Chapter 5

Dynamics of DON

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I. INTRODUCTION

Dissolved organic nitrogen (DON) is that subset of the dissolved organic matter (DOM) pool that contains N. From the perspective of a microorganism, this is where the action is—one-stop shopping for N, carbon (C), and energy. Research into DON, however, has lagged far behind that of the larger dissolved organic carbon (DOC) pool as clearly seen by the C:N ratio of chapters in this volume. This situation is primarily the result of the substantial analytical challenges

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inherent in DON research. DON exists in substantially lower concentrations than DOC, multiple chemical analyses are required for a single DON measurement, inorganic N removal is a nightmarish undertaking, and unless you have easy access to a nuclear reactor manufacturing short-lived ^{13}N, one must be content with labor-intensive stable isotopes rather than the quicker and more sensitive radiotracers.

The objectives of this chapter are to review available data specific to DON on the concentration and composition of the pool, to describe recent findings on the sources of DON to aquatic systems, and to survey data on rates and mechanisms of DON uptake and other sinks. An exhaustive review of DON was published by Antia *et al.* (1991). Therefore, this review will focus on work published largely after 1990 and topics not included in the earlier review. As a subset of the DOM pool, much of the information presented on DOC throughout this volume holds equally true for DON.

II. CONCENTRATION AND COMPOSITION OF THE DON POOL

Measurements of DON concentrations have become a routine component of many studies. This section reviews methods for measuring DON and then presents a survey of recent literature values of DON concentrations, relationships between DON and other parameters, data on the chemical composition of the pool, and suggested research priorities for the future. Due to space limitations, DON concentrations in lakes, streams, or groundwater, with some exceptions, are not included.

A. Methods for Measuring DON Concentrations

Studies of any aspect of DON cycling require first and foremost a reliable method of quantifying DON concentrations with high precision (Bronk *et al.*, 2000; see Sharp, Chapter 2). To calculate DON concentrations, one must first obtain an accurate total dissolved N (TDN) concentration. The TDN pool consists of an inorganic fraction, composed of ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-), and an organic fraction (i.e., DON), the composition of which is largely unknown (see Section II.C). There are presently three methods commonly used to measure TDN concentrations in aquatic systems: persulfate oxidation (Menzel and Vaccaro, 1964; Sharp, 1973; Valderrama, 1981), ultraviolet oxidation (Armstrong *et al.*, 1966; Armstrong and Tibbitts, 1968), and high-temperature oxidation (Sharp, 1973; Suzuki and Sugimura, 1985). After a TDN concentration has been measured, the sum of the NH_4^+ and combined NO_3^- / NO_2^- concentrations are subtracted from it, with the residual being defined as DON. This approach is problematic

because estimates of DON concentrations have the combined analytical error and uncertainty of three analyses: TDN, NH_4^+, and combined NO_3^-/ NO_2^-.

The first broad community comparison of the three methods used to measure DON was recently completed (Sharp *et al.,* in press; see Sharp, Chapter 2). It consisted of 29 sets of analyses done on five natural samples. The coefficient of variations for the five samples range from 19 to 46%, with the poorest replication observed on deep ocean samples. No one method emerged as clearly superior.

B. DON Distributions and Correlative Relationships between DON and Other Parameters

Here DON concentrations are presented and discussed with respect to global distributions, vertical profiles, seasonal variability, and the link between DON and inorganic N distributions.

1. Concentrations of DON in Aquatic Environments

In general, the lowest mean concentrations of DON are found in the deep ocean and the highest mean concentrations are found in rivers (Fig. 1A). Concentrations in Table I for the surface ocean range from 0.8 to 13 μM with a mean of 5.8 $\pm$ 2.0 μM. Note that many open ocean studies present data on total organic N (TON), rather than DON. Most researchers working in oligotrophic waters forego the filtration step because the particulate N (PN) pool is generally so small (<10% of TON; Abell *et al.,* 2000) and the risk of contamination and cell breakage during filtration is so high (Libby and Wheeler, 1997; Abell *et al.,* 2000). Concentrations in the deep ocean are lower with most measurements in the 2 to 5 μM range (Table I); if the very high Tupas and Koike (1990) data are excluded, the mean deep ocean concentration is 3.9 $\pm$ 1.8. Concentrations tended to be progressively higher in coastal, then estuarine, and then riverine waters, but the ranges in concentrations are much greater as well (Table I). In all environments, except the deep ocean, the bulk of the TDN pool is organic in form, averaging 60–69% of the TDN pool (Fig. 1B). The high NO_3^- concentrations in the deep ocean, results in the relatively small contribution of DON to the TDN pool in that environment (10 $\pm$ 3%, Fig. 1B). The C:N ratio of DOM increases from $\sim$14 in the surface ocean along a decreasing salinity gradient to a maximum mean of 26 in riverine systems (Fig. 1C; see Karl and Björkman, Chapter 6).

2. Global Distributions

Our understanding of global distributions of DON is still incomplete. Fortunately, the larger data sets needed to give a more holistic picture of DON

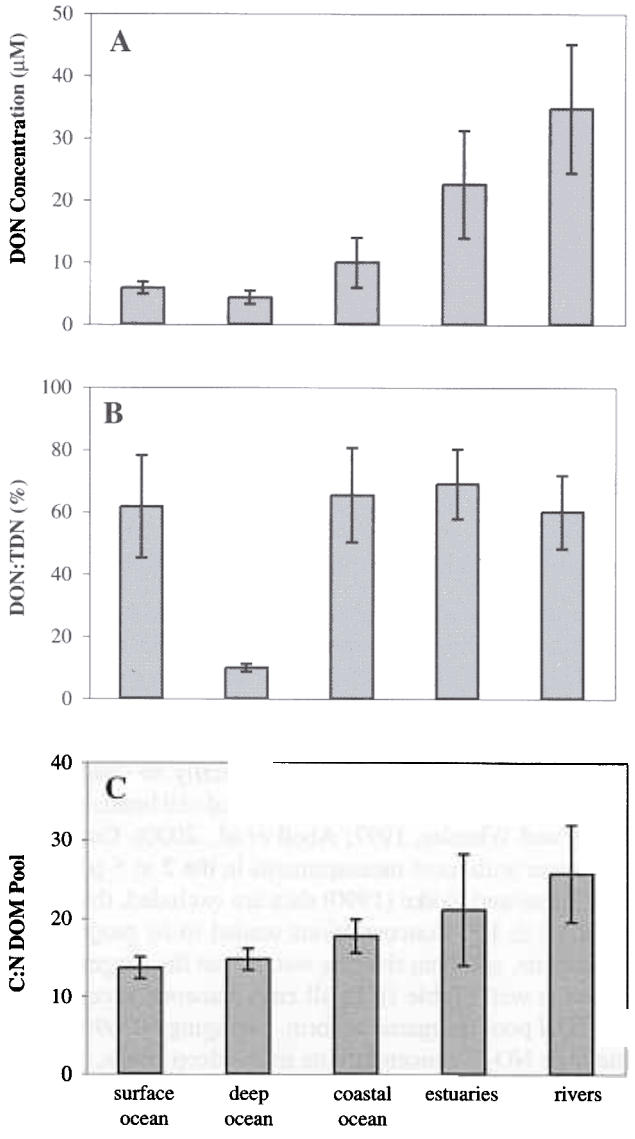

Figure 1 Summary of the data in Table 1 on A) dissolved organic nitrogen (DON) concentrations, B) the ratio of DON to total dissolved nitrogen (TDN, DON plus nitrate, nitrite, and ammonium), and C) the carbon (C) to N ratio (C:N) of the dissolved organic matter (DOM) pool.

distributions are becoming more common. In general, the lowest TON concentrations occur right at the equator, with the highest concentrations occurring just to the north and south (~3°N and S; Libby and Wheeler, 1997; Raimbault *et al.,* 1999; Hansell and Waterhouse, 1997). The pattern emerging in the Pacific is that increased biological production of DON occurs near the equator, via a number of release processes, and is fueled by primary production resulting from upwelled NO_3^- (see Hansell, Chapter 15). The released DON is then exported north or south from the equator in the meridonal Ekman transport to N depleted subtropical waters. The meridonal transport is likely one mechanism for moving organic N to the oligotrophic central gyres where it can fuel autotrophic growth and therefore support export production (Hansell and Waterhouse, 1997; Libby and Wheeler, 1997).

Consistent with the picture above, TON concentrations along a transect from 45°N to 10°N in the North Pacific exhibit a gradual decline, and the TOC:TON ratio increases, as the water is transported northward (Fig. 2; Abell *et al.,* 2000); continuing north (north of ~30°N), the reverse pattern is observed. One intriguing observation is a significant correlation between TON concentrations and apparent oxygen utilization along the four isopycnals surfaces studied (Abell *et al.,* 2000). It was suggested that TON distributions are primarily the result of degradation of organic matter along isopycnal surfaces, although the degradation does not follow Redfield stoichiometry (Abell *et al.,* 2000).

In the Atlantic, patterns in surface DON concentrations are similar to those in the Pacific; concentrations are low at the equator and then increase to the north and south, again indicating the possibility of a meridonal flux moving away from the equator (Vidal *et al.,* 1999). Continuing further south, however, DON concentrations reach a minimum of 5 to 7 μM.

Another trend is that concentrations of DON generally increase along ocean margins. This reflects the higher concentrations of DON in estuaries and rivers, which transport DON to the coastal ocean (Table I). From the little data available, it also appears that concentrations of DON tend to decline beyond the frontal zones to the poles (Table I).

3. Vertical Profiles

Vertical profiles of DON (or TON) generally show a surface enrichment relative to concentrations deeper in the water column. This has been observed in a wide number of environments including the equatorial Pacific (Libby and Wheeler, 1997), Monterey Bay and the Bering Sea (Hansell, 1993), the Santa Monica Basin (Hansell *et al.,* 1993), the Mississippi-Atchafalaya river plume (Lopez-Veneroni and Cifuentes, 1992), the Southern Ocean (Ogawa *et al.,* 1999; Kähler *et al.,* 1997), Drake Passage (Sanders and Jickells, 2000), Georges Bank (Hopkinson

Table I

Literature Values of Concentrations of Total Dissolved Nitrogen (TDN) and Dissolved Organic Nitrogen (DON) for Oceanic, Coastal, Estuarine, and Riverine Systems

Location	Sampling date	Sample depth (m)	TDN concentration (μM)	DON concentration (μM)	DON: TDN (%)	C:N DOM Pool	Method	Reference
Oceanic—surface				5				Range in Antia *et al.*, 1991
Greenland Sea	June 1991	Upper 100	~11.7	4.3 ± 0.9	~37			Lara *et al.*, 1993
Greenland Sea	June 1991	< 100		4.6 ± 0.6			PO	Hubberten *et al.*, 1995
Bering Sea, North Pacific	June 1990	Upper 30	8.6 ± 2.9	2.5 ± 1.9	37.0 ± 37.0		HTO	Hansell, 1993
Bering Sea, North Pacific	July 1986	Upper ~250		7 to 9			HTO	Koike and Tupas, 1993
Northern North Pacific	June 1986	Upper ~100		8 to 10			HTO	Koike and Tupas, 1993
Western North Pacific	July 1986	Upper ~250		10 to 13			HTO	Koike and Tupas, 1993
Western tropical Pacific (10–20S)	March–April 1996	Upper 50		5.4 ± 0.3[a]		15.1	UV	Hansell and Feely, 2000
Western tropical Pacific (25–35S)	March–April 1996	Upper 50		4.8 ± 0.4[a]		15.5	UV	Hansell and Feely, 2000
Santa Monica Basin, Pacific	April, July, Aug 1990	Upper 100	11.9 ± 6.2	5.2 ± 1.9	57.2 ± 35.2	16.7 ± 4.6	HTO	Hansell *et al.*, 1993

Eastern N. Pacific	June 1995	Upper 85	11.1 ± 6.4	4.1 ± 0.5	48.1 ± 29.5	15.7 ± 0.6	PO	Loh and Bauer, 2000
Subtropical Pacific (5–21N)	Feb–April 1994	Upper 50	5.8 ± 1.4	5.5 ± 0.91[a]	97.9 ± 10.8	15.2 ± 3.0	UV	Hansell and Waterhouse, 1997
Equatorial Pacific (6S–2N)	Feb–April 1994	Upper 50	16.0 ± 6.1	5.0 ± 0.71[a]	36.4 ± 15.6	13.1 ± 2.3	UV	Hansell and Waterhouse, 1997
Equatorial Pacific	Sep–Nov 1992	Upper 40	13.9 ± 4.0	8.4 ± 1.0[a,b]	66.0 ± 22.0	8.0 ± 0.9	PO	Libby and Wheeler, 1997
Equatorial Pacific (6–15S)	Feb–April 1994	Upper 100	7.9 ± 3.5	5.5 ± 0.69[a]	77.2 ± 21.4	12.3 ± 1.5	UV	Hansell and Waterhouse, 1997
Subtropical Pacific (16–35S)	Feb–April 1994	Upper 150	4.8 ± 0.4	4.5 ± 0.42[a]	96.6 ± 8.9	14.8 ± 2.4	UV	Hansell and Waterhouse, 1997
Subpolar Pacific (35–64S)	Feb–April 1994	Upper 150	18.3 ± 6.8	4.3 ± 0.59[a]	28.5 ± 14.3	11.4 ± 2.2	UV	Hansell and Waterhouse, 1997
Pacific Equatorial Transition	November 1997	Upper 50	5.8 to 6.0	5.7 to 5.9[a]	98.3		UV	Abell *et al.*, 2000
Pacific Subtropical Gyre	November 1997	Upper 50	5.3 to 6.3	5.2 to 6.2[a]	98.1		UV	Abell *et al.*, 2000
Pacific Subtropical Transition	November 1997	Upper 50	4.7 to 5.5	4.5 to 5.3[a]	95.3		UV	Abell *et al.*, 2000
Equatorial Pacific (16S–1N)	November 1994	Upper 200		~3.0 to 7.0			PO	Raimbault *et al.*, 1999
Southern California Bight (offshore)	October 1992	Upper 55	9.7 ± 2.4	7.0 ± 0.4	74.9 ± 15.9		UV	Ward and Bronk, 2001

Table I (***Continued***)

Location	Sampling date	Sample depth (m)	TDN concentration (μM)	DON concentration (μM)	DON: TDN (%)	C:N DOM Pool	Method	Reference
Southern California Bight (offshore)	April 1994	Upper 43	10.8 ± 5.8	6.6 ± 1.4	74.7 ± 31.1		UV	Ward and Bronk, 2001
Southern Ocean Polar Front	Oct–Nov 1993	Upper 200		6.9 to 11.0			HTO	Kahler *et al.*, 1997
North of Antarctic Peninsula	Spring 1997	Surface		0.8 to 6.3			UV	Karl *et al.*, 1996
Pacific Subarctic Frontal	November 1997	Upper 50	5.3 to 7.9	5.1 to 5.2[a]	96.2		UV	Abell *et al.*, 2000
Southern Ocean (56S–144E)	January 1995	Upper 150	32.8 ± 2.8	6.0 ± 2.1	18.2 ± 6.0	8.1 ± 3.9	HTO	Ogawa *et al.*, 1999
Southern Ocean (60S–142E)	January 1995	Upper 150	30.5 ± 2.3	4.6 ± 0.4	15.2 ± 2.2	9.4 ± 0.9	HTO	Ogawa *et al.*, 1999
Southern Ocean (64S–141E)	January 1995	Upper 75	28.4 ± 4.0	3.2 ± 0.2	11.4 ± 1.9	14.2 ± 1.1	HTO	Ogawa *et al.*, 1999
Southern Ocean (65S–140E)	January 1995	Upper 150	32.2 ± 1.8	4.3 ± 0.3	13.3 ± 1.0	10.4 ± 0.7	HTO	Ogawa *et al.*, 1999
Southern Ocean (St. F)	December 1995	Upper 94	20.9 ± 1.1	4.2 ± 0.2	20.4 ± 1.7	12.0 ± 0.6	PO	Loh and Bauer, 2000
Ross Sea Polynya	Nov 1994 and Jan 1997	Upper 150		2.1 to 6.3		8.1 to 23.0	UV	Carlson *et al.*, 2000

Antarctic waters	December 1991	<100	3.9 ± 1.3			PO	Hubberten *et al.*, 1995
Drake Passage (61–50S)	Dec 1997–Jan 1998	Upper 50	3.1 to 7.3	~10.25		UV	Sanders and Jickells, 2000
North Atlantic (33–60N)	Summer 1996	Surface	4.4 to 7.4		.0 to 12.0	HTO	Kähler and Koeve, 2001
Arctic Ocean (shelf)	September 1994	Upper 55[c]	3.6 ± 0.7		3.4 ± 6.6	PO	Wheeler *et al.*, 1997
Arctic Ocean (slope)	September 1994	Upper 100[c]	5.2 ± 1.6		5.1 ± 4.7	PO	Wheeler *et al.*, 1997
Arctic Ocean (basin)	September 1994	Upper 100[c]	5.3 ± 1.4		6.0 ± 4.0	PO	Wheeler *et al.*, 1997
Sargasso Sea	September 1996	Surface	5.8 ± 0.8[a,b]	> 95		UV	Bates and Hansell, 1999
Sargasso Sea (BATS)	1994–1998	Surface	4.0 to 5.5	> 95	13.8 to 14.2	UV	Hansell and Carlson, 2001
Equatorial Atlantic (15–25N)	Oct–Nov 1995	Upper 100	10.9 ± 9.1	~20 to > 90		PO	Vidal *et al.*, 1999
Equatorial Atlantic (15S–15N)	Oct–Nov 1995	Upper 100	9.5 ± 4.1	70 to > 90		PO	Vidal *et al.*, 1999
Equatorial Atlantic (35–15S)	Oct–Nov 1995	Upper 100	5.2 ± 2.9	> 90		PO	Vidal *et al.*, 1999
Pacific (HMW DON >1kDa)[d]		Upper 100	1.2 ± 0.2		16.3 ± 0.6	UV	Benner *et al.*, 1997

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Table I (*Continued*)

Location	Sampling date	Sample depth (m)	TDN concentration (μM)	DON concentration (μM)	DON: TDN (%)	C:N DOM Pool	Method	Reference
Atlantic (HMW DON >1kDa)[d]		Surface		1.0		17.1	UV	Benner *et al.*, 1997
Gulf of Mexico (HMW DON >1kDa)[d]		10		1.2		17.8	UV	Benner *et al.*, 1997
		Mean ± std	**14.2 ± 9.4**	**5.8 ± 2.0**	**61.6 ± 32.9**	**13.6 ± 2.8**		
Oceanic—deep								
				3				Range in Antia *et al.*, 1991
Northeast Pacific	Oct 1986–May 1988	Upper 150	4.82[e]	4.5 ± 0.4	~92		UV	Harrison *et al.*, 1992
Greenland Sea	June 1991	>100		3.5 ± 0.8			PO	Hubberten *et al.*, 1995
Bening Sea	July 1986	500–4000		5 to 9			HTO	Koike and Tupas, 1993
Northern North Pacific	June 1986	200–4000		6 to 8			HTO	Koike and Tupas, 1993
Western North Pacific	July 1986	500–4000		6 to 12			HTO	Koike and Tupas, 1993
Santa Monica Basin	April and Aug 1990	110–800	36.7 ± 5.7	4.3 ± 1.2	11.9 ± 3.0	16.7 ± 4.5	HTO	Hansell *et al.*, 1993
Subtropical Pacific (5–21N)	Feb–April 1994	51–1000	36.9 ± 5.7	2.7 ± 0.73[a]	7.6 ± 2.5	16.8 ± 8.0	UV	Hansell and Waterhouse, 1997

Equatorial Pacific (6S–2N)	Feb–April 1994	1–1000	38.8 ± 4.1	2.6 ± 0.64[a]	6.9 ± 2.2	18.4 ± 4.6	UV	Hansell and Waterhouse, 1997
Equatorial Pacific (6–15S)	Feb–April 1994	101–3000	37.1 ± 7.1	2.9 ± 0.82[a]	8.4 ± 4.0	16.9 ± 5.2	UV	Hansell and Waterhouse, 1997
Subtropical Pacific (16–35S)	Feb–April 1994	151–3000	28.3 ± 12.2	3.0 ± 0.65[a]	14.0 ± 12.2	14.5 ± 2.7	UV	Hansell and Waterhouse, 1997
Subpolar Pacific (35–64S)	Feb–April 1994	151–3250	31.2 ± 4.7	2.8 ± 0.64[a]	9.5 ± 3.6	15.0 ± 3.6	UV	Hansell and Waterhouse, 1997
Pacific Equatorial Transition	November 1997	~205		2.8			UV	Abell *et al.*, 2000
Pacific Subtropical Gyre	November 1997	~305		2.8 to 3.7			UV	Abell *et al.*, 2000
Pacific Subtropical Transition	November 1997	~185		4.4			UV	Abell *et al.*, 2000
Pacific Subarctic Frontal	November 1997	~145		3.7			UV	Abell *et al.*, 2000
Eastern North Pacific	June 1995	100–4097	39.0 ± 5.2	2.4 ± 0.4	6.4 ± 1.6	17.3 ± 4.3	PO	Loh and Bauer, 2000
Southern Ocean Polar Front	Oct–Nov 1993	200–1500		7.9 to 9.8			HTO	Kähler *et al.*, 1997
Southern Ocean (56S–144E)	January 1995	200–3400	38.2 ± 1.8	4.6 ± 0.5	12.1 ± 1.0	9.4 ± 1.2	HTO	Ogawa *et al.*, 1999

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Table I (*Continued*)

Location	Sampling date	Sample depth (m)	TDN concentration (μM)	DON concentration (μM)	DON: TDN (%)	C:N DOM Pool	Method	Reference
Southern Ocean (60S–142E)	January 1995	200–4150	35.8 ± 2.1	3.4 ± 0.8	9.3 ± 1.8	13.5 ± 3.1	HTO	Ogawa *et al.*, 1999
Southern Ocean (64S–141E)	January 1995	100–3450	34.7 ± 0.8	3.1 ± 0.8	8.8 ± 2.2	14.3 ± 4.5	HTO	Ogawa *et al.*, 1999
Southern Ocean (65S–140E)	January 1995	200–1480	36.2 ± 0.4	5.1 ± 1.0	14.2 ± 2.5	8.7 ± 1.0	HTO	Ogawa *et al.*, 1999
Southern Ocean (St. F)	December 1995	142–5408	32.2 ± 5.4	3.5 ± 0.6	11.0 ± 2.0	12.5 ± 2.0	PO	Loh and Bauer, 2000
Ross Sea Polynya	Nov 1994 and Jan 1997	150–600		2.4 ± 0.3		14.1 to 20.1	UV	Carlson *et al.*, 2000
Antarctic waters	December 1991	>100		3.0 ± 1.1			PO	Hubberten *et al.*, 1995
Sargasso Sea (BATS)	1994–1998	250–1000		2.1 to 5.0		13.4 to 14.7	UV	Hansell and Carlson, 2001
Sargasso Sea (BATS)	1994–1998	1000–4000		3.1 ± 0.4		13.9 to 14.5	UV	Hansell and Carlson, 2001
Drake Passage (61–50S)	Dec 1997–Jan 1998	Upper 50		1.4 to 2.9			UV	Sanders and Jickells, 2000
Equatorial Atlantic (15–25N)	Oct–Nov 1995	110–1000		4.9 ± 4.1	~20 to 40		PO	Vidal *et al.*, 1999
Equatorial Atlantic (15S–15N)	Oct–Nov 1995	110–1000		9.8 ± 3.8	~20 to >90		PO	Vidal *et al.*, 1999
Equatorial Atlantic (35–15S)	Oct–Nov 1995	110–1000		4.4 ± 2.5	~20 to >90		PO	Vidal *et al.*, 1999

Pacific (HMW DON> 1kDa)[d]		200–400		0.54 ± 0.15		18.2 ± 2.1	UV	Benner *et al.*, 1997
Atlantic HMW DON> 1kDa)[d]		900–2400		0.51 ± 0.53		5.6 to 18.1	UV	Benner *et al.*, 1997
Gulf of Mexico (HMW DON > 1kDa)[d]		750		0.56		16.9	UV	Benner *et al.*, 1997
		Mean ± std	**33.1 ± 9.1**	**4.3 ± 2.1**	**9.9 ± 2.6**	**14.7 ± 2.8**		
Coastal/Continental shelf								
				3 to 10				Range in Antia *et al.*, 1991
Gulf of Mexico (LA–TX coast)	July, Apr, May, Oct 1990	Surface		1.9 to 52.5			HTO	Lopez-Vancroni and Cifuentes, 1994
Gulf of Riga, Baltic Sea	April 1995	Surface	26.7[f]	18.0 to 19.0	67.0 to 71.0		PO	Tamminen and Seppälä, 1999
Gulf of Riga, Baltic Sea	August 1993	Surface	29.4[f]	26.4	~90		PO	Tamminen and Seppälä, 1999
Gulf of Riga, Baltic Sea	May–Nov 1996	2.5	15.5 to 40.2	9.0 to 23.0[g]			HTO	Jørgensen *et al.*, 1999
Gulf of Riga, Baltic Sea	May–Nov 1996	30.0	25.0 to 30.5	5.4 to 21.0[g]			HTO	Jørgensen *et al.*, 1999
Georges Bank	April 1993	Surface		4.8 to 5.4	Up to 58%	11.0 to 15.0	UV	Hopkinson *et al.*, 1997
Georges Bank	April 1993	200–1500		2.5 to 3.4	As low as 9%	14.7 to 22.8	UV	Hopkinson *et al.*, 1997

(*Continues*)

Table I (*Continued*)

	Sampling date	Sample depth (m)	TDN concentration (μM)	DON concentration (μM)	DON: TDN (%)	C:N DOM Pool	Method	Reference
Middle Atlantic Bight	September 1996	Surface		7.4 ± 1.1[a,b]			UV	Bates and Hansell, 1999
Monterey Bay	August 1990	Upper 100	18.5 ± 6.1	1.9 ± 1.6	15.0 ± 16.0		HTO	Hansell, 1993
Monterey Bay	August 1990	200–400	33.9 ± 2.8	1.1 ± 1.4	3.5 ± 4.4		HTO	Hansell, 1993
Monterey Bay	March 1993	Upper 20	6.5 ± 1.9	5.2 ± 1.8	79.0 ± 12.0		PO	Bronk and Ward, 1999
Monterey Bay	Sept 1993	Upper 40	6.5 ± 1.2	4.8 ± 0.5	75.0 ± 10.0		PO	Bronk and Ward, 1999
Northeast Greenland Shelf	May–August 1993	Upper 70	7.2	5.9[b]	81.9	19.3	PO	Daly *et al.*, 1999
Akkeshi Bay, Japan	August 1998	Surface	7.7 ± 2.3	6.7 ± 1.0	89.7 ± 15.3		PO	Hasegawa *et al.*, 2000c
Japanese (2) Bays	June, Sept, Oct	Surface	12.0 ± 1.6	8.7 ± 1.6	72.4 ± 4.4	21.5 ± 6.6	HTO	Tupas and Koike, 1990
Southern California Bight (nearshore)	October 1992	Upper 55	10.2 ± 2.5	7.7 ± 1.3	77.0 ± 14.2		UV	Ward and Bronk, 2001
		Mean ± std	**17.8 ± 10.6**	**9.9 ± 8.1**	**65.3 ± 30.4**	**17.7 ± 4.3**		

Estuarine								
				5 to 150				Range in Antia *et al.*, 1991
Shinnecock Bay, NY	July–Aug 1995	Surface	2.0 to 4.9	0.6 to 4.3[i]	30.1 to 88.9		PO	Lomas *et al.*, 1996
Shinnecock Bay, NY	July 1995	Surface	3.2 to 4.8	2.7 to 4.3[i]	84.4 to 90.4		PO	Berg *et al.*, 1997
Waquoit Bay, MA	Late summer/fall 1995	Surface	140	40.0	28.6	15.5	NP	Hopkinson *et al.*, 1998
Chesapeake Bay, mesohaline	May 1988	Surface	31.0 ± 6.6	7.1 ± 7.5	37.0 ± 14.8	36.8 ± 20.5	PO	Bronk *et al.*, 1998
Chesapeake Bay, mesohaline	August 1988	Surface	47.4 ± 3.9	41.6 ± 1.9	88.0 ± 4.1	8.8 ± 0.4	PO	Bronk *et al.*, 1998
Chesapeake Bay, mesohaline	October 1988	Surface	22.7 ± 5.8	15.4 ± 6.3	64.8 ± 14.4	17.7 ± 16.1	PO	Bronk *et al.*, 1998
Chesapeake Bay, mesohaline	May 1990	Surface	42.5 ± 3.7	22.3 ± 9.2	51.3 ± 19.2		PO	Bronk and Glibert, 1993a
Chesapeake Bay, mesohaline	August 1990	Surface	23.1 ± 1.7	22.2 ± 1.6	96.1 ± 1.7		PO	Bronk and Glibert, 1993a
Chesapeake Bay, mouth	September 1996	Surface		16.3 ± 5.5[b]			UV	Bates and Hansell, 1999
Apalachicola Bay	May 1994–May 1996	Surface	23	14.8 ± 1.0	61.0		PO	Mortazavi *et al.*, 2000
Delaware Estuary	Jan and April 1988	Surface		40.8 ± 29.3			PO	Keil and Kirchman, 1991b

Table I (*Continued*)

Location	Sampling date	Sample depth (m)	TDN concentration (μM)	DON concentration (μM)	DON: TDN (%)	C:N DOM Pool	Method	Reference
Elbe Estuary	Aug–Oct 1997		72.2 ± 17.6	65.0 ± 12.2	91.4 ± 11.0	6.0 ± 1.0	PO	Kerner and Spitzy, 2001
North Inlet, SC	Monthly 1994–1996	Surface	19.4 to 35.3	18.0 to 30.8	87.3 to 92.7		NP	Lewitus *et al.*, 2000
Lake Kinneret, Israel (freshwater)	Aug 1996–Sept 1997	Surface	24.9 ± 6.8	18.3 ± 3.3	71.6 ± 29.5		PO	Berman *et al.*, 1999
Tomales Bay	June 1987–July 1989	Surface		5.8 to 12.6			UV	Smith *et al.*, 1991
		Mean ± std	**38.5 ± 37.0**	**22.5 ± 17.3**	**68.9 ± 22.4**	**21.1 ± 14.3**		
Selected Rivers								
Russian rivers (7) draining into Arctic				27.0 ± 5.0		20.5 ± 2.6	NP	Gordeev *et al.*, 1996; In Wheeler *et al.*, 1997
Rivers (5) entering the Baltic Sea	June–July 1999	Surface	48.9 ± 41.9	29.8 ± 14.8	73.8 ± 19.0	30.7 ± 12.1	HTO	Stepanauskas *et al.*, in press
Susquehanna River, MD	Late summer/fall 1995	Surface	116	23.0	20	9	NP	Hopkinson *et al.*, 1998
Satilla River, GA	Late summer/fall 1995	Surface	62.6	59.0	94	29	NP	Hopkinson *et al.*, 1998

Parker River, MA	Late summer/fall 1995	Surface	37	26.0	70		NP	Hopkinson *et al.*, 1998
Delaware River	April and June 1992	Surface		29.7 ± 23.7			HTO	Seitzinger and Sanderson, 1997
Hudson River	April 1992	Surface		33.5			HTO	Seitzinger and Sanderson, 1997
Rivers (17) in USA and Europe		Surface				7.1 ± 19.8	NP	Table in Seitzinger and Sanderson, 1997
Choptank River (subestuary of CBay)	August 1990	Surface	41.3	26.9	65		PO	Bronk and Glibert, 1993b
Georgia and South Carolina Rivers (8)[j]	Annual averages 1974–1993	Surface		35.9 ± 10.7	72.0 ± 15.8	22.0 ± 8.6	NP	Alberts and Takács, 1999
Streams (2) in Sweden[k]	February–May	Surface		24.3 ± 7.4		37.9 to 64.9	HTO	Stepanauskas *et al.*, 2000
Wetland (3) in Sweden (bulk DON)[l]	Winter, summer, fall samples	Surface		90.0 ± 68.0	49.0 ± 25.0	10 to 42	PO	Stepanauskas *et al.*, 1999a

(*Continues*)

Table I (*Continued*)

Location	Sampling date	Sample depth (m)	TDN concentration (μM)	DON concentration (μM)	DON: TDN (%)	C:N DOM Pool	Method	Reference
Lagunitas Creek (flows to Tomales Bay)	June 1987–July 1989	Surface		3.9 to 17.9			UV	Smith *et al.*, 1991
		Mean ± std	**61.2 ± 32.2**	**34.7 ± 20.7**	**60.1 ± 23.5**	**25.7 ± 12.5**		

Note. Data were taken from tables, estimated from graphs, or obtained from the authors. Methods used were the persulfate oxidation (PO), ultraviolet oxidation (UV), and high-temperature oxidation (HTO). NP: not presented. Means were calculated for individual sections using the average values of any ranges presented; Antia *et al.* (1991) data, high-molecular-weight (HMW) data, and approximations are not included in the means. Data are mean ± standard deviation. Concentrations in the surface ocean are separated from concentrations in the deep ocean; admittedly, this was often a judgement call based on hydrographic and/or inorganic nutrient data as available.

[a] Samples were not filtered so data represent TON; it was assumed that <10% N was particulate.

[b] Ammonium is included in the TON concentration.

[c] Data were converted from g m^{-2}; mean and std at stations within each area are reported.

[d] HMW DON only (>1 kDa).

[e] Estimated from integrated values throughout the upper 150 m.

[f] Sum of the average DON, nitrate, and ammonium concentrations.

[g] Jørgensen *et al.* (1999) listed urea separately; it was added back into the DON pool.

[h] Median values

[i] Measured during a bloom of *Aureococcus anophagefferens*.

[j] Averages for eight rivers (Altamaha, Black, Edsto, Ogeechee, Eden and Oliver, Peedee, Satilla, Savannah, and St. Marys).

[k] The two streams were Lillån and Stridbäcken.

[l] The three wetlands were Amboke, Isgrannatorp, and Vomb.

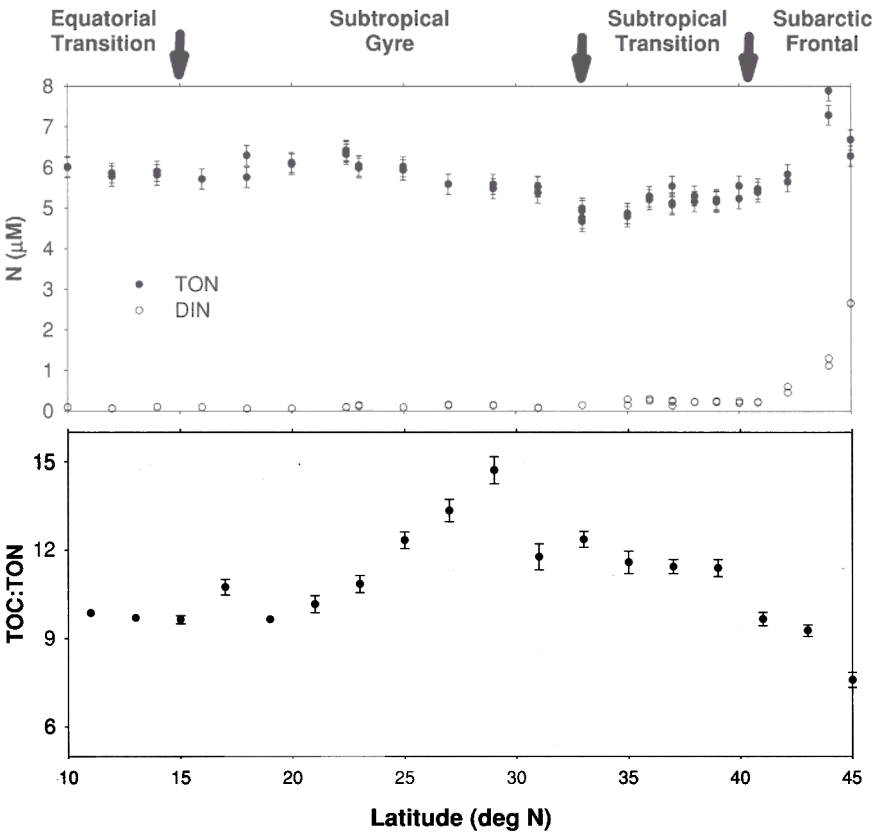

Figure 2 (Top) Concentrations of dissolved inorganic nitrogen (DIN) and total organic N (TON) and (Bottom) the total organic carbon (TOC) to TON ratio along a transect in the North Pacific (modified with permission from Abell *et al.*, 2000).

et al., 1997), the oligotrophic North Pacific (Maita and Yanada, 1990; Harrison *et al.*, 1992; Loh and Bauer, 2000), along a transect from Bermuda to Chesapeake Bay (Bates and Hansell, 1999), the Arctic (Wheeler *et al.*, 1997), the North Pacific (Abell *et al.*, 2000), and the equatorial Atlantic (Vidal *et al.*, 1999). In the Southern California Bight, DON concentrations are generally uniform in the surface layer but become more variable and often increase within the nitracline (Hansell *et al.*, 1993).

Elevated DON concentrations at the surface suggest that DON can be exported to depth (Toggweiler, 1989; Hopkinson *et al.*, 1997). DON export, and subsequent ammonification and nitrification, is estimated to supply 19% of remineralized NO_3^- at depth off Georges Bank (Hopkinson *et al.*, 1997); 15% in the Bering Sea

(Koike and Tupas, 1993), 10% at various sites in the Pacific (Jackson and Williams, 1985), and 25% in the North Pacific (Maita and Yanada, 1990). Vidal *et al.* (1999) calculated vertical gradient-driven fluxes of DON in the equatorial Atlantic using vertical profiles of DON concentrations and estimates of a vertical eddy diffusion coefficient. They found that surface DON did appear to be transported to depth at times, however, the direction of the dominant flux varied along the north–south transect.

The DOC pool is commonly envisioned as being composed of a labile, semilabile, and refractory component based on vertical profile data (Kirchman *et al.*, 1993; Carlson and Ducklow, 1995; see Carlson, Chapter 4). In a similar fashion, the refractory TON pool is estimated at 4 μM in equatorial Pacific waters, based on TON concentrations in the deep ocean (Libby and Wheeler, 1997). Assuming this recalcitrant fraction is present throughout the water column, refractory TON is $\sim$ 60% of the TON in the upper 40 m; the C:N of the refractory TON is 9.9. The semilabile pool in the upper 40 m ranges from 3.4 to 5.8 μM TON and has a lower C:N ratio (5.1 to 8.5) than the refractory pool.

4. Seasonal Variations

The question of whether DON concentrations exhibit a seasonal pattern is an open one. There are areas where no seasonal pattern is indicated, including the Santa Monica Basin (Hansell *et al.*, 1993) and at the Bermuda Atlantic Time Series (BATS) site in the Sargasso Sea (Hansell and Carlson, 2001). In contrast, some studies suggest that DON increases in late spring and summer, including work in the Gulf of Mexico (Lopez-Veneroni and Cifuentes, 1994), Chesapeake Bay (Bronk *et al.*, 1998), North Inlet, SC (Lewitus *et al*, 2000), and a suite of rivers draining into the Baltic Sea (Stepanauskas *et al.*, in press). The most compelling evidence for a seasonal cycle is presented by Butler *et al.* (1979), who conducted an 11-year study of DON concentrations in the English Channel. They documented a steady increase in DON concentrations from January through August and then a steady decline from August to December. The clear seasonal pattern observed by Butler *et al.* (1979) highlights the importance of long-term data sets in defining these types of patterns. In general, oligotrophic environments do not show seasonality in DON, as would be anticipated given the scant supply of N.

5. Link between DON Distributions and Inorganic N

There have been a number of observations linking decreases in NO_3^- or elevations in N_2 fixation and accumulations of DON in near surface waters. In the Pacific, an increase in DON/TON concentrations and a concomitant decrease in NO_3^- concentrations as one moves away from the equator is shown by a number of studies (Libby and Wheeler, 1997; Hansell and Waterhouse, 1997; Raimbault

et al., 1999). This pattern suggests that new TON production is fueled by high equatorial new production and subsequent organic N release. An estimated 37 ± 14 and 81 ± 54% of net NO_3^- depletion accumulates as DON during the movement of upwelled equatorial water to the north and south, respectively (Libby and Wheeler, 1997). In the Ross Sea, approximately 10% of the net NO_3^- draw down in surface waters accumulates as DON (Carlson *et al.*, 2000). Similar relationships between NO_3^- consumption or disappearance and TON/DON production have been observed in the English Channel (Butler *et al.*, 1979), in the subarctic Pacific (Maita and Yanada, 1990), in Chesapeake Bay (Bronk *et al.*, 1998), and in a coastal pond (Collos *et al.*, 1996).

In the Mississippi River plume, Benner *et al.* (1992a) used $\delta^{15}N$ data to demonstrate the conversion of NO_3^- to high-molecular-weight (HMW) DON, isolated using a >1-kDa ultrafiltration unit. The DON produced is likely the result of phytoplankton uptake and subsequent conversion to DON that is then released. The $\delta^{15}N$ of the DOM pool is ~3‰ at both the river and Gulf endpoints. At intermediate salinities, however, the $\delta^{15}N$ of the DOM pool increases to ~9‰. The likely cause for this increase is the conversion of NO_3^- to DON; the NO_3^- in this region has a $\delta^{15}N$ of ~10‰.

In the Pacific, Atlantic, and Gulf of Mexico, the $\delta^{15}N$ of the HMW DON ranges from a mean of 7.9 ± 0.7 in the Pacific to 9.9 ± 0.5‰ in the Gulf of Mexico (Benner *et al.*, 1997). There is no relationship between the concentration of HMW DON and the $\delta^{15}N$ of the material, suggesting that the isotopic signature reflects the source of the N, not isotopic fractionation during decomposition. The lowest $\delta^{15}N$ values (6.6‰) are observed in the surface waters at the BATS site in the Sargasso Sea, and are likely the result of the use of isotopically light new NO_3^-, which has a $\delta^{15}N$ of ~3.5‰ in the region (Altabet, 1988). These low values can also indicate the addition of isotopically depleted N from N_2 fixation (atmospheric N_2 is ~0‰) and then subsequent release of DON from N_2 fixers such as *Trichodesmium* (see Section III. A.2). In the Pacific, the lightest $\delta^{15}N$ values are measured at the equator where new NO_3^- is upwelled (Benner, *et al.*, 1997). The $\delta^{15}N$ of DON increases to the north and south of the equator, suggesting that the DOM is being produced biologically during meridonal transport as described above.

In the reverse of the NO_3^- to DON conversion discussed above, Kerner and Spitzy (2001) documented that between 75 and 100% of the LMW DON and NH_4^+ is consumed and converted to NO_3^- in the Elbe estuary via nitrification. This is the analogous process that produces the inverse relationship between DON and NO_3^- concentrations when moving from the surface into the deep ocean (Lara *et al.*, 1993).

Finally, there are examples where increases in DON concentrations do not correlate well with decreases in NO_3^-. For example, along the NW African coast, Vidal *et al.* (1999) found that the downward flux of DON exceeds the upward supply of NO_3^-, indicating an additional supply of N from meridonal transport

(Libby and Wheeler, 1997) or perhaps atmospheric inputs (Cornell *et al.*, 1995). At the station with the highest DON flux, in excess of NO_3^- influx, there were significant concentrations of *Trichodesmium*.

C. Chemical Composition of the DON Pool

DON is a heterogeneous mixture of compounds composed of biologically labile moieties, which likely turn over on the order of days to weeks, and refractory components, which persist for months to hundreds of years, and comprise the bulk of the DON measured in the ambient DON pool (see Section V). The more refractory forms are quantitatively dominant with respect to ambient concentrations, but their importance as a potential N source is far exceeded by the smaller, more labile compounds. A large number of compounds have been identified within the DON pool, including urea, dissolved combined amino acids (DCAAs), dissolved free amino acids (DFAA), humic and fulvic substances, and nucleic acids. The remainder of the DON pool is a heterogeneous mixture of unidentified compounds. In this section, individual organic compounds are discussed including measurement techniques and a review of recently measured concentrations, followed by a discussion of recent efforts to chemically characterize the HMW fraction and research priorities for the future.

1. Urea

Urea is a low-molecular-weight (LMW) organic compound, which is a product of organic matter decomposition and organismal excretion. The two methods commonly used to measure urea concentrations are the urease method, which involves enzymatic hydrolysis of urea to carbon dioxide and ammonia (McCarthy, 1970), and the direct colorimetric measurement of urea using diacetyl monoxime (Price and Harrison, 1987). Note that urea is occasionally treated as an inorganic N form (Capone, 2000; Jørgensen *et al.*, 1999). The rationale for this practice is that urea is used primarily as a N source and not as a form of energy. Out of solidarity with poor researchers assembling large tables, I suggest this practice be discontinued, because it confuses the calculation of DON concentrations. Urea contains C, as well as N, and so should sit squarely in the DON pool.

Urea concentrations range widely from 0 to 13 μM in the studies surveyed (Table II). In general, urea concentrations in open ocean systems tend to be very low (<0.3 μM), coastal systems tend to be slightly higher (<0.7 μM, Metzler *et al.*, 2000), and estuarine and riverine systems are higher still (<3 μM). The highest urea concentrations were measured in polar regions affected by sea ice formation (Conover *et al.*, 1999). In the studies where urea concentrations are presented as part of the total DON pool, urea averages 5.2 $\pm$ 3.4% (Table II).

2. DCAA

The chemical structure of DCAA is largely unknown but can include a suite of bound amino acids including proteins and oligopeptides (Lee and Bada, 1977), amino acids bound to humic or fulvic materials (Lytle and Perdue, 1981; Poutanen and Morris, 1985), and amino acids adsorbed to clays or other materials (Hedges and Hare, 1987). Billen (1991) provided indirect evidence that protein is the dominant form of DCAA in eutrophic waters. Though protein may be a major component of DCAA, abiotic transformations of protein can produce recalcitrant DOM, which is not recognizable as protein in routine chemical analyses, via such processes as glucosylation or the Maillard reaction (Hedges, 1988; see the end of this section).

Concentrations of DCAA are typically measured using HPLC after liquid hydrolysis with 6 N HCl at 110°C for 20–24 h (Parsons *et al.,* 1984). A quicker vapor phase hydrolysis technique was introduced by Tsugita *et al.* (1987). DCAA concentrations measured with the vapor phase method were found to be 1.5 ± 0.4 times higher than those found with the traditional hydrolysis method (Keil and Kirchman, 1991b).

Concentrations of DCAA often constitute the largest identifiable pool of DON in the ocean (Sharp, 1983). In the studies surveyed here, DCAA concentrations range from 0.15 to 4.20 μM and represent $7.2 \pm 4.3\%$ of total DON (Table II). DCAA are present in at least three forms (Keil and Kirchman, 1993). First, it can exist as protein similar to that freshly extracted from phytoplankton (<10% of the total DCAA); this material appears to be rapidly assimilated by bacteria with turnover times of hours to days. Second, it can exist as protein kinetically similar to abiotically glucosylated protein (~50% of the DCAA pool); this material appears to turn over much slower. Third, it can exist as nonproteinaceous DCAA that can contribute up to 50% of the DCAA pool; this material is resistant to standard liquid hydrolysis and likely represents bound or sorbed amino acids with an unknown turnover time. Consistent with this scenario, the proportion of DCAA identifiable as protein in the northern Sargasso Sea ranges from 40 to 100% in surface waters but only 20 to 50% in deeper waters (Keil and Kirchman, 1999).

Depth profiles suggest that levels of dissolved proteins, measured with tangential flow ultrafiltration and gel electrophoresis, are low in the surface and higher below the euphotic zone; the electrophoretic technique as applied, however, is not quantitative (Tanoue *et al.,* 1995, 1996). One protein (48 kDa) is present at all depths examined, and the amino acid sequence indicates that it is a homolog of porin P found in Gram-negative bacteria (see Section II.C.6); porin P specifically facilitates P utilization and is induced by P limitation. In general, porins are very resistant to breakdown by proteases (Cowan *et al.,* 1992), which likely explains why they are so prevalent in the water column. The electrophoretograms of protein dissolved in seawater are very different from the protein in the particulate fraction

Table II

Literature Values of Concentrations of Dissolved Organic Compounds in Aquatic Systems

Location	Sampling date	Sampling depth (m)	Compound concentration (μM)	% DON Pool	Method	Reference
Urea						
			0 to 23			Range in Antia *et al.*, 1991[a]
Gulf of Riga, Baltic Sea	May–Nov 1996	3 and 30	0.40 to 3.20			Jørgensen *et al.*, 1999
Straits of Georgia, Canada	July–Aug 1984	Upper 15	0.17 to 0.72		Monoxime	Cochlan *et al.*, 1991
North Sea	March–April 1994	10	0.04 ± 0.03		Monoxime	Riegman *et al.*, 1998
North Sea	July–Aug 1994	10 and 40	0.14 ± 0.07		Monoxime	Riegman and Noordeloos, 1998
Resolute Passage	Feb–Oct 1993	Upper 100	0.00 to 2.28		Urease	Conover *et al.*, 1999
Allen Bay, Resolute Passage	November 1993	Upper 75	0.12 to 13.03		Urease	Conover *et al.*, 1999
North of Antarctic Peninsula	November 1992	Surface	0.2 to 0.7		NP	Bury *et al.*, 1995
Bellingshausen Sea	Nov–Dec 1992	Upper 100	0.20 to 2.28[b]		Monoxime	Waldron *et al.*, 1995
Brazilian coast—oceanic	March 1994	Upper 15	< 0.03 to 0.26		NP	Metzler *et al.*, 2000
Brazilian coast—coastal	December 1995	Upper 4	0.53 to 0.67		NP	Metzler *et al.*, 2000
Chesapeake Bay plume	Feb, June, Aug 1985, Apr 1986	Surface	0.04 to 1.41		Urease	Glibert *et al.*, 1991
Chesapeake Bay, mesohaline	May, Aug, Oct 1988	Surface	0.49 ± 0.28	2.2 ± 2.4	Urease	Bronk *et al.*, 1998
Chesapeake Bay, mesohaline	August 1990	Surface	0.26 ± 0.08		Urease	Bronk and Glibert, 1993a
Chesapeake Bay	1973, 1988–1998		0.48 to 0.91	0.5 to 4.7		Lomas *et al.*, in press
Chesapeake Bay	1988–1998		0.51 to 1.49			Lomas *et al.*, in press
Shinnecock Bay, NY	July–Aug 1995		0.04 to 0.48[c]	0.9 to 16.9		Lomas *et al.*, 1996

Shinnecock, Bay, NY	July 1995	Surface	0.04 to 0.16[c]	0.9 to 5.9	Urease	Berg *et al.*, 1997
Rivers (5) entering the Baltic Sea	June–July 1999	Surface	2.79 ± 1.53	10.4 ± 4.4	Monoxime	Stepanauskas *et al.*, in press
Streams (2) in Sweden[d]	February–May	Surface	0.56 ± 0.80	2.3 ± 2.6	Monoxime	Stepanauskas *et al.*, 2000
Lake Kinneret, Israel (freshwater)	Jan–Sept 1997	Surface	1.25 ± 1.59	6.9 ± 8.4	Urease	Berman *et al.*, 1999
			Mean ± std	**5.2 ± 3.4**		
Dissolved combined amino acids						
Gulf of Riga, Baltic Sea	May–Nov 1996	3 and 30	0.55 to 4.20	0.6 to 4.2	LH-HPLC	Jørgensen *et al.*, 1999
Subarctic Pacific (Stn. P)	September 1987	0–80	0.43 ± 0.06		VPH-HPLC	Keil and Kirchman, 1991b
Japanese (2) Bays	June, Sept, Oct	Surface	0.64 ± 0.45	8.2 ± 7.3	LH-HPLC	Tupas and Koike, 1990
Northern Sargasso Sea	July 1990, Feb 1991	Upper 100	0.60 to 0.81		VPH-HPLC	Keil and Kirchman, 1999
Northern Sargasso Sea	July 1990, Feb 1991	100–3000	0.15 to 0.55		VPH-HPLC	Keil and Kirchman, 1999
Delaware Estuary	January and April 1988	Surface	3.74 ± 1.68	12.6 ± 7.5	VPH-HPLC	Keil and Kirchman, 1991b
Rivers (5) entering the Baltic Sea	June–July 1999	Surface	2.21 ± 1.00	8.3 ± 3.1	LH-HPLC	Stepanauskas *et al.*, in press
Streams (2) in Sweden[d]	February–May	Surface	1.50 ± 0.67	5.7 ± 1.9	LH-HPLC	Stepanauskas *et al.*, 2000
			Mean ± std	**7.2 ± 4.3**		
Dissolved free amino acids/DPA						
Amino acids in general			< 0.01 to 69			Range in Antia *et al.*, 1991[a]
Gulf of Riga, Baltic Sea	May–Nov 1996	2.5 and 30	0.04 to 0.35	0.5 to 9.1	HPLC	Jørgensen *et al.*, 1999
Northern North Sea	March–April 1976	Upper 145	0.10 to 0.30		HPLC	Hammer and Kattner, 1986
Greenland Sea	June 1991	<100	0.50 ± 0.14	11.0 ± 3.0	HPLC	Hubberten *et al.*, 1995
Greenland Sea	June 1991	>100	0.28 ± 0.17	8.0 ± 3.0	HPLC	Hubberten *et al.*, 1995
Subarctic Pacific (Stn. P)	September 1987	0–80	0.08 ± 0.03		HPLC	Keil and Kirchman, 1991b
Japanese (2) Bays	June, Sept, Oct	Surface	0.17 ± 0.09	1.9 ± 0.8	HPLC	Tupes and Koike, 1990
North Atlantic	May 1989	Upper 50	~0.05		HPLC	Kirchman *et al.*, 1994
North Atlantic	May 1989	>50	~0.005		HPLC	Kirchman *et al.*, 1994

(*Continues*)

Table II (*Continued*)

Location	Sampling date	Sampling depth (m)	Compound concentration(μM)	% DON Pool	Method	Reference
Northern Sargasso Sea		Upper 100	0.003 to 0.009		HPLC	Keil and Kirchman, 1999
Northern Sargasso Sea		100–3000	0.001 to 0.004		HPLC	Keil and Kirchman, 1999
Central Arctic		Upper 50	0.18 to 0.27		HPLC	Rich *et al.*, 1997
Antarctic waters		<100	0.44 ± 0.16	12.0 ± 3.0	HPLC	Hubberten *et al.*, 1995
Antarctic waters		>100	0.28 ± 0.04	11.0 ± 3.0	HPLC	Hubberten *et al.*, 1995
Chesapeake Bay Plume		Surface	0.003 to 0.074		HPLC	Furhman, 1990
Hudson River Plume		Surface	0.002 to 0.016		HPLC	Furhman, 1990
Chesapeake Bay, mesohaline		Surface	0.30 ± 0.26	1.7 ± 2.1	F	Bronk *et al.*, 1998
Chesapeake Bay, mesohaline	May 1990	Surface	0.47 ± 0.15		F	Bronk and Glibert, 1993a
Delaware Estuary	October 1993	Surface	0.30 to 0.70		HPLC	Middelboe *et al.*, 1995
Thames Estuary	February 1999	Surface	0.40 ± 0.10		F	Middelburg and Nieuwenhuize, 2000
Santa Rosa Sound, FL		Surface	0.2		HPLC	Jørgensen *et al.*, 1993
Flax Pond, NY		Surface	0.18 to 0.22		HPLC	Jørgensen *et al.*, 1993
Rivers (5) entering the Baltic Sea	June–July 1999	Surface	0.30 ± 0.26	1.1 ± 0.7	HPLC	Stepanauskas *et al.*, in press
Streams (2) in Sweden[d]	February–May	Surface	0.30 ± 0.21	1.2 ± 1.3	HPLC	Stepanauskas *et al.*, 2000
			Mean ± std	**5.9 ± 4.6**		
Nucleic acids—DNA						
Oceanic			0.20 to 4.10[e]			Range in Karl and Bailiff, 1989
Coastal/estuarine			0.05 to 80.6[e]			Range in Karl and Bailiff, 1989
Tokyo Bay	Apr, May, Sept, Nov 1983, May 1984	Surface	11.9 ± 8.7[e]			Sakano and Kamatani, 1992
Gulf of Trieste	October 1987	NP	2 to 7[f]			Turk *et al.*, 1992
Baltic Sea	July 1988	NP	17.1 ± 12.7[f]			Turk *et al.*, 1992
Scripps Pier, CA	NP	0–50	1.4 to 2.2[f]			Turk *et al.*, 1992

Santa Rosa Sound, FL		Surface	3.7[e]			Jørgensen *et al.*, 1993
Flax Pond, NY		Surface	5 to 7[e]			Jørgensen *et al.*, 1993
Nucleic acids—RNA						
			0.5 to 1.6[f]			Range in Antia *et al.*, 1991[a]
Oceanic			4.0 to 13.9[e]			Range in Karl and Bailiff, 1989
Coastal/estuarine			6.7 to 193[e]			Range in Karl and Bailiff, 1989
Tokyo Bay	Apr, May, Sept, Nov 1983, May 1984	Surface	11.6 ± 8.2[e]			Sakano and Kamatani, 1992
Methylamines						
Flax Pond, NY (mono-)		Surface	0.050			Jørgensen *et al.*, 1993
Flax Pond, NY (di-)		Surface	0.185			Jørgensen *et al.*, 1993
Flax Pond, NY (tri-)		Surface	0.035			Jørgensen *et al.*, 1993
Irish Sea (mono-)			0.000 to 0.619			Abdul-Rashid, 1990[g]
Irish Sea (di-)			0.000 to 0.100			Abdul-Rashid, 1990[g]
Irish Sea (tri-)			0.000 to 0.004			Abdul-Rashid, 1990[g]
Mediterranean Sea (mono-)			0.008 to 0.018		FIGD-IC	Gibb *et al.*, 1999
Mediterranean Sea (di-)			4.6×10^{-3} to 0.012		FIGD-IC	Gibb *et al.*, 1999
Mediterranean Sea (tri-)			1.4×10^{-3} to 0.010		FIGD-IC	Gibb *et al.*, 1999
Arabian Sea (mono-)	Aug–Nov 1994	Up to 4000	0.006 to 0.022	< 1	FIGD-IC	Gibb *et al.*, 1999
Arabian Sea (di-)	Aug–Nov 1994	Up to 4000	2.8×10^{-3} to 4.2×10^{-3}	< 1	FIGD-IC	Gibb *et al.*, 1999
Arabian Sea (tri-)	Aug–Nov 1994	Up to 4000	0.05×10^{-3} to 0.45×10^{-3}	< 1	FIGD-IC	Gibb *et al.*, 1999

Note. Data were taken from tables, estimated from graphs, or obtained from the authors. Methods are liquid hydrolysis followed by high-pressure liquid chromatography (LH-HPLC), vapor phase HPLC (VP-HPLC), fluorometry (F), and flow injection gas diffusion coupled to ion chromatography (FIGD-IC). NP: not presented. Data are mean ± standard deviation.

[a] Data from lakes, estuaries, and marine systems.

[b] Converted from urea concentrations integrated throughout the euphotic zone.

[c] Measured during a bloom of *Aureococcus anophagefferens*.

[d] The two streams were Lillån and Stridbäcken.

[e] Units for DNA are $\mu g\ L^{-1}$.

[f] Units for DNA are $\mu mol\ L^{-1}$.

[g] Data from Gibb *et al.* (1999).

or in bacteria, suggesting that the proteins isolated in seawater do not originate directly from living organisms (Tanoue *et al.,* 1996).

Another important component of the DON pool are the proteolytic enzymes, which are well characterized for a number of bacterial sources (see Chrost, 1991; Hoffman and Decho, 2000). Much less is known about proteolytic enzymes associated with microalgae, though recent work has investigated cell-associated proteases in a number of phytoplankton (Hooper and Hughes, 1992; Berges and Falkowski, 1996) and cyanobacteria (Martinez and Azam, 1993).

One interesting area of ongoing research is determining why some organic compounds persist in the ocean for hundreds to thousands of years. Specifically, what is the mechanism that transforms a labile compound to a refractory one (see Section IV.C.3 and Carlson, Chapter 4, and Benner, Chapter 3)? Bacterial assimilation of protein decreases when the protein is aged for as little as 6 h (Keil and Kirchman, 1994). When the protein is aged for 40 days, it degrades fourfold more slowly than unaged protein. No aging affect is observed in organic-free water, indicating that organic–organic interactions produce the refractory protein. Keil and Kirchman (1994) demonstrate that protein comprises 1–10% of the DCAA pool, that glucosylated protein comprises 5–66%, and that glucosylation inhibits bacterial protein degradation.

3. DFAA

Concentrations of free amino acids are reported either as DFAA (measured with HPLC; Mopper and Lindroth, 1982) or dissolved primary amines (DPA, estimated fluorometrically; Parsons *et al.,* 1984); in waters with low NH_4^+ concentrations, the two measurements are generally equal (Kirchman *et al.,* 1989). DFAA concentrations range from 0.001 to 0.70 μM in the studies surveyed, and represent only 5.9 $\pm$ 4.6% of the total DON pool (Table II). Though concentrations of amino acids tend to be very low due to the close coupling between uptake and release (Fuhrman, 1990), this is not always the case. For example, extremely high levels of DPA (up to 17 μM) were measured during a dinoflagellate bloom in Chesapeake Bay (Sellner and Nealley, 1997). Concentrations of DFAA vary with season, depth, location, and time of day (Mopper and Lindroth, 1982; Williams and Poulet, 1986; Fuhrman, 1987, 1990). A likely source of DFAA are primary producers, many of which have large intracellular pools of amino acids that can be released via a number of processes (see Section III.A; Brown, 1991; Marsot *et al.,* 1991). Laboratory culture experiments indicate that intra- and extracellular amino acids can vary as a function of growth phase (Admiraal *et al.,* 1986; Marsot *et al.,* 1991), and thus can be very important indicators of cellular metabolic state in phytoplankton.

One area that is receiving attention of late is the analysis of amino acid enantiomeric ratios (McCarthy *et al.,* 1998; Jørgensen *et al.,* 1999; see Section III.C.3).

The D enantiomers are abundant in bacterial cell walls and are indicative of refractory components, such that they can be used as an indicator of the source and diagenetic state of DOM. During a 10-day decomposition experiment with fresh phytoplankton-derived DOM from an Arctic ice floe, the concentration of the D enantiomer did not change but the D/L ratio increased during the course of the incubation indicating a trend toward the presence of more refractory DOM (Amon *et al.*, 2001).

4. Humic and Fulvic Substances

Humic substances are the most hydrophobic component of the DON pool, composed of organic acids (500 to 10,000 MW) and operationally defined based on their retention on hydrophobic resins (Thurman, 1985, Aiken, 1988; see Benner, Chapter 3). Humic substances generally range in color from yellow to dark brown, and can fall into one of three categories: humic acids, which are not soluble in water under acid conditions (<pH 2) but become soluble at higher pHs (isolated using XAD-8 resin); fulvic acids, which are hydrophilic acids soluble under all pH conditions (isolated using XAD-4 resin), and humin, which is the fraction that is insoluble under any pH condition (Ishiwatari, 1992). In seawater, humic substances typically make up 10–20% of the DOM pool, while hydrophilic fulvic acids can contribute 50% or more (Thurman, 1985). For a review of humic substances in aquatic systems, see Hessen and Tranvik (1998) and Benner (Chapter 3).

Humic substances isolated from natural waters originate in either a terrestrial or a marine environment. Humics from both environments are colored organic acids that have similar metal complexing capabilities and redox functions (Harvey and Boran, 1985). Humic substances of terrestrial origin are mostly aromatic and have a higher C:N ratio than do marine humics, which are more aliphatic in nature (Stuermer *et al.*, 1978). The building blocks of marine humics are believed to be biosynthetic compounds such as amino acids, sugars, amino-sugars, and fatty acids (Gagosian and Lee, 1981). The general consensus is that both marine and terrestrial humic substances arise from microbial degradation of plant material, but the exact mechanisms of humification are unknown (Hedges, 1988; Hatcher and Spiker, 1988).

Collating a table of humic N concentrations proved to be frustrating (Table III). Researchers routinely report concentrations of DOC in humic substances or elemental analyses of C:N ratios. In most cases, however, both pieces of information are not presented for a given sample so that the concentration of DON can be estimated. Of the literature data found, concentrations of humic substances range from 0.4 to 12.3 μM (Table III). The mean C:N ratio is 16 ± 5 for humic acids and 33 ± 20 for fulvic acids (Table III). In general, the percentage of N ranges from 2 to 6% for humic acids and <1–3% for fulvic acids in natural waters (Schnitzer, 1985; Thurman, 1985; Hedges, 1988). There is still some question as to how this N

Table III

Literature Values of Concentrations of N Associated with Humic and Fulvic Acids and Their C:N Ratios

Location	Sampling date	Sampling depth (m)	Concentration (μM)	C:N	Reference
Humic acids					
Mangrove swamp	October 1992	Surface	5.3	22.3	Moran and Hodson, 1994
Altamaha River, GA	Annual means 1996–1998	Surface	12.33 ± 5.48		Bronk *et al.*, unpub. data
Savannah River, GA	Annual means 1996–1998	Surface	11.65 ± 7.14		Bronk *et al.*, unpub. data
Crab Cay, Bahamas	October 1992	Surface	1.9	13.4	Moran and Hodson, 1994
Gulf Stream	October 1992	Surface	1.7	14.4	Moran and Hodson, 1994
Marine (6) waters				11.1 to 13.3	Reviewed in Ishiwatari, 1992
Greenland Sea	June 1991	0 to 3650	1.00 ± 0.2[a]		Lara *et al.*, 1993
Greenland Sea	June 1991	0 to 3650	0.77 ± 0.2[b]		Lara *et al.*, 1993
Antarctic waters	December 1991	<100	0.45 ± 0.09[a]		Hubberten *et al.*, 1995
Antarctic waters	December 1991	>100	0.41 ± 0.19[a]		Hubberten *et al.*, 1995
Antarctic waters	December 1991	<100	0.67 ± 0.12[b]		Hubberten *et al.*, 1995
Antarctic waters	December 1991	>100	0.69 ± 0.10[b]		Hubberten *et al.*, 1995
Greenland Sea	June 1991	<100	1.05 ± 0.23[a]		Hubberten *et al.*, 1995
Greenland Sea	June 1991	>100	0.86 ± 0.20[a]		Hubberten *et al.*, 1995
Greenland Sea	June 1991	<100	0.83 ± 0.17[b]		Hubberten *et al.*, 1995
Greenland Sea	June 1991	>100	0.65 ± 0.12[b]		Hubberten *et al.*, 1995
			Mean ± std	**15.6 ± 4.6**	
Fulvic acids					
Sargasso Sea				7.8	Harvey and Boran, 1985
Loch Vale watershed, Colorado				28.3 to 34.5	Reviewed in McKnight and Aiken, 1998

(*Continues*)

Table III (*Continued*)

Location	Sampling date	Sampling depth (m)	Concentration (μM)	C:N	Reference
Pacific Ocean				37.0	Reviewed in McKnight and Aiken, 1998
Lake, rivers, and ponds (14)				14.0 to 96.0	Reviewed in McKnight and Aiken, 1998
Greenland Sea	June 1991	0 to 3650	2.3 ± 0.7[c]		Lara *et al.*, 1993
			Mean ± std	**32.8 ± 19.5**	

Note. Data are mean ± standard deviation.
[a]Hydrophobic neutral fraction isolated using XAD-2 (Fu and Pocklington, 1983); represented 56 ± 10% of the total DON pool.
[b]Hydrophobic acid fraction isolated using XAD-2 (Fu and Pocklington, 1983); represented 25 ± 70% of the total DON pool.
[c]Hydrophilic fraction isolated using XAD-2 (Fu and Pocklington, 1983); represented 19 ± 4% of the total DON pool.

is associated with the humic substances. Schnitzer (1985) suggested that there are two types of N associations. The first group (~50% of the humic associated N), contains N compounds that have distinct characteristics such as amino acids, amino sugars, ammonium, nucleic acid bases, and purines. The second group includes compounds in which N is an integral part of the humic substance itself. The first group of compounds is the most likely source of the bioavailable N associated with humics (see Sections IV.C.4 and IV.D).

5. Other Organic Compounds

There has been a suite of other organic compounds identified in seawater including nucleic acids, purines and pyrimidines, pteridines, methylamines, and creatine (see review by Antia *et al.*, 1991). The nucleic acids include dissolved deoxyribonucleic acids (D-DNA) and dissolved ribonucleic acids (D-RNA). There are a number of methods used to measure nucleic acid concentrations in seawater (reviewed in Karl and Bailiff, 1989). D-DNA is produced by bacteria during growth and can be consumed by bacteria through metabolism and hydrolysis reactions involving cell-surface and extracellular nucleases (Paul *et al.*, 1987). Most DNA is present in the nucleus of the cell, while most RNA is located in ribosomes in the cytoplasm; ribosomes are the sites of protein synthesis. Accordingly, RNA concentrations within a cell are dependent on the cell's growth rate, while DNA

concentrations are not nearly as variable. In general, D-DNA concentrations are highest in nearshore surface waters, with concentrations decreasing with depth and distance from shore (reviewed by Karl and Bailiff, 1989). In Tokyo Bay, concentrations of both D-DNA and D-RNA decrease from the head to the mouth, and vertical profiles have surface maxima with lower concentrations deeper in the water column (Sakano and Kamatani, 1992). Concentrations of particulate DNA and RNA are greater than the dissolved forms, and both D-DNA and total nucleic acids (D-DNA + RNA) concentrations are correlated with DOP concentrations.

Purines and pyrimidines are heterocyclic bases that contain N. The major purine bases found in nucleic acids are adenine and quanine and the major pyrimidine bases are thymine, cytosine, and uracil. Some purines and pteridines are primary excretory products that are the end products of N catabolism (Antia *et al.*, 1991). These compounds have received little attention in the literature. The range of concentrations reported in Antia *et al.* (1991) is 4–24 $\times$ 10^{-5} to 12.6 μM.

Methylamines are another organic compound that has received attention of late. Methylamines come in mono-, di-, and tri-methyl forms that are primary, secondary, and tertiary methylated homologs of NH_3. In the Arabian Sea, concentrations of methylamines are low in oligotrophic open ocean regions and higher in productive coastal areas influenced by upwelling (Gibb *et al.* (1999). Concentrations of the different forms generally follow the pattern of mono- > di- > tri-methylamines (Table II; Gibb *et al.*, 1999). Overall, methylamines contribute less than 1% of the measured DON pool, and their distributions appear to be biologically controlled with maxima in the mono- and di- forms associated with diatom abundance and microzooplankton grazing.

6. Characteristics of HMW DON

The introduction of ultrafiltration techniques has greatly expanded our knowledge of the HMW DON fraction, referred to as ultrafiltered DON (UDON). Ultrafiltration through a nominal 1-kDa ultrafilter routinely isolates approximately 20–40% of total DON (Benner *et al.*, 1992b, 1997; see Benner, Chapter 3). It is unknown how compositionally representative UDON is to the LMW fraction that passes through the ultrafilter, but based on C:N ratios and overall amino acid content, ultrafiltration does not appear to fractionate DOM in terms of major N forms (McCarthy *et al.*, 1997).

UDON has a characteristic organic composition that appears to be highly conserved across the ocean basins sampled to date (McCarthy *et al.*, 1996). Chemically, the material appears very different from that of humic substances, phytoplankton, or particles. McCarthy *et al.* (1997) analyzed ocean samples, with no terrestrial input, and found that retention by a 1-kDa filter ranges from 19% in the deep Pacific to 38% in Pacific surface waters and that the C:N ratio of the HMW fraction ranges from 15.6 to 18.4. By weight, 17–29% of the UDON can be

recovered as hydrolyzable amino acids, and this percentage is invariant with depth (McCarthy *et al.,* 1997). McCarthy *et al.* (1997) analyzed the remaining 70–80% of the UDON that was not hydrolyzable using ^{15}N NMR and found that virtually the entire UDON fraction is amide in form. Amides are common linkages in major biomolecules, which do not form abiotically, indicating that the source of the bulk of HMW DON is biological. In the past, the large uncharacterized fraction of the DON pool was assumed to consist predominantly of complex macromolecules produced during biological degradation and spontaneous abiotic condensation reactions (Harvey *et al.,* 1983). The amide fraction could be proteinaceous material that is resistant to conventional hydrolysis and could include hydrolysis-resistant amides produced by some phytoplankton (Derenne *et al.,* 1992), acetylated amino sugars such as chitin (an important structural component of many plankton), or mureins and lipopolysaccharides (found in bacterial cell walls); *N*-acetyl amino sugars have been identified as a major component of UDOM by Aluwihare *et al.* (1997). There is also evidence for the presence of small amounts of highly stable indole-like or pyrrole-like N forms in this fraction (McCarthy *et al.,* 1997). These forms may be derived from the bases of DNA, RNA, or the porphyrin ring of photosynthetic pigments. These data are also consistent with the presence of melanoidins, which are the end-products of abiotic sugar and amino acid condensation.

UDOM material isolated from surface and deep waters in the central Pacific, Gulf of Mexico, and North Sea shows enrichment in the D enantiomers of four amino acids (McCarthy *et al.,* 1998). These data are interpreted as evidence that peptidoglycan remnants from bacterial cell walls are a major component of the UDON pool. The material could enter the dissolved phase during bactivory by protozoans or viral infection and likely accumulates and persists because the cell-wall matrix renders the material resistant to degradation.

In another study of HMW material (i.e., UDOM), three phytoplankton species were shown to release HMW DOM rich in polysaccharides (Aluwihare and Repeta, 1999). The HMW DOM produced by *Thalassiosira weisflogii* has a C:N ratio of 14 early in the culture, but this ratio consistently decreases to a low of 5.6 after ~225 days of decomposition. Surprisingly, this suggests the accumulation of a more N-rich DOM fraction over time.

In the same vein, Lara *et al.* (1997) performed a 3-month incubation with a nonaxenic diatom culture to determine the chemical evolution of DOM. During active growth there is a net increase in DON that is largely hydrophilic in nature, and bacterial uptake of DCAA and nonamino DON is observed. In the stationary phase, DON (largely hydrophilic) is consumed but there is an increase in hydrophobic algal exudates. Lara *et al.* (1997) found evidence for the formation of humic substances and suggested that the production of refractory DOM may begin in the hydrophilic fraction because a portion of the particulate amino N pool is transformed into hydrophilic DON during the degradation phase.

D. Concentration and Composition of the DON Pool: Research Priorities

The past decade has been a productive one for research into DON distributions and chemical composition. There are a number of areas, however, where additional research is desperately needed. First, there has just got to be an easier way to measure DON. As long as a DON concentration is determined by taking the difference between TDN and dissolved inorganic nitrogen (DIN) measurements, analytical errors will be a problem and our ability to resolve small but significant changes in DON will be limited. Second, there is a need for large, high-quality data sets of DON concentrations comparable to what is being assembled for DOC (see Hansell, Chapter 15). Third, the information assembled on UDON is impressive, but we must remember that this is a small fraction of the total DON pool. One of the highest research priorities should be to crack the composition of the quantitatively dominant <1-kDa fraction, a task that will require the development of innovative isolation and concentration technologies.

III. SOURCES OF DON

DON in the ocean can originate from a number of sources—both abiotic and biotic. Abiotic sources will be considered only briefly. They include terrestrial inputs, such as DON transport via overland runoff, rivers, streams, and groundwaters (Valiela *et al.*, 1990; Tobias *et al.*, 2001) and atmospheric inputs (Cornell *et al.*, 1995). Meybeck (1993) estimated that ~70% of the N entering the coastal ocean via rivers is DON (10×10^{12} gN/year). Galloway *et al.* (1995) predicts that future changes in local precipitation will increase the amount of DON transported to the coastal ocean via this mechanism. Recent data from a wide range of environments indicate that DON is also a substantial fraction of the N in rainwater, representing 2 to 84% of the total N deposited annually (Seitzinger and Sanders, 1999). Bioassay studies indicate that 45 to 75% of this DON is bioavailable on the time scales of days (Seitzinger and Sanders, 1999).

This section will focus on biotic sources of DON in the water column. Each source will be reviewed, followed by methods for measuring rates of DON release, a summary of available data on release rates, and suggested research priorities for the future.

A. Biotic Sources of DON in the Water Column

Biotic inputs discussed in this chapter include extracellular phytoplankton production, either through active exudation or passive diffusion of metabolites through

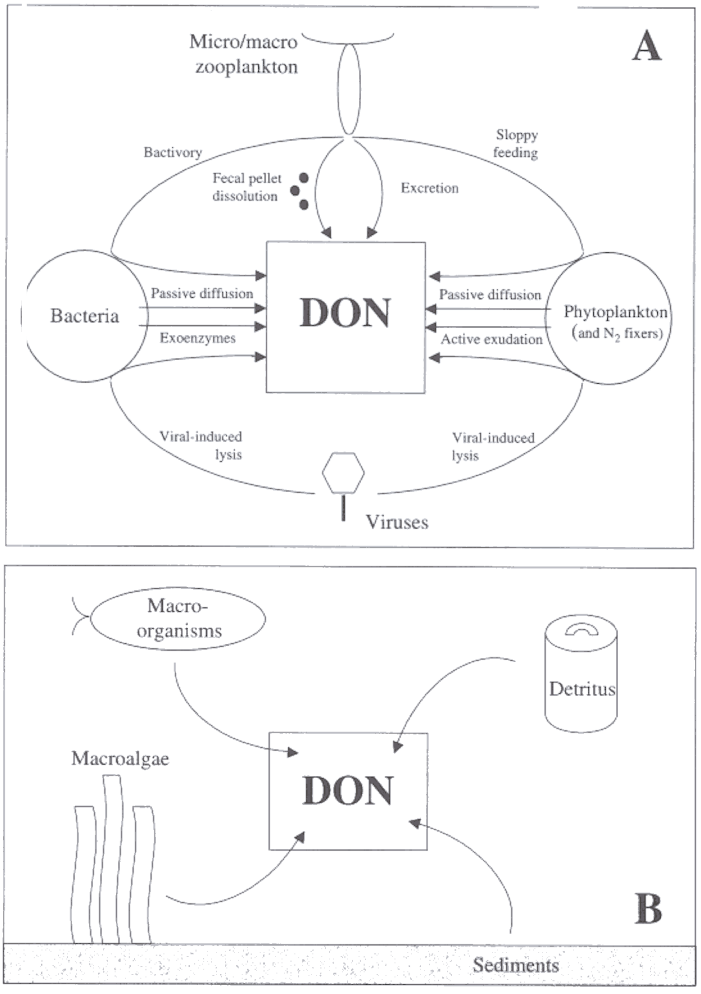

Figure 3 Conceptual diagram of processes involved in dissolved organic nitrogen (DON) release in aquatic systems including (A) processes that are covered in this chapter and (B) additional processes not discussed.

membranes; bacterial release via active release of exoenzymes, or passive diffusion; micro- and macrozooplankton release via fecal pellet dissolution, excretion, or bactivory or sloppy feeding (i.e., trophic mediated release); and viral release via lysis both of autotrophs and heterotrophs (Fig. 3A). The information on DOC release due to grazing, virus induced lysis, and enzymatic hydrolysis of particles in Carlson (Chapter 4) are all relevant to this discussion.

Additional biotic sources that will not be considered here due to space limitations include release from macroorganismal excretion (Tupas and Koike, 1990), direct release from macroalgae (Mann, 1982; Branch and Griffiths, 1988); detrital particle release via dissolution (see Carlson, Chapter 4); and release from sediments via diagenesis (see Burdige, Chapter 13; Fig. 3B).

1. Phytoplankton

When discussing DON release from phytoplankton, it is important to clearly discriminate *direct release* from phytoplankton, including passive or active release, from *mediated release,* where the phytoplankton are acted on by other trophic levels. Regarding direct release from phytoplankton, there have been two models proposed: the outflow model (Fogg, 1966) and the passive diffusion model (Fogg, 1966; Bratbak and Thingstad, 1985; Bjørnsen, 1988; see Carlson, Chapter 4).

Active release (i.e., overflow model) includes release of excess photosynthates that accumulate when C fixation exceeds incorporation into new cellular materials due to nutrient limitation (termed exudation by Fogg, 1983). The overflow model is unlikely to impact DON release significantly because most environments that are lacking in phosphorus (i.e., another limiting nutrient), generally do not have an excess of N. Other processes that would be considered direct release are release due to osmostic changes, and release of reduced inorganic or organic N in response to elevations in light (Lomas and Glibert, 1999). A specialized form of direct release is autolysis — the disruption of cell membranes of an organism by enzymes produced by the same organism. It has been suggested that autolysis in phytoplankton may be a significant death term, and by implication, a significant source of DOM (Agusti *et al.,* 1998). Another specialized form of release that has received little attention is protoplasm lysis during spermatogenesis, which occurs in response to N starvation (Sakshaug and Holm-Hansen, 1977; Collos, 1986).

Passive release (i.e., passive diffusion model) includes the permeation of presumably LMW compounds through the cell membrane in response to the large concentration gradient that exists between intracellular and extracellular pools. Passive release would potentially vary depending on such things as physiological stress, exposure to UV radiation, temperature, and light levels. Bjørnsen (1988) suggested that bacteria act as ectoparasites by continually assimilating extracellular DOM and thus maintaining the concentration gradient between intracellular and extracellular LMW organic pools. Hasegawa *et al.* (2000a) provided evidence that smaller plankton release $DO^{15}N$ more efficiently than larger ones. These data support Bjørnsen's hypothesis, because smaller cells have a larger surface to volume ratio. Phytoplankton can also be a source of DON when other trophic levels act on them such as during zooplankton sloppy feeding (i.e., grazing; Dagg, 1974; Lampert, 1978), and lysis due to viral infection (Bratbak *et al.,* 1993; Murray, 1995; Gobler *et al.,* 1997; Suttle, 1994; Fuhrman, 1999).

Much of what we know about DON release from phytoplankton was learned from culture work done in the 1960s and 1970s (reviewed in Antia *et al.,* 1991). For example, extracellular N as a percentage of total N is highest immediately after transfer of cells from one set of environmental conditions to another (Jones and Stewart, 1969; Collos *et al.,* 1992; Slawyk and Raimbault, 1995). If these results accurately reflect the phytoplankton's response to changing environmental conditions and are not an artifact of stressing cells during transfer, than the percentage of extracellular release in the turbulent natural environment is likely much higher than longer-term laboratory studies imply.

The decline of phytoplankton blooms has also been shown to be a period of significant DOM release from phytoplankton due to such processes as physiological stress or high grazing pressure (Carlson *et al.,* 1994; Jenkinson and Biddanda, 1995). There seems to be a pattern of low rates of release in actively growing cells, such as those found at the beginning of a bloom, and high rates of release when cells are stressed by nutrient limitation, light inhibition, etc., such as at the end of a bloom (Larsson and Hagström, 1979). Consistent with this scenario, Flynn and Berry (1999) found that the highest rates of DCAA release occur during stationary phase and that release of DCAA is low during active growth.

Other recent work conflicts with this view, however. Biddanda and Benner (1997) found that most of the DOM produced in their cultures is released during nutrient replete conditions. In batch cultures of marine *Synechococcus,* grown under N-sufficient and N-deficient conditions, DOC release increases under N-deficient conditions, consistent with previous work (Bronk, 1999). Consistent with Biddanda and Benner (1997), however, Bronk (1999) found that the highest rates of DON release, both absolute and as a percentage of gross N uptake, occur during N sufficient growth, and release rates decrease by a factor of 4 to 7 when NH_4^+ is depleted in the medium.

One specialized route of DON release that may be quite important involves vertically migrating mats of *Risoselenia* (Villareal *et al.,* 1993). The mats migrate into the nitracline and fill large intracellular pools with NO_3^-. Once at the surface, the potential for DON release exists via direct release or during slopping feeding. The magnitude of DON released via this route has yet to be quantified.

2. N_2 Fixers

N_2 fixation by *Trichodesmium* spp. has been shown to be a significant source of new N to tropical and subtropical marine systems in which they occur (Lipschultz and Owens, 1996; Karl *et al.,* 1997; Capone *et al.,* 1997; Hansell and Feely, 2000). *Trichodesmium* contribute to N turnover in oceanic systems both directly, through the release of amino acids, DON, and NH_4^+, and indirectly through regeneration of DIN and DON by bacteria and grazers living in association with the colonies (Sellner, 1992).

In natural populations of *Trichodesmium* from the Atlantic Ocean and Caribbean Sea, up to half of the recently fixed N_2 is released directly as DON during growth, primarily as DFAA (Capone *et al.*, 1994; Glibert and Bronk, 1994). Data from the subtropical North Pacific station ALOHA also shows enrichment of N pools (NH_4^+, NO_3^-, DON) within *Trichodemsium* blooms (Karl *et al.*, 1992; Letelier and Karl, 1996). In natural populations from the Caribbean Sea and cultured populations of *Trichodesmium* NIBB1067, lysogenic phages have also been identified that can produce cell lysis and the release of cellular contents (Ohki, 1999). Nausch (1996) estimated that 0.32 to 15 nmol N colony^{-1}h^{-1} is released by peptidase and b-glucosamidase activity associated with bacteria residing among *Trichodesmium* colonies in the subtropical Atlantic Ocean. As one of the few known grazers of *Trichodesmium* spp., *Macrosetella gracilis* provides an important link in introducing new N from N_2 fixation into the food web through sloppy feeding or excretion (O'Neil and Roman, 1992; O'Neil *et al.*, 1996). *M. gracilis* ingest *Trichodesmium* at high rates but do not appear to make solid fecal pellets, suggesting that much of the N they release during excretion remains in the dissolved fraction.

In a study in the Baltic, Ohlendieck *et al.* (2000) measured the accumulation of N recently fixed by two other N_2 fixers, *Aphanizomenon* and *Nodularia*. In two experiments in July 1995 and July 1996, they found that 7.7 ± 2.1 and 6.7 ± 2.1% of the recently fixed ^{15}N was present in the picoplankton, indicating organic release and subsequent reincorporation.

3. Bacteria

Bacteria are generally thought of as DON consumers, but they can also be important producers and remineralizers of DON as noted above. Berman *et al.* (1999) demonstrated that urea (and NH_4^+) can be produced from DON by natural bacterial populations or via extracellular enzymes from DON in Lake Kinneret, the Charente Estuary, France, and the French coast of the Atlantic. Addition of guanine, hypoxanthine, and arginine results in significant increases in urea concentrations; the organic compounds were added at environmentally unrealistic levels (40 μM), however, which raises questions as to the importance of this process in the environment. Carlsson and Granéli (1993) and Carlsson *et al.* (1993) also provide evidence that DON is utilized by phytoplankton indirectly through bacterial incorporation of the DON and then release of NH_4^+ during bactivory. In another study, Jørgensen *et al.* (1999) documented urea release in bioassays in the Gulf of Riga. Bacteria are also known to release DON through the mineralization of organic aggregates (Smith *et al.*, 1992).

Therkildsen *et al.* (1997) measured urea production in commercially available cultures of two marine bacteria and found that the highest accumulation occurs during the growth deceleration phase and at the beginning of stationary phase. They argued that internal RNA provides the precursors for the release of urea.

During growth, the intracellular RNA pool is dynamic with some portion of it being degraded to urea and NH_4^+, particularly during exponential growth (Mason and Engli, 1993).

4. Micro- and Macrozooplankton

The processes of grazing and bactivory are known to be important in transforming and partitioning C and N within planktonic systems (see reviews by Nagata, 2000; and Strom, 2000). These processes can result in DON release via sloppy feeding (Dagg, 1974; Lampert, 1978) or bactivory, where cells are not ingested whole but are broken, resulting in release of dissolved intracellular materials, via excretion, where DON compounds are released as waste (Miller and Glibert, 1998; Conover and Gustavson, 1999) or via diffusion away from or the dissolution of fecal pellets (Jumars *et al.,* 1989; Fig. 3A).

Microzooplankton tend to ingest whole cells, such that the release of DOM during sloppy feeding is relatively minor, although some workers have found that microzooplankton enhance DOM fluxes as well as influence the composition of the DOM pool (Flynn and Davidson, 1993; Strom *et al.,* 1997). In the studies reviewed in Table IV in Carlson (Chapter 4), $9 \pm 6\%$ ($n = 5$) of the N ingested by a number of microzooplankton species is released as DFAA or DFAA and DCAA. Ferrier-Pagès *et al.* (1998) measured release of DPA from two flagellates (*Strombidium sulcatum,* cilitate, and *Pseudobodo* sp., aplastidic flagellate) grazing on bacteria in culture. They found high rates of DPA release during the exponential phase, when ingestion rates were at a maximum, but lower rates during the other growth phases. In another bactivory study, Alonso *et al.* (2000) found rates of up to 281 μg DNA L^{-1} h^{-1} in bacterial cultures with the ciliate *Uronema* sp. and the flagellate *Pseudobodo* sp. In the Adriatic Sea, concentrations of D-DNA and nanoflagellates were found to covary during a study of diel dynamics, and D-DNA release rates increase sixfold when the nanoflagellate, *Ochromonas* sp., is present (Turk *et al.,* 1992).

In contrast to the microzooplankton, it is generally believed that sloppy feeding by macrozooplankton is responsible for the generation of significant amounts of labile DOM (Dagg, 1974; Lampert, 1978; Urban-Rich, 1999). In Table IV in Carlson (Chapter 4), macrozooplankton release $11 \pm 12\%$ ($n = 11$) of their body N as DON, often measured as DFAA, urea, or DCAA. In other studies, $25 \pm 12\%$ ($n = 6$) of the TDN released is organic in form (Table IV in Carlson, Chapter 4). The relative coupling of C and N during this release, however, is poorly known. Daly *et al.* (1999) suggested that C and N release by copepods results in quantitatively different fluxes of DOC and DON, which ultimately results in non-Redfieldian ratios within those pools.

Lampert (1978) found that 4 to 17% of particulate organic C (POC) *Daphnia pulex* ingested was released as DOC as a result of sloppy feeding alone. Release is

Table IV

Summary of Published Rates of DON Release and Ratios of DON Release to Gross N Uptake, Expressed as a Percentage, Determined Using ^{15}N Tracer Techniques (^{15}N) or Changes in Concentrations (CC)

Location	Date/Culture	Substrate	DON release rate (ng-at N $L^{-1}h^{-1}$)	DON release: Gross Uptake (%)	Method	Reference
Oceanic						
Caribbean Sea	November 1988	NH_4^+	9.8 ± 3.0	27.8 ± 8.0	^{15}N IRC	Bronk *et al.*, 1994
Ross Sea, Antarctica	Nov–Dec 1994	NO_3^-	66.5[a]	19.0	^{15}N IRC	Hu and Smith, 1998
Ross Sea, Antarctica	Dec–Jan 1995/6	NO_3^-	27.2[a]	8.0	^{15}N IRC	Hu and Smith, 1998
Oligotrophic North Pacific	Sept–Oct 1992	NH_4^+	1.6 to 3.1[b]	19.7 to 71.6[b]	^{15}N WC	Slawyk and Raimbault, 1995
Oligotrophic North Pacific	Sept–Oct 1992	NO_3^-	0.2 to 0.5[b]	25.8 to 98.5[b]	^{15}N WC	Slawyk and Raimbault, 1995
Equatorial and oligotr. Pacific	November 1994	NH_4^+ NO_3^-		15.3 ± 13.4	^{15}N WC	Slawyk *et al.*, 1998
Equatorial and oligotr. Pacific	November 1994	NH_4^+ NO_3^-		20 to 100	^{15}N WC	Raimbault *et al.*, 1999
Southern California Bight	Oct 1992 and April 1994	NH_4^+	0.6 to 31.1[c]	13.2 to 89.0	^{15}N WC	Ward and Bronk, 2001
Southern California Bight	Oct 1992 and April 1994	NH_4^+	0.7 to 19.1[d]	14.4 to 79.7	^{15}N WC	Ward and Bronk, 2001
Southern California Bight	Oct 1992 and April 1994	NO_3^-	1.1 to 72.3[c]	22.2 to 96.0	^{15}N WC	Ward and Bronk, 2001

Southern California Bight	Oct 1992 and April 1994	NO_3^-	1.1 to 385.6[d]	22.0 to 99.0	^{15}N WC	Ward and Bronk, 2001
		Mean ± std	**40.2 ± 61.0**	**41.4 ± 20.2**		
Coastal						
Southern California Bight	October 1992	NH_4^+	12.4 ± 3.2	20.5 ± 1.6	^{15}N IRC	Bronk *et al.*, 1994
Southern California Bight	October 1992	NO_3^-	3.4 ± 0.2	34.3 ± 3.6	^{15}N IRC	Bronk *et al.*, 1994
Monterey Bay, CA	March 1993	NH_4^+	61.9 ± 47.2	16.2 ± 12.0	^{15}N WC	Bronk and Ward, 1999
Monterey Bay, CA	March 1993	NO_3^-	1.4 ± 0.7	22.2 ± 33.6	^{15}N WC	Bronk and Ward, 1999
Monterey Bay, CA	September 1993	NH_4^+	20.8 ± 20.1	64.7 ± 22.1	^{15}N WC	Bronk and Ward, 1999
Monterey Bay, CA	September 1993	NO_3^-	12.2 ± 2.2	85.7 ± 14.3	^{15}N WC	Bronk and Ward, 1999
Akkeshi Bay, Japan	May 1998	NH_4^+		3.6 ± 0.1[e]	^{15}N WC	Hasegawa *et al.*, 2000a
Akkeshi Bay, Japan	June 1998	NH_4^+		4.9 ± 0.4[e]	^{15}N WC	Hasegawa *et al.*, 2000a
Akkeshi Bay, Japan	August 1998	NH_4^+		2.7 ± 0.1[e]	^{15}N WC	Hasegawa *et al.*, 2000a
Akkeshi Bay, Japan	March–Nov 1998	NH_4^+	6.0 to 15.0[f]		^{15}N WC	Hasegawa *et al.*, 2000b
Gulf of Lions (Mediterranean Sea)	March–May 1997	NH_4^+	~0 to 1.46	26.0	^{15}N WC	Diaz and Raimbault, 2000

(*Continues*)

Table IV (*Continued*)

Location	Date/Culture	Substrate	DON release rate (ng-at N $L^{-1}h^{-1}$)	DON release: Gross Uptake (%)	Method	Reference
	March–May 1997	NO_3^-		**24.0**		Diaz and Raimbault, 2000
	October 1992	NH_4^+	**16.9 to 360**[g]	**29.6 to 97.2**	^{15}N WC	Ward and Bronk, 2001
	October 1992	NO_3^-	**5.0 to 26.8**[g]	**53.0 to 95.4**	^{15}N WC	Ward and Bronk, 2001
	March and Sept 1993	NH_4^+	3.5 to 263.4[c]	21.1 to 94.0	^{15}N WC	Ward and Bronk, 2001
	March and Sept 1993	NH_4^+	19.5 to 334.0[d]	14.1 to 97.7	^{15}N WC	Ward and Bronk, 2001
	March and Sept 1993	NO_3^-	0.7 to 26.7[c]	9.3 to 95.0	^{15}N WC	Ward and Bronk, 2001
	March and Sept 1993	NO_3^-	1.4 to 21.5[d]	4.1 to 92.0	^{15}N WC	Ward and Bronk, 2001
		Mean ± std	**44.1 ± 65.5**	**38.6 ± 26.0**		
Estuarine						
Chesapeake Bay, north	April 1989	NH_4^+	51.8	34.0	^{15}N IRC	Bronk *et al.*, 1994
Chesapeake Bay, north	April 1989	NO_3^-	60.6	11.0	^{15}N IRC	Bronk *et al.*, 1994

Chespeake Bay, south	April 1989	NH_4^+	36.8 ± 32.1	**26.3 ± 12.6**	^{5}N IRC	Bronk *et al.*, 1994
Chespeake Bay, mesohaline	May 1988	NH_4^+	71.6 ± 59.2	**27.8 ± 18.3**[h]	^{5}N IRC	Bronk *et al.*, 1998
Chesapeake Bay, mesohaline	August 1988	NH_4^+	55.3 ± 47.0	**14.2 ± 8.3**[h]	^{5}N IRC	Bronk *et al.*, 1998
Chesapeake Bay, mesohaline	October 1988	NH_4^+	33.4 ± 39.1	**28.4 ± 25.4**[h]	^{5}N IRC	Bronk *et al.*, 1998
Choptank River, MD	August 1990	NH_4^+	193.1 ± 118.4	**22.1 ± 15.1**[h]	^{15}N IRC	Bronk and Glibert, 1993b
		Mean ± std	**71.8 ± 55.1**	**23.4 ± 8.2**		
Culture						
Trichodesmium	Jan/Feb 1992	N_2 gas	**114.0 ± 83.4**[l]	**44.4 ± 31.8**	^{15}N IRC	Glibert and Bronk, 1994
Synchococcus WH7803 & 3018		NH_4^+	0.017 ± 0.012[l]	11.1 ± 5.5	^{15}N IRC	Bronk, 1999
P. tricornutum and D. tertiolecta		NO_3^-		3.9[k]	^{15}N WC	Pujo-Pay *et al.*, 1997
Dunaliella tertiolecta		NO_3^-		6 to 21	^{15}N WC	Slawyk *et al.*, 1998
Microcystis novacekii		NH_4^+	106.7 ± 35.1	20.9 ± 3.7[l]	^{15}N IRC	Nagao and Miyazaki, 1999

(*Continues*)

Table IV (*Continued*)

Location	Date/Culture	Substrate	DON release rate (ng-at N $L^{-1}h^{-1}$)	DON release: Gross Uptake (%)	Method	Reference
Synechococcus bacillaris		DIN	0.053	18.2[m]	CC	Biddanda and Benner, 1997
Phaeocystis sp.		DIN	0.080	27.7[m]	CC	Biddanda and Benner, 1997
Emiliana huxleyi		DIN	0.050	20.5[m]	CC	Biddanda and Benner, 1997
Skeletonema costatum		DIN	0.030	19.3[m]	CC	Biddanda and Benner, 1997
Synedra planctonica		NO_3^-	119	36.0	CC	Collos *et al.*, 1992
Heterosigma carterae	DCAA release only	NH_4^+	119.4[n]	37.7[o]	CC	Flynn and Berry, 1999
Heterosigma carterae	DFAA release only	NH_4^+	50.4[n]	15.9[o]	CC	Flynn and Berry, 1999
Mantoniella squamata	DCAA release only	NH_4^+	214.1[n]	32.9[o]	CC	Flynn and Berry, 1999
Mantoniella squamata	DFAA release only	NH_4^+	24.4[n]	3.8[o]	CC	Flynn and Berry, 1999
Thalassiosira psuedonana	DCAA release only	NH_4^+	99.4[n]	18.5[o]	CC	Flynn and Berry, 1999
Thalassiosira psuedonana	DFAA release only	NH_4^+	39.5[n]	.4[o]	CC	Flynn and Berry, 1999

Mesocosms	Various additions	11.7 to 30.8	CC	Søndergaard *et al.*, 2000
	Mean ± std	**21.8 ± 13.7**		

Note. Tracer methods include ion retardation column (IRC) and wet chemical (WC) isolation as described in the reference. Data are presented as mean ± standard deviation. When ranges are presented, the mean % release was calculated using the median value in the range.

[a] Calculated from uptake and percentage release data.

[b] Calculated using raw data from manuscript.

[c] <10-μm size fraction

[d] <202-μm size fraction

[e] Calculated with data from the <90-μm fraction so grazing is likely reduced or absent.

[f] Release mediated by grazers.

[g] Combined data for <10 and <202 μm.

[h] Gross uptake rates calculated from original data.

[i] *Trichodesmium* colonies from the Caribbean, units are pmol N colony^{-1} h^{-1}.

[j] In units of fg-at N cell^{-1} h^{-1}

[k] Estimated using ^{15}N mass balance not actual uptake and release rates.

[l] Cells preserved with formalin prior to filtering.

[m] Calculated by converting the change in DON conc. over 14 days into a per hour rate.

[n] Uptake rate calculated as increase in algal N over first day in cultures with added P.

[o] Percentage release is release divided by uptake + DCAA release + DFAA release.

independent of excretory processes or diffusion or dissolution of fecal pellets and is highly dependent on the size and morphology of the phytoplankton prey—those algae that can be consumed whole release 3.5 to 4.0% of their POC as DOC while those that cannot be consumed whole release 10 to 17% of their POC as DOC. Similar studies have not been done with DON.

It has been hypothesized that the majority of DOM diffuses away from fecal pellets within minutes of its release, assuming that the peritrophin membrane surrounding the pellet is permeable (Jumars *et al.*, 1989). The mucus coating of some fecal pellets, however, may restrict this avenue of exchange. Other studies suggest that fecal pellets must be broken up mechanically before a substantial amount of DON is released (Lampitt *et al.*, 1990; Strom *et al.*, 1997). Urban-Rich (1999) measured abiotic and biotic release from copepod fecal pellets using ^{14}C tracers in the Greenland Sea and found that 86% of the DOC is utilized or leached from fecal pellets in the first 6 h. Shorter term incubations were not done, however, that could address the issue of time scale raised by Jumars *et al.* (1989).

Roy *et al.* (1989) investigated the release of DFAA during sloppy feeding by two copepod species fed a large diatom, known to have large intracellular pools. Although the presence of particulate debris indicates that sloppy feeding occurs, total DFAA concentrations and extracellular composition are not significantly different after copepod grazing. This suggests that the DFAA released are rapidly taken up by bacteria or other cells or that adsorption onto debris produced by the copepods occurs. Fuhrman (1987) found that combinations of copepods and microplankton had a much higher release rate of DFAA than either alone (Table V). He also found that release of DFAA due to sloppy feeding by copepods or excretion can be similar in magnitude to direct release by microzooplankton.

In estuarine mesocosms, rates of urea and DPA release from the copepod *Acartia tonsa* tend to be higher during early morning and early evening and are of the same order of magnitude as NH_4^+ regeneration (Miller and Glibert, 1998). Micrograzers are important agents of DON release and bacteria rapidly consume 58 to 103% of the recently released DON in Japanese coastal waters (Hasegawa *et al.*, 2000b). The magnitude of DON release is ~40% of the rate of NH_4^+ regeneration in the Southern California Bight and Monterey Bay (Bronk and Ward, 1999) and 59% of NH_4^+ regeneration in Japanese coastal waters (Hasegawa *et al.*, 2000b). A tight positive correlation between rates of DON release and NH_4^+ regeneration ($P<0.00001$) has also been observed, suggesting that the same process is likely responsible for both (Ward and Bronk, 2001).

5. Viruses

Viruses are unique in that they can be agents of DON release while being a component of the DON pool itself. Viruses are contributors to DON production because in the final stages of viral infection, the phage increase to such numbers

within the cell that the cell bursts, releasing its cellular contents. Viruses may influence both the production of DOM, through lysis, as well as the character of DOM by shaping the metabolic characteristics of primary and secondary producer communities (see reviews by Fuhrman, 1999; Wommack and Colwell, 2000; Fuhrman, 2000; see Carlson, Chapter 4).

Viruses typically outnumber their potential autotrophic and heterotrophic hosts by at least a factor of 10 making them the most abundant component of the plankton with concentrations ranging from 10^9 to 10^{11} viral particles L^{-1}(Wommack and Colwell, 2000). While estimates of virus-mediated mortality exhibit a wide range, studies indicate that 10 to 20% of heterotrophic bacteria and 3–5% of phytoplankton are lysed daily due to viral infection (Suttle, 1994). A conceptual model of the incorporation of viruses and viral lysis into the aquatic food web was offered by Wommack and Colwell (2000) that emphasizes the importance of viral lysis in enhancing the flux of autotrophic and heterotrophic biomass into the DOM pool (Fig. 4). Each lysis event releases the entire contents of the host cell into the DOM pool in the form of macromolecules, cell organelles, and viral particles, making viral lysis a highly efficient mechanism for transferring living biomass to the DOM pool. The efficiency of this transfer is large when one considers that only one virus from each lysis event needs to survive to infect another host in order to maintain the lytic cycle (Fuhrman, 1992). The theoretical effect of viral lysis is to divert C and N, fixed by phytoplankton and transformed into bacterial biomass, away from zooplankton consumers into the DOM pool (Fuhrman, 1992; Bratbak *et al.,* 1994; Murray and Eldridge, 1994; Fuhrman and Noble, 1995).

Numerous studies have been done to examine the effects of viral lysis on the flux and composition of the DOM pool. In mesocosm experiments it was found that phage lysis products stimulate bacterial growth and metabolic activity, indicating that viral lysis can contribute to a loop in which a portion of available nutrients cycle between the DOM pool and bacterial biomass without contributing to higher trophic levels (Middelboe *et al.,* 1996). In another study, viral lysis of a chrysophyte alga (*Aureococcus anophagefferens*) was responsible for significant changes in the partitioning of nutrients (i.e., C, N, P, Fe, and S), between dissolved and particulate phases (Gobler *et al.,* 1997). Similarly, Bratbak *et al.* (1998) found that viral lysis of *Phaeocystis pouchetii* cultures results in a nearly complete conversion of lost algal biomass to bacterial biomass through production of excess DOC. Finally, changes in DOM composition with viral lysis have been demonstrated in mesocosm experiments. Slight (i.e., 2.5-fold) increases in virioplankton concentration results in measurable changes in the chemical characteristics of the DOM compared to unamended controls (Weinbauer and Peduzzi, 1995). These changes are likely due to the increased incidence of viral lysis in virus-enriched mesocosms.

As an interesting twist on phytoplankton DOM release, Murray (1995) used a modeling approach to suggest that DOM exudation can be a cost-effective, indirect means of reducing viral infection in phytoplankton. The reasoning is that DOM

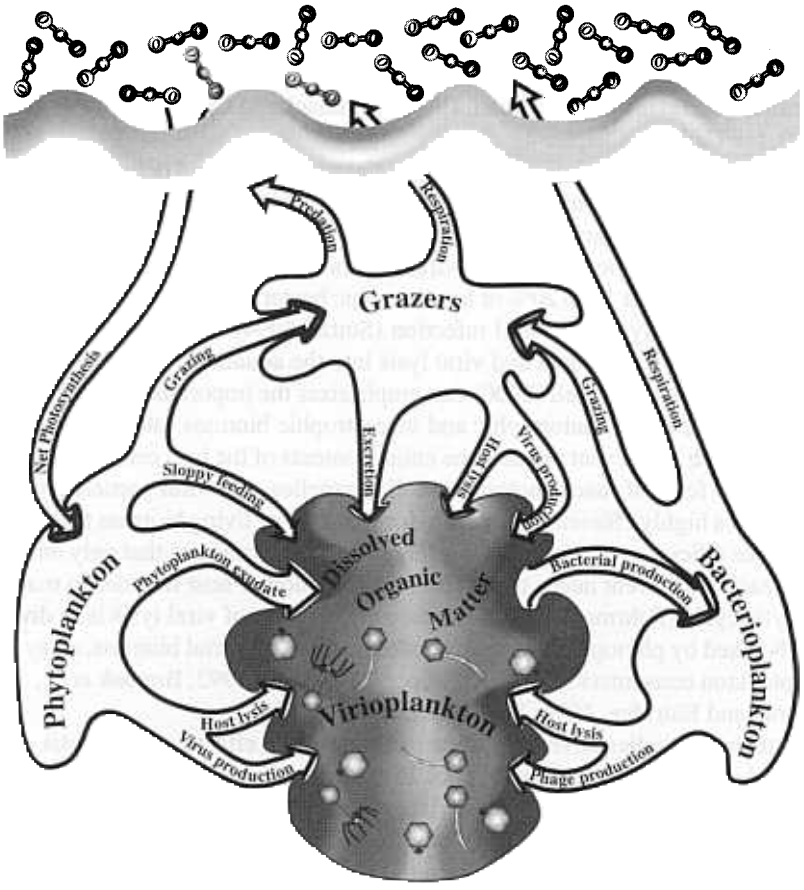

Figure 4 Conceptual model of the incorporation of viruses and viral lysis into the microbial loop as presented by Wommack and Colwell (2000).

exudation supports bacterial populations that can kill viruses, which the bacteria contact with much greater frequency because of their small size. If DOM exudation leads to a reduction in phytoplankton losses from infection greater than the cost of the exudation, then DOM exudation is a cost-effective strategy.

B. Methods for Estimating Biotic DON Release Rates

To measure rates of DON release and uptake there are two main methods–monitoring changes in ambient concentrations and ^{15}N tracer techniques. In the