ecol. Prog. Ser. 51: 201–213

Smith DC, Simon M, Aldedge AL & Azam F (1992) Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution. Nature 359: 139–142

Sorokin YI (1977) The heterotrophic phase of plankton succession in the Japan Sea. Mar. Biol. 41: 107–117

Søndergaard M & Schierup HH (1982) Release of extracellular organic carbon during a diatom bloom in Lake Møsso: molecular weight fractionation. Freshw. Biol. 12: 313–320

Søndergaard M, Riemann B & Jørgensen NOG (1985) Extracellular organic carbon (EOC) released by phytoplankton and bacterial production. Oikos 45: 323–332

Søndergaard M, Rieman B, Møller-Jensen L, Jørgensen NOG, Bjørnsen PK, Olesen M, Larsen JB, Geertz-Hensen O, Hansen J, Christoffersen K, Jespersen AM, Andersen F & Bosselmann S (1988) Pelagic food web processes in an oligotrophic lake. Hydrobiologia 164: 271–286

Stabel HH (1977) Gebundene Kohlenhydrate als stabile Komponenten im Schöhsee und in *Scenedesmus*-Kulturen. Arch. Hydrobiol. Suppl. 53: 159–254

Stabel HH, Moaledj J & Overbeck J (1979) On the degradation of dissolved organic molecules from Plußsee by oligocarbophilic bacteria. Arch. Hydrobiol. Ergebn. Limnol. 12: 95–104

Stabel HH & Steinberg C (1976) Cleavage of macromolecular allochthonous soluble organic matter. Naturwiss. 63: 533

Steinberg C (1977) Schwer abbaubare, stickstoffhaltige gelöste Substanzen im Schöhsee und in Algenkulturen. Arch. Hydrobiol. Suppl. 53: 48–158

Steinberg C & Münster U (1985) Geochemistry and ecological role of humic substances in lakewater. In: Aiken GR, McKnight DN, Wershaw RL & MacCarthy P (Eds) Humic Substances in Soil, Sediment, and Water. Geochemistry, Isolation, and Characterization (pp 105–145) Wiley & Sons, NY

Storch TA & Saunders GW (1978) Phytoplankton extracellular release and its relation to the seasonal cycle of dissolved organic carbon in a eutrophic lake. Limnol. Oceanogr. 23: 112–119

Sundh I (1992) Biochemical composition of dissolved organic carbon derived from phytoplankton and used by heterotrophic bacteria. Appl. Environ. Microbiol. 58: 2938–2947

Suttle CA, Chan AM & Fuhrman JA (1991) Dissolved free amino acids in the Sargasso Sea: uptake and respiration rates, turnover times, and concentrations. Mar. Ecol. Prog. Ser. 70: 189–199

Tamminen T, Kuparinen J & Lignell R (1984) Diurnal cycles of phytoplankton exudation and bacteria uptake of organic substrates. Arch. Hydrobiol. Ergebn. Limnol. 19: 267–279

Taylor GT, Iturriaga R & Sullivan CW (1985) Interactions of bacteriovorous grazers and heterotrophic bacteria with dissolved organic matter. Mar. Ecol. Prog. Ser. 22: 129–141

Thienemann A (1925) Die Binnengewässer Mitteleuropas. Binnengewässer Vol 1: 1–255

Thompson LA & Nedwell DB (1985) Existence of different pools of fatty acids in anaerobic model ecosystems and their availability to microbial metabolism. FEMS Microb. Ecol. 31: 141–146

Thurman M (1985) Organic geochemistry of natural waters (p 497) Nijhoff/Junk Publ., Boston

Tilzer MM & Horne AJ (1979) Diel patterns of phytoplankton productivity and extracellular release in ultra-oligotrophic Lake Tahoe. Int. Rev. Ges. Hydrobiol. 64: 157–176

Tolbert NE (1974) Photorespiration by algae. In: Stewart WDP (Ed) Algal Physiology and Biochemistry (pp 474–504) Blackwell, Oxford

Tolbert NE & Zill LP (1956) Excretion of glycolic acid by algae during photosynthesis. J. Biol. Chem. 22: 895–906

Tranvik L (1988) Availability of dissolved organic carbon for planktonic bacteria in oligotrophic lakes of differing humic content. Microb. Ecol. 16: 311–322

— (1989) Bacterioplankton growth, grazing mortality and quantitative relationship to primary production in a humic and clearwater lake. J. Plankt. Res. 11: 985–1000

— (1990) Bacterial growth on fractions of dissolved organic carbon of different molecular weights from humic and clear waters. Appl. Environ. Microbiol. 56: 1672–1677

— (1992) Allochthonous dissolved organic matter as energy source for pelagic bacteria and the concept of the microbial loop. Hydrobiologia 229: 107–114

Tranvik L & Höfle M (1987) Bacterial growth in mixed cultures on dissolved organic carbon from humic and clear waters. Appl. Environ. Microbiol. 53: 482–488

Vadstein O, Harkjerr BO & Jensen A (1989) Cycling of organic carbon in the photic zone of a eutrophic lake with special reference to the heterotrophic bacteria. Limnol. Oceanogr. 34: 840–855

Vaughan GM & Mopper K (1987) Dissolved free amino acid enantiomeric composition of deep Sargasso seawater using a new HPLC technique. EOS 68: 1741–

Waksman SA (1936) Humus (p 289) Williams & Wilkins, Baltimore

Watanabe Y (1980) A study of the excretion and extracellular products of natural phytoplankton in lake Nakonuma, Japan. Int. Rev. Hydrobiol. 65: 809–834

