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Low molecular weight and colloidal DOC production during a phytoplankton bloom

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ABSTRACT: Dissolved organic carbon (DOC) in seawater collected during a spring bloom in Bedford Basin, Nova Scotia, Canada, was separated into low molecular weight and colloidal size fractions by cross-flow ultrafiltration. Total DOC and the organic carbon in the 2 size fractions were analyzed by high temperature catalytic oxidation. DOC accumulated in the mixed layer at the beginning of the bloom and contained a substantial amount of surface active material associated with an increase in river discharge. There was little variation in total DOC at the height of the bloom. Instead, the low molecular weight fraction increased and reached a maximum 3 to 6 d after the chlorophyll maximum. The colloidal fraction of DOC also increased but, at its maximum, accounted for only 16 % of the total. This maximum in colloidal DOC was achieved 8 d after the low molecular weight maximum and almost 2 wk after the chlorophyll maximum. Colloidal material may have coagulated with phytoplankton aggregates at the height of the bloom and limited the accumulation of DOC in the mixed layer. During the decline of the bloom, the downward transport of this material associated with aggregates may have contributed to the eventual accumulation of DOC below the mixed layer As a result, the downward transport of DOC should be determined from estimates of the low molecular weight and colloidal DOC produced by phytoplankton and include the colloidal carbon associated with aggregates.

INTRODUCTION

Dissolved organic carbon (DOC) in the ocean is 1 of the 3 main reservoirs of organic material on the planet, equal to the carbon stored in terrestrial plants or soil humus (Hedges 1987). The results from analytical developments in high temperature catalytic oxidation (Sugimura & Suzuki 1988) suggest that DOC outweighs particulate organic carbon (POC) in surface waters by at least a factor of 10. However, given the conflicting results obtained with this technique (Benner et al. 1992, Martin & Fitzwater 1992, Ogawa & Ogura 1992, Tanoue 1992), it is important to remember that the size of the DOC pool is still open to question. In addition, a number of questions about the biological lability of DOC (the rate at which it is broken down and respired to CO_2) have not been answered.

The lability of DOC has become a key issue (Toggweiler 1992) in models of carbon cycling between the atmosphere and oceans (Bacastow & Maier-Reimer 1991), but the quantitative definition of lability requires accurate estimates of the rate of DOC production by phytoplankton and the resolution of a long-standing dilemma. DOC appears to be largely unreactive over time spans on the order of decades to hundreds of years (Williams & Druffel 1987, Bauer et al. 1992), yet it must be more reactive to maintain a balance between organic carbon and CO_2 inputs to the surface and deep oceans (Hedges 1987). A partial answer to the dilemma lies in observations that DOC degradation in the mixed layer near the ocean surface is enhanced by coupled physical and microbial processes.

For example, Johnson & Kepkay (1992) have shown that DOC in the colloid size range of 0.001 to 1.0 µm (Stumm 1977, Heimenz 1987) can escape bacterial degradation by virtue of its particle size characteristics. Once this untapped pool of organic material is brought into close contact with the bacteria by coagulation onto bubble surfaces, respiration increases dramatically (Kepkay & Johnson 1989). The heterotrophic community associated with the increase in respiration is

capable of rapidly turning over colloidal DOC, but only when the carbon is concentrated into microaggregates that are hundreds of µm across (Kepkay et al. 1990).

The results of Sugimura & Suzuki (1988), Koike et al. (1990) and Wells & Goldberg (1991) also suggest that colloidal DOC (variously described as 'submicrometer' or 'high molecular weight' carbon) is a predominant fraction of dissolved organic material in the upper ocean (Toggweiler 1990, 1992). Results from the ultrafiltration of seawater (Benner et al. 1992, Ogawa & Ogura 1992) suggest the opposite, that low molecular weight material (< 0.001 µm diameter) is the predominant fraction, accounting for 65 to 80 % of total DOC. Benner et al. (1992) have gone on to state that, even though their estimates of colloid-sized DOC are less than 10 % of the values obtained by Sugimura & Suzuki (1988), this DOC includes a substantial carbohydrate content, making it the most likely candidate for labile material that is turned over rapidly by the heterotrophic community.

The production of DOC by the phytoplankton is a more difficult issue to address. The majority of DOC originates either directly or indirectly from primary production in the photic zone (Druffel et al. 1992) but, with the exception of 2 studies of DOC release by phytoplankton in culture (Sharp 1973, Chen & Wangersky 1993a), there is very little information on the relationship between organic exudates released by the phytoplankton and DOC. There are, however, a number of studies (reviewed by Van Es & Meyer-Reil 1982, Fogg 1983, 1986) that delineate the production of extracellular exudates by ^{14}C-labelled phytoplankton in natural waters, and the rapid turnover of these exudates by heterotrophic activity. In addition, Kepkay & Wells (1992) have found positive linear correlations of DOC with chlorophyll and inverse correlations of DOC with apparent oxygen utilization (AOU) in the upper 100 m of both coastal and oceanic waters. While these correlations may lend substance to the notion that the DOC produced by phytoplankton is labile, they do not provide information on the size characteristics of a given DOC pool in relation to its production. In response to this lack of information, we describe here the size fractionation of DOC during a coastal spring bloom.

MATERIALS AND METHODS

Seawater collection and filtration. During March, April and May 1992, seawater was collected from Bedford Basin, Nova Scotia, Canada. The basin is a small (3 × 1.5 km) coastal bay connected to the Atlantic Ocean through Halifax Harbour and is subject to fresh water discharge from the Sackville River. One set of water samples was collected by 12 l Niskin bottle cast at 5 m intervals from the surface to 20 m. At the same time as the Niskin casts, a second set of large volume samples was taken for ultrafiltration using a peristaltic pump (to collect water from 5 m) or a 100 l GoFlo bottle (to collect water from 20 m).

Samples collected from the Niskin casts were analyzed for bulk chlorophyll *a* (chl *a*), suspended particulate material (SPM) and dissolved nutrients. Additional samples taken from the 5 m Niskin cast for total DOC analysis were filtered on board ship through fiberglass filters (Whatman GFF) that had been precombusted for 2 h at 450 °C; large volume samples were prepared for ultrafiltration by filtering on board ship through 0.2 µm cartridge filters (Gelman) that had been precleaned by flushing with 0.05M HCl, followed by deionized water (Millipore super Q) and seawater rinses. There were no discernable differences between the total DOC measured in large volume samples or in those passed through fiberglass filters (Kepkay unpubl. data). As a result, we concluded that the passage of ultrafiltration samples through precleaned 0.2 µm cartridges did not introduce detectable contamination.

All of the samples for DOC analysis were transferred as 100 ml aliquots to 250 ml pyrex bottles equipped with plastic caps, acidified to pH 1.6 with concentrated phosphoric acid and stored at 5 °C in the dark. We found that the bottles did not introduce contamination provided they were soaked overnight in 2 % NaOH (w/v), rinsed 5 times in distilled water and dried in an oven at 80 °C. As an additional safeguard against contamination, samples were taken for DOC analysis before sampling for chl *a*, dissolved nutrients and suspended particulates.

Temperature, salinity, chl *a*, nutrients and river discharge. Water temperature and salinity were monitored as continuous profiles by a Seabird CTD. Samples were taken for the analysis of chl *a* on Whatman GFF filters (Holm-Hansen et al. 1965) and for the analysis of dissolved nutrients (Irwin et al. 1988). Data on the discharge of Sackville River into Bedford Basin were provided by the Water Resources Branch of Environment Canada (A. Gilmore unpubl.)

Suspended particulate material. Size distribution and the total particle volume of suspended particulates were analyzed using a Coulter Multisizer II and the methods of Kranck & Milligan (1979). Fresh seawater from the Niskin bottles was counted with 30, 200 and 400 µm orifice tubes to produce a size distribution between 1 and 240 µm. The volume concentrations in each size class were plotted as log-log size spectra (see Fig. 7). As Kranck & Milligan (1988) have pointed out, these spectra represent distributions that are intermediate between a true, *in situ* aggregate size distribution and the single constituent particle or grain distribution.

Smaller aggregates and aggregate fragments are included in the size spectra, but larger aggregates are broken up by sample handling and shear in the orifice tubes (Kranck 1984).

Ultrafiltration. We adopted a modified version of Whitehouse et al.'s (1990) ultrafiltration procedure, incorporating a Millipore Pellicon cross-flow ultrafiltration system equipped with a Millipore PTGC filter cassette. A polysulfone membrane with a molecular weight (MW) cutoff of 10000 was installed in the cassette and retained material greater than 1 to 2 nm (0.001 to 0.002 µm) in diameter. This means that the term 'low molecular weight fraction' was applied to material less than 0.001 µm in diameter. The term 'colloidal fraction' was applied to material greater than 0.001 µm in diameter, but less than the 0.2 µm cutoff of the cartridge prefilter. These experimental definitions of the 2 ultrafiltration fractions were based on commonly-accepted descriptions (Stumm 1977, Heimenz 1987) of low molecular weight and colloidal material.

A large volume peristaltic pump was used to pass water from a polypropylene reservoir into the ultrafiltration membrane housing. The reservoir and housing assembly was cleaned and conditioned before each seawater ultrafiltration by leaching with 0.1 M HCl for at least 12 h, flushing with 30 l Milli-Q water, circulating 0.05 M NaOH for at least 30 min, flushing with an additional 30 l of Milli-Q water and soaking for at least 4 h with seawater that had been previously ultrafiltered. Approximately 100 l of 0.2 µm filtered seawater were then transferred from clean polypropylene jerricans to the reservoir and the system flushed with 10 l of the seawater. Ultrafiltration of the 100 l sample was then continued until the retentate (containing material that did not pass through the membrane) was reduced to 1 to 2 l. The time from sample collection and 0.2 µm prefiltration to completion of the ultrafiltration was typically 5 h.

The large ultrafiltration volumes were required for measurements of ^{234}Th, which were carried out on the samples analyzed for DOC. Material larger than the 1 to 2 nm pore size of the filter membrane became concentrated in the retentate while material smaller than the pore size remained at its original concentration in both the retentate and ultrafiltrate. This means that the concentration of DOC and ^{234}Th in the retentate had to be corrected for the concentration of smaller material (equal to the DOC and ^{234}Th measured in the ultrafiltrate) and for the reduction in retentate volume during ultrafiltration (Hoffmann et al. 1981). We have concentrated here on the results from DOC analyses; the ^{234}Th measurements (Niven unpubl.) will be discussed elsewhere.

Total DOC in the large volume samples was similar to the total DOC in samples filtered through precombusted Whatman GFF filters (Kepkay unpubl.) to within the standard deviation of quadruplicate analyses (2 to 6 µM C). This means that there was no discernable contamination introduced into the large volume samples by prefiltration through the 0.2 µm cartridges. However, when mass balances were calculated and the sum of low molecular weight and colloidal DOC compared to total DOC, there was considerable loss of organic carbon to the ultrafiltration system (see Tables 1 & 2) between 24 March and 22 April (Days 84 to 113), a period of time associated with heavy discharge of the Sackville River (see Figs. 2 & 3). Our ultrafiltration methods were the same throughout, and good mass balances (98.6 ± 4.8 %, n = 5) were achieved before and after the period of DOC loss. As a result, we attributed the loss to surface active material retained by the ultrafiltration system and reported the loss as surface active DOC.

Dissolved organic carbon. In the laboratory, filtered and acidified samples were transferred as 5 ml aliquots into pre-cleaned 10 ml pyrex test-tubes and analyzed for DOC by high temperature catalytic oxidation in an Ionics Model 1500 Carbon Analyzer (Watertown, MA, USA) equipped with a ceramic slider auto-injection valve and auto-sampler. We employed a sample sequence of repeatedly injecting 2 acidified aliquots of seawater followed by 2 injections of acidified distilled water into the oxidation furnace to avoid rapid salt build-up on the catalyst. Prior to analysis, the acidified seawater samples were sparged in batches with CO_2 free oxygen for 10 min to remove inorganic carbon. Each sample of acidified water was then sparged for a further 90 s just prior to injection into a quartz combustion tube to ensure the complete removal of inorganic carbon. Once this final sparge was complete, the acidified sample was then aspirated into a teflon sample loop and 80 µl were drop-injected onto a platinum catalyst in the combustion tube. Effluent from the rapid combustion of the 80 µl drop at 790 °C was swept by the carrier gas (CO_2 free oxygen) through a series of traps before entering a Horiba non-dispersive infrared (NDIR) analyzer. After passing through a water separator, the effluent passed through a tin-shot trap to remove HCl vapour, a pyrex U-tube at 1 °C and a $Mg(ClO_4)_2$ trap to remove water vapour, and a particle filter (Balston type 9900-05-BK) to remove sea-salt and phosphoric acid aerosols before entering the NDIR analyzer. The signal generated by the NDIR detection of CO_2 was quantified as peak area on a Hewlett Packard model 3396 integrator.

The concentration of DOC in each sample was determined from standard curves generated daily by the analysis of 50, 100, 150 and 200 µM C (as glucose) in acidified photo-oxidized seawater or distilled water. The analysis of standards in either the salt-free or salt-

bearing analytical matrix resulted in standard curves with slopes that were similar to within 2 to 5 % (the standard deviations of 2 to 6 µM C that were typical of standard and sample analyses). Slopes of the standard curves varied by 5 to 7 % from day to day, but care had to be taken to avoid the long term accumulation of salt on the catalyst. This salt buildup took place despite the repeated injection of acidified distilled water and, over time, caused relatively large (20 to 50 %) variations in curve slopes. Salt accumulation also tended to increase the *y*-axis offset of curves and the apparent concentration of DOC in photo-oxidized seawater or distilled water.

The analysis of standard additions of glucose to distilled water resulted in an analytical blank of 35 to 45 µM C when curves were extrapolated back to *x*-axis intercepts. This was not a true instrument blank (which should be subtracted from a given DOC analysis) because it included the organic carbon that was oxidized in the distilled water. We determined the carbon content of the distilled water independently by subjecting samples to the high temperature distillation and combustion process of Chen & Wangersky (1993b). From DOC analyses before and after high temperature distillation and combustion, we were able to determine that the contribution of distilled water to the analytical blank was no greater than 10 µM C. This means that the instrument blank was 25 to 35 µM C out of a total analytical blank of 35 to 45 µM C; the instrument blank was subtracted from all of our DOC measurements. Even though this blank reflects the current state of the art in DOC analysis, it does not include the effect of salt accumulated in the combustion tube (Tanoue 1992). As a result, it cannot be regarded as a true instrument blank until the carbon associated with salt residues from a seawater analytical matrix are accounted for explicitly.

RESULTS

DOC, river discharge and chl *a*

Between 10 March (Day 70) and 27 May (Day 148) chl *a* increased at 5 m, reaching a small preliminary maximum of 3.4 µg l^{-1} at 90 to 94 d and an overall maximum of 13.0 µg l^{-1} by 115 d (Fig. 1A). Dissolved nutrients decreased by only small amounts from 94 to 105 d (Fig. 1B), suggesting that the small increase in chl *a* was associated with a short-lived, preliminary phytoplankton bloom. True bloom conditions (Irwin et al. 1988), when nutrients dropped to low concentrations (Fig. 1B), were not apparent until 110 d and were associated with the development of the chlorophyll maximum at the height of the bloom (Fig. 1A). The dominant phytoplankton species at the height of the bloom was *Chaetoceros socialis*, accounting for 61 to 77 % of microplankton numbers between 105 and 128 d (S. R. Durvasula unpubl.); there was no discernable increase in zooplankton number throughout the bloom (A. Ciotti unpubl.).

During the preliminary bloom (from 70 to 105 d), discharge of the Sackville River increased, reaching a maximum at 90 to 94 d (Fig. 2A). This maximum in river discharge caused an abrupt decrease in salinity at 5 m (Fig. 2B) and was associated with a storm from the northwest. The storm interrupted the preliminary bloom by diluting the mixed layer and flushing it out of Bedford Basin into Halifax Harbour. After the storm and during the height of the bloom (from 105 to 142 d), river discharge and salinity both remained low (Fig. 2).

During the preliminary bloom (from 10 March to 14 April), surface active and total DOC increased (by 47.4 and 79.9 µM respectively), reaching maximum concentrations at Day 94 (Fig. 3B, Table 1), 4 d after the weak chlorophyll maximum (Fig. 3A). Low molecular weight DOC also increased by 15.8 µM C (Fig. 3C, Table 1),

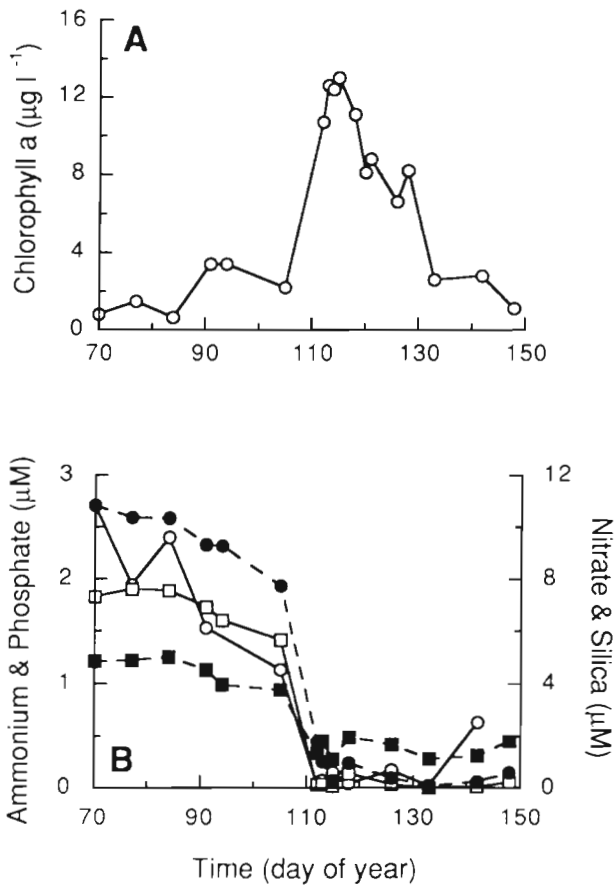

Fig. 1 (A) Chl *a* concentration and (B) dissolved silicate (●), phosphate (■), ammonia (○) and nitrate (□) at a depth of 5 m in the mixed layer from 10 March (Day 70) to 27 May (Day 148) 1992

Table 1. Low molecular weight, colloidal, surface active and total DOC at 5 m in Bedford Basin during the preliminary bloom in spring 1992 (Days 70 to 105)

Date	Day of year	Low MW DOC (µM C)	(% of total)	Colloidal DOC (µM C)	(% of total)	Surface active DOC (µM C)	(% of total)	Total DOC (µM C)
10 Mar	70	69.4	88.7	12.9	16.5	-4.1	-5.2	78.2
17 Mar	77	64.0	90.8	7.5	10.6	-1.0	-1.4	70.5
24 Mar	84	63.8	74.3	7.2	8.4	14.9	17.3	85.9
31 Mar	91	77.9	73.3	4.7	4.4	23.7	22.3	106.3
3 Apr	94	86.9	55.0	8.9	5.6	62.3	39.4	158.1
14 Apr	105	85.2	74.3	5.5	4.8	22.1	19.3	114.7

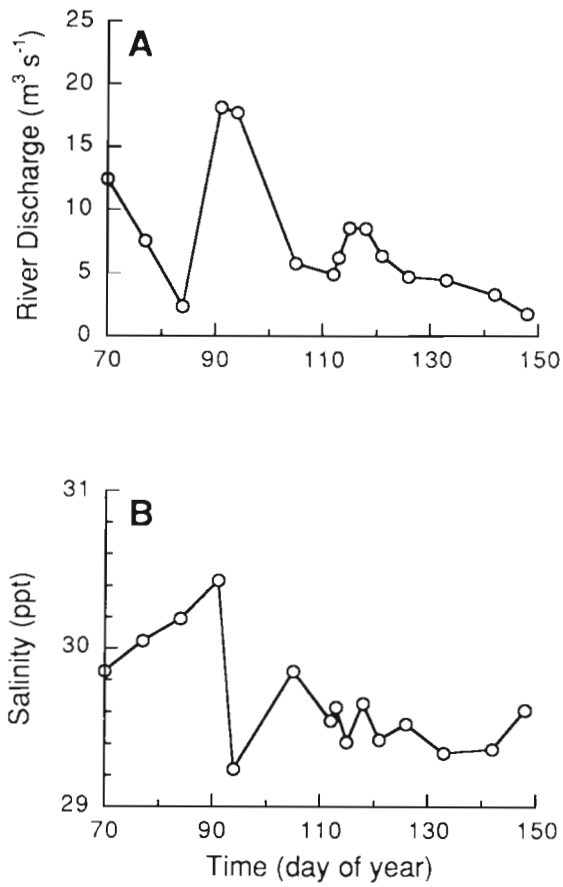

Fig. 2. (A) Discharge of the Sackville River into Bedford Basin and (B) salinity at a depth of 5 m in the mixed layer from 10 March (Day 70) to 27 May (Day 148) 1992

but colloidal DOC actually decreased (by 7.4 µM C) from 70 to 105 d. The increase in total DOC during this period was primarily related to the increase in a surface active fraction (Fig. 3B), which was between 11.4 and 39.4 % of the total (Tables 1 & 2) and was associated with the maximum in river discharge at 90 to 94 d (Fig. 3A). The surface active fraction was defined as the DOC lost to the ultrafiltration system. This loss was apparent only when the river discharge was near its maximum (Tables 1 & 2). Before and after the maximum, the mass balances for accumulated ultrafiltration fractions were 98.6 ± 4.8 % (n = 5) of the total DOC.

In contrast to results from the preliminary bloom, a far greater increase in chl *a* at 5 m (Fig. 4A) was found at the height of the bloom between 14 April and 21 May (Days 105 and 142). While the mean value for total DOC within this time period was slightly greater than the mean calculated for the preliminary bloom (Table 3), total DOC (Fig. 4B) did not increase or decrease in association with chl *a*. Surface active DOC decreased by 15.1 µM C from 105 to 133 d (Fig. 4B, Table 3), as river discharge remained low (Fig. 4A). Low molecular weight DOC increased by almost the same amount, i.e. 16.4 µM C (Fig. 4C), reaching a maximum 3 to 6 d after the chlorophyll maximum (at Day 118). Colloidal DOC increased by 12.8 µM C (Fig. 4C) reaching a maximum at 126 d, 11 to 14 d after the chlorophyll maximum and 8 d after the maximum in low molecular weight DOC.

When salinity and nutrient analyses from the 100 l

Table 2. Low molecular weight, colloidal, surface active and total DOC at 5 m in Bedford Basin at the height of the bloom in spring 1992 (Days 105 to 133)

Date	Day of year	Low MW DOC (µM C)	(% of total)	Colloidal DOC (µM C)	(% of total)	Surface active DOC (µM C)	(% of total)	Total DOC (µM C)
14 Apr	105	85.2	74.3	5.5	4.8	22.1	19.3	114.7
21 Apr	112	87.0	80.6	8.6	8.0	12.3	11.4	107.9
22 Apr	113	88.6	75.5	8.3	7.1	20.4	17.4	117.3
27 Apr	118	101.6	82.9	14.4	11.7	6.6	5.4	122.6
5 May	126	94.2	82.6	18.3	16.1	2.3	2.0	114.0
12 May	133	94.7	85.2	9.4	8.5	7.0	6.3	111.1

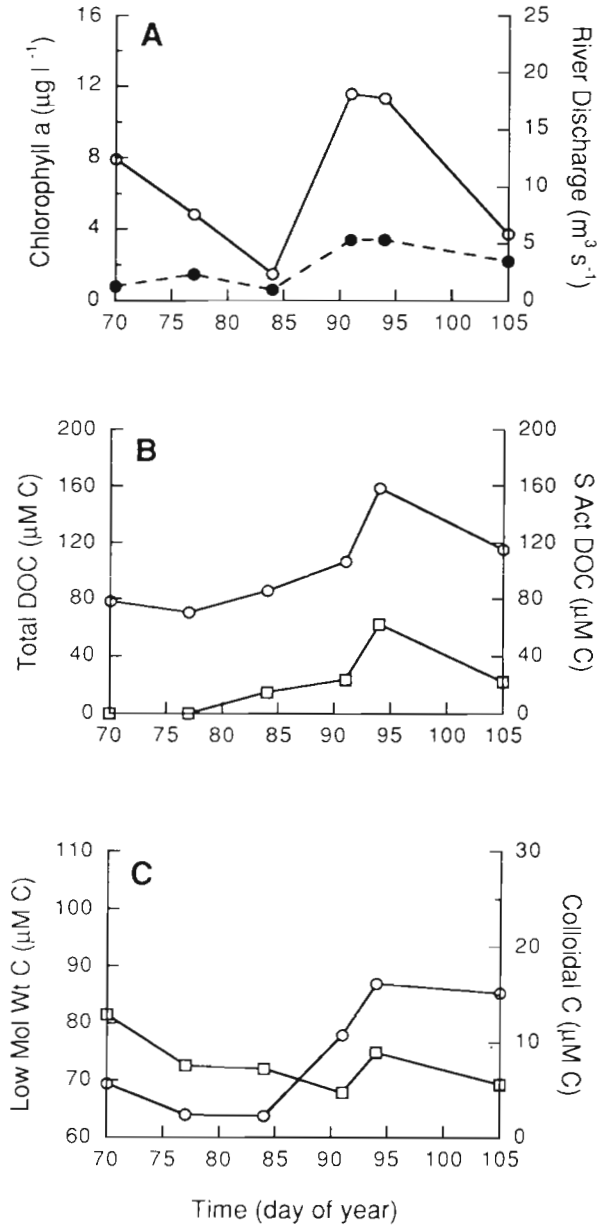

Fig. 3. (A) River discharge (○) and chl *a* (●) at 5 m during the preliminary bloom in Bedford Basin from 10 March (Day 70) to 14 April (Day 105) 1992. (B) Total DOC (○) and surface active DOC (□). (C) Low molecular weight DOC (◌) and colloidal DOC (□)

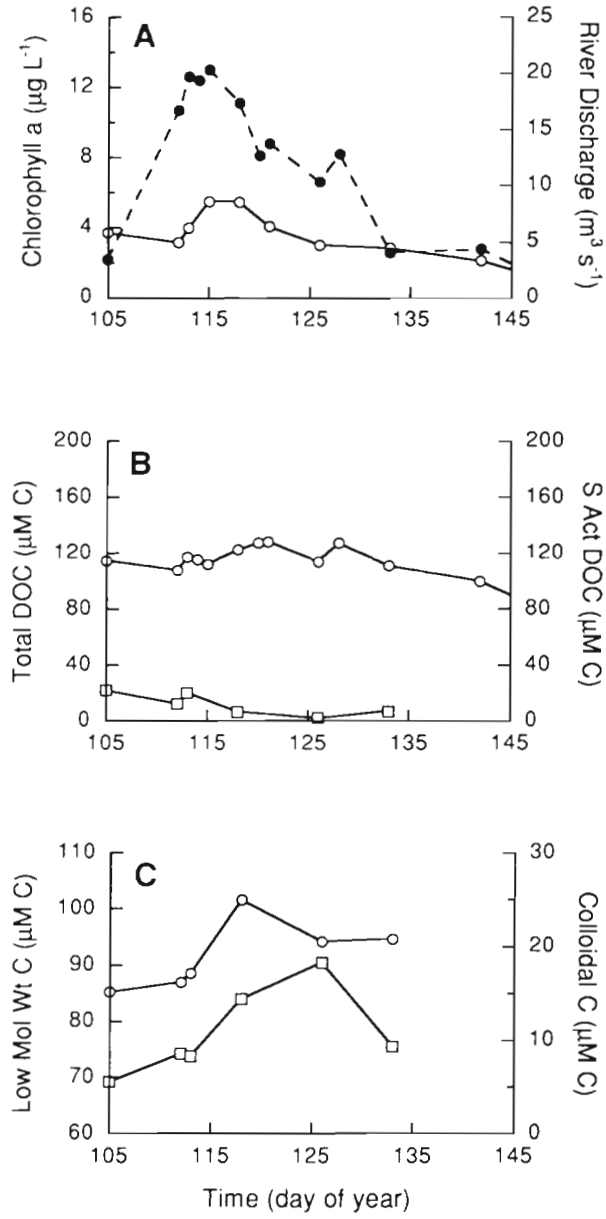

Fig. 4. (A) River discharge (◌) and chl *a* (●) at 5 m during the height of the bloom in Bedford Basin from 14 April (Day 105) to 21 May (Day 142) 1992. (B) Total DOC (◌) and surface active DOC (□). (C) Low molecular weight DOC (○) and colloidal DOC (□)

Table 3. Mean DOC concentration at 5 m in Bedford Basin during the preliminary bloom (Days 70 to 105) and at the height of the bloom (Days 105 to 133) in spring 1992. The data used to calculate the means appear in Tables 1 & 2. n = 6 for each period

Date	Day of year	DOC concentration (µM C) Mean	Range	SD
10 Mar–14 Apr	70–105	102.3	70.5–158.1	32.1
14 Apr–12 May	105–133	114.6	107.9–122.6	5.1

GoFlo bottle were compared with the equivalent data from 12 l Niskin casts, it was clear that surface water was not completely flushed out of the larger volume GoFlo before samples were retrieved. As a result, we have not reported data collected from large volume samples taken at 20 m. However, independent measurements of DOC from Niskin casts (W. Chen unpubl.) showed that DOC at 20 m increased after the chlorophyll maximum, reaching 140.5 µM C by 142 d.

Suspended particulate material and chl *a*

The time series of total particle volume of suspended particulate material (SPM) was similar to that of chl *a* at both 5 and 20 m (Fig 5). This covariation of chl *a* and SPM agrees with Kranck & Milligan's (1988) observation that Coulter counts are estimates of the number of small diatom aggregates, the prime constituent of microplankton populations during blooms in Bedford Basin. The variations in chl *a* and SPM at 5 m reached a small maximum at 94 d during the preliminary bloom (Fig. 5A) and a far greater maximum at 112 to 115 d, during the height of the bloom. There was an overall migration of the SPM maximum downward from 5 to 20 m between 115 and 142 d (Fig. 5C); at 20 m, chl *a* and SPM reached a maximum at 142 d (Fig. 5B), well after the height of the bloom.

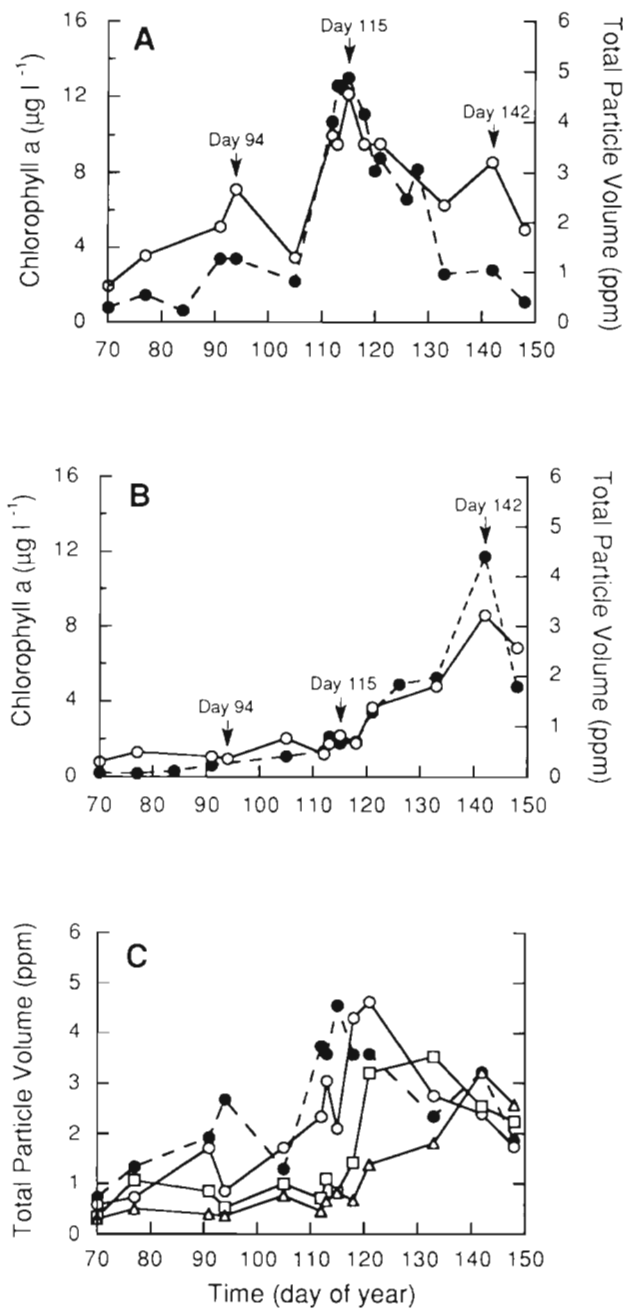

Fig. 5. Chl *a* (●) and total particle volume (ppm) of suspended particulate material (○) at (A) 5 m and (B) 20 m from 10 March (Day 70) to 27 May (Day 148) 1992. Arrows indicate preliminary bloom (Day 94), height of the bloom (Day 115) and a time point after the bloom (Day 142). (C) Total particle volumes of SPM at 5 m (●), 10 m (○), 15 m (□) and 20 m (△)

CTD profiles from 94, 115 and 142 d (Fig. 6) delineate the overall sequence of physical and biological events during the bloom. At Day 94, the relatively low temperature and salinity of surface water extended down to about 10 m (Fig. 6A) and was associated with a relatively small increase in chl *a* over almost the entire mixed layer (Fig. 6B). At the height of the bloom, a mixed layer of warmer saline water (Fig. 6C) extended down to about 7 m at 115 d and was associated with far greater concentrations of chl *a* (Fig. 6D). Finally, as the bloom declined, a mixed layer of even warmer surface water extended down to about 6 m at 142 d (Fig. 6E) with a relatively small chlorophyll maximum at 5 m (Fig. 6F). By this time, the main chlorophyll maximum had developed well below the mixed layer, presumably as phytoplankton settled out to a depth of 20 to 25 m (Fig. 6F).

The size spectra of SPM at 5 and 20 m underwent considerable changes between 94, 115 and 142 d (Fig. 7). During the preliminary bloom, the size spectra at 94 d (Fig. 7A) were dominated by 2 peaks between particle or aggregate diameters of 6 to 15 µm and 40 to 80 µm. These peaks were particularly pronounced at the higher particle volumes recorded at 5 m and were an order of magnitude greater than concentrations of particles in other size classes. Kranck & Milligan (1988) have suggested that particles contributing to a 30 to 80 µm peak during the 1986 spring bloom at the same site were probably aggregates of chain-forming diatoms, such as the predominant genus in this study – *Chaetoceros*. The cells of *Chaetoceros socialis*, which accounted for 61 to 77 % of total microplankton counts at the height of the bloom (S. R. Durvasula unpubl.), were typically 6 to 12 µm across and often imbedded as chains in a mucus matrix. These cells may have been responsible for the 6 to 15 µm peak in the Coulter size spectra (Fig. 7A).

By 115 d, when the bloom had reached its height, size spectra had progressed toward peaks between 6 and 60 µm at 5 m and 30 to 60 µm at 20 m (Fig. 7B). Particle or aggregate concentrations at 20 m were between 2 and 10 times less than the concentrations found at 5 m. In contrast, the size spectra at 5 and 20 m were similar in shape at 142 d, with peaks between 6

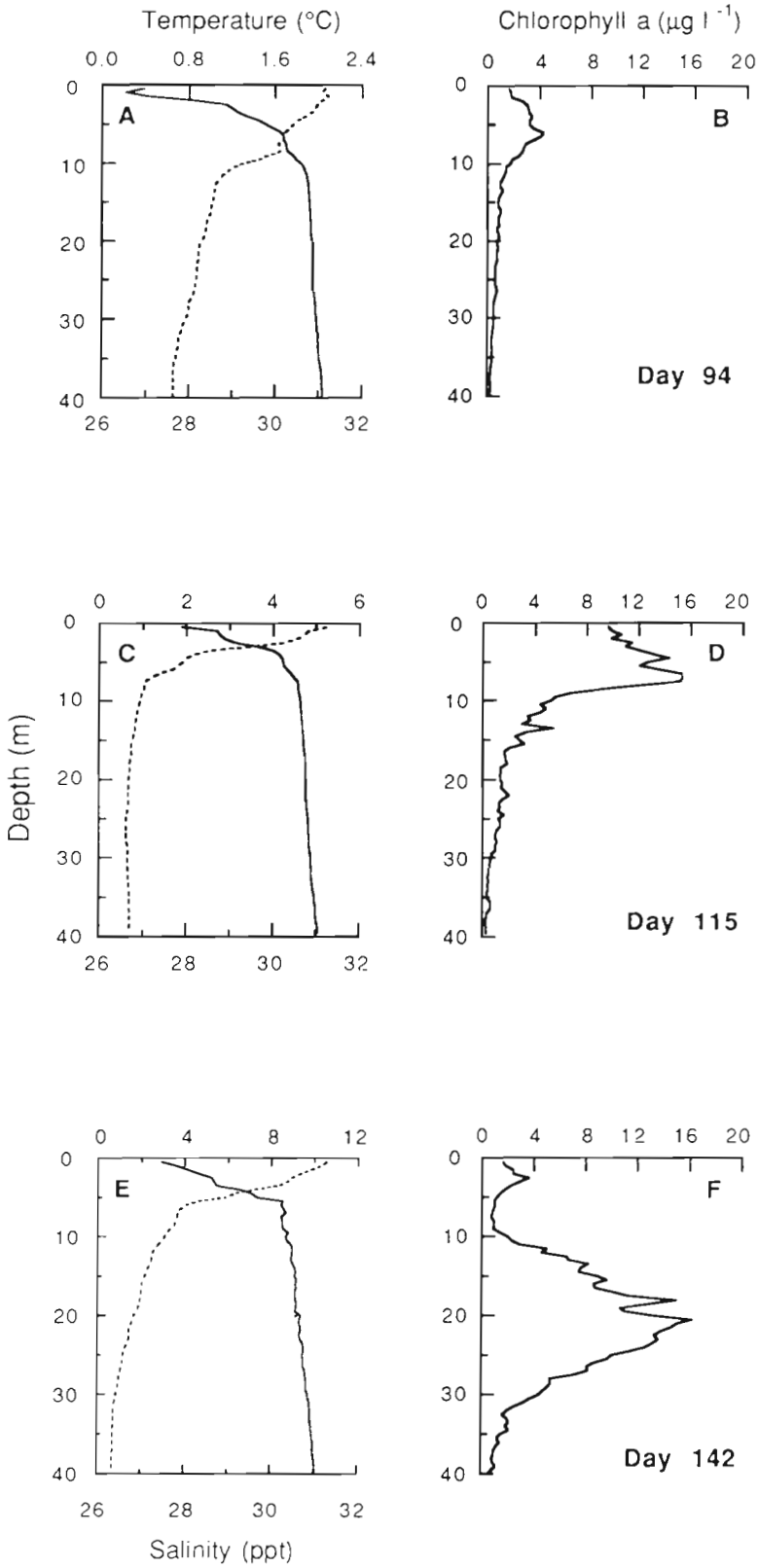

Fig. 6. Salinity (——) and temperature (– – –) profiles (A, C, E), and chl *a* profiles (B, D, F) from CTD casts during the preliminary bloom (Day 94), the height of the bloom (Day 115) and after the bloom (Day 142)

and 60 µm (Fig. 7C). More importantly, the particle or aggregate concentrations at 20 m were far higher than previously recorded (Fig. 7A, B) and, for the first time, were similar to those found at 5 m (Fig 7C).

DISCUSSION

The spring bloom at 5 m in the mixed layer of Bedford Basin (Figs. 1 & 2) can be described in terms of 2 main events: (1) a preliminary bloom (from 70 to 105 d), which was interrupted by a northwesterly storm and an increase in river discharge (Fig. 3); (2) the bloom at its height (from 105 to 142 d), which was associated with a sharp decrease in dissolved nutrients and low river discharge (Fig. 4). During the preliminary bloom (Fig. 3), an approximately 70 µM C increase in total DOC (Fig. 3B) lagged behind a small (3 µg l^{-1}) increase in chl *a* by 4 d (Fig. 3A). Chen & Wangersky (1993b) found a similar (5 d) lag between chlorophyll and DOC maxima in the 1991 spring bloom in Halifax Harbour; they attributed the lag to the production of DOC from ageing phytoplankton cells.

The increase in total DOC that we measured could not be attributed to the phytoplankton. When a carbon to chl *a* ratio (Θ) of between 40 and 100 (Li et al. 1993, B. Irwin unpubl.) was applied to our data (Fig. 3A), the phytoplankton biomass associated with a 3 µg l^{-1} increase in chl *a* was 10 to 25 µM C. This is 3 to 5 times less than the carbon required to produce the observed 70 µM C increase in total DOC (Table 1). The increase in total DOC was coincident with an increase in the DOC lost to the ultrafiltration system during separation of low molecular weight and colloidal fractions. The same ultrafiltration methods were used throughout the bloom and there was good agreement between the mass balances obtained before and after the DOC maximum (with the sum of fractions accounting for 98.6 ± 4.8 % of the total). As a result, we attributed this DOC loss to an increase in surface active material in the mixed layer (Fig 3B, Table 1).

The increase in total and surface active DOC (Fig. 3B) coincided with the increase in river discharge (Fig. 3A). Studies of the 'flushing effect' of rivers (reviewed by

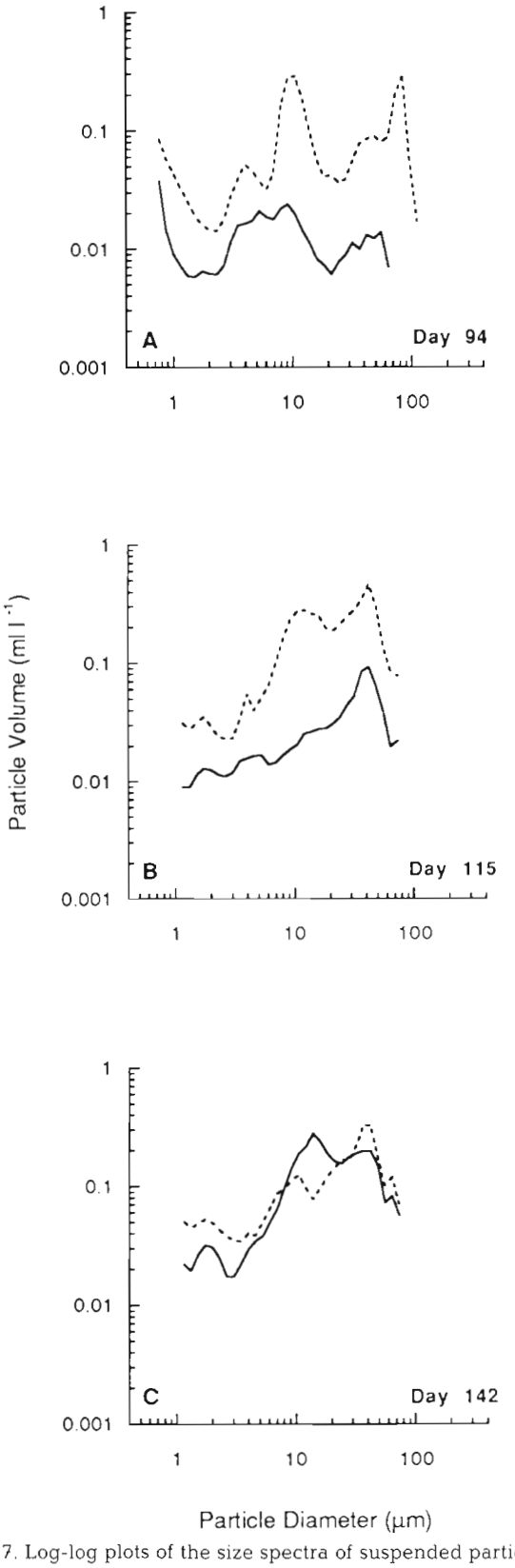

Fig. 7. Log-log plots of the size spectra of suspended particulate material at 5 m (- - - -) and 20 m (——) during the preliminary bloom at (A) Day 94, (B) the height of the bloom at Day 115 and (C) after the bloom at Day 142

Spitzy & Leenheer 1991) suggest that the concentration of DOC in a river increases as discharge increases and that the primary source of this DOC is terrestial material that can resist degradation. We could not determine whether surface active DOC from the mixed layer was terrestrial in origin, or even if it was in the low molecular weight or colloidal size range. However, our results do suggest that freshwater runoff and river discharge should be carefully monitored when measuring DOC