Webb KL & Johannes RE (1967) Studies of release of dissolved free amino acids by marine zooplankton. Limnol. Oceanogr. 12: 376–384

Weinmann G (1970) Gelöste Kohlenhydrate und andere organische Stoffe in natürlichen Gewässern und in Kulturen von *Scenedesmus quadricauda.* Arch. Hydrobiol. Suppl. 37: 164–242

Wetzel RG (1972) Functions and interactions of dissolved organic matter and the littoral zone in lake metabolism and eutrophication. In: Kajak Z & Hilbricht-Ilkowska A (Eds) Productivity Problems of Freshwater (pp 333–347) PWN, Warszawa

— (1979) The role of the littoral zone and detritus in lake metabolism. Arch. Hydrobiol. Ergebn. Limnol. 13: 145–161

— (1983) Limnology, 2nd ed. (p 755) Saunders College, Philadelphia

— (1984) Detrital dissolved and particulate organic carbon functions in aquatic ecosystems. Bull. Mar. Sci. 35: 503–509

— (1990) Land-water interfaces: metabolic and limnological regulators. Verh. Internat. Ver. Limnol. 24: 6–24

— (1991) Extracellular enzymatic interactions in aquatic ecosystems: storage, redistribution, and interspecific communication. In: Chróst JR (Ed) Microbial Enzymes in Aquatic Environments (pp 6–28) Brock/Springer Series in Contemporary Bioscience. Springer Verlag, Berlin

— (1992) Gradient-dominated ecosystems: sources and regulatory functions of dissolved organic matter in freshwater ecosystems. Hydrobiologia 229: 181–198

Whittaker RH & Likens GE (1973) Carbon in the Biota. In: Woodwell GM & Pecan EV (Eds) Carbon and the Biosphere (pp 281–302) AEC 30 Technical Information Center, Washington, DC

Wicks RJ, Moran MA, Pittman LJ & Hodson RE (1991) Carbohydrate signatures of aquatic macrophytes and their dissolved degradation products as determined by a sensitive high-performance ion chromatography method. Appl. Environ. Microbiol. 57: 3135–3143

Williams LeB PJ (1981) Incorporation of microheterotrophic processes into the classical paradigm of the planktonic food web. Kieler Meeresforsch. Sonderh. 5: 1–28

— (1990) The importance of losses during microbial growth: commentory on the physiology, measurement and ecology of the release of dissolved organic material. Mar. Microb. Food Webs 4: 175–206

Williams LeB PJ & Yentsch CS (1976) An examination of photosynthetic production, excretion of photosynthetic products, and heterotrophic utilization of dissolved organic compounds with reference to results from coastal subtropical sea. Mar. Biol. 35: 41–47

Williams PM (1971) The distribution and cycling of organic matter in the ocean. In: Faust SJ & Hunter JV (Eds) Organic Compounds in Aquatic Environments (pp 145–163) Marcel Dekker, New York

— (1986) Chemistry of the dissolved and particulate phases in the water column. In: Eppley RW (Ed) Plankton Dynamics of the Southern California Bight. Lecture Notes on Coastal and Estuarine Studies (pp 53–83) Vol 15

Williams R & Poulet SA (1986) Relationship between the zooplankton, phytoplankton, particulate matter and dissolved free amino acids in the Celtic Sea. Mar. Biol. 90: 279–284

Wommack KE, Hill RT, Kessel M, Russek-Cohen E & Colwell RR (1992) Distribution of viruses in the Chesapeake Bay. Appl. Environ. Microbiol. 58: 2965–2970

Wood TM (1985) Properties of the cellulolytic enzyme systems. Biochem. Soc. Trans. 13: 407–410

Wood TM & McCrea SI (1979) Synergism between enzymes involved in the solubilization of native cellulose. Adv. Chem. Ser. 181: 181–209

Woodwell GM, Whittaker RH, Reiners WA, Likens GE, Delwiche CC & Botkin (1978) The biota and the world carbon budget. Science 199: 141–146

Wright RT (1970) Glycolic acid uptake by planktonic bacteria. In: Hood DW (Ed) Organic Matter in Natural Waters (pp 521–536) Institute of Marine Sciences, Alaska

— (1975) Studies on glycolic acid metabolism by freshwater bacteria. Limnol. Oceanogr. 20: 626–633

— (1984) Dynamics of pools of dissolved organic carbon. In: Hobbie JE & Wright RT (Eds) Heterotrophic Activity in the Sea (pp 121–154) Plenum Publ. Co, New York

— (1988a) Methods for evaluating the interaction of substrate and grazing as factors controlling planktoning bacteria. Arch. Hydrobiol. Ergebn. Limnol. 31: 229–242

— (1988b) A model for short-term control of the bacterioplankton by substrate and grazing. Hydrobiologia 159: 111–117

Wright RT & Hobbie JE (1965) The uptake of organic solutes in lake water. Limnol. Oceanogr. 10: 22–28

— (1966) The use of glucose and acetate by bacteria and algae in aquatic ecosystems. Ecology 47: 447–464

Wright RT & Shah N (1975) The trophic role of glycolic acid in coastal seawater. I. Heterotrophic metabolism in seawater and bacterial cultures. Mar. Biol. 33: 175–183

Zehr JP, Axler RP & Goldman CR (1985) Heterotrophic mineralization of amino acid nitrogen in subalpine Castle lake, California. Mar. Chem. 16: 343–350

Zeikus JG (1981) Lignin metabolism and the carbon cycle. In: Marshall KC (Ed) Advances in Microb. Ecol. 8: 211–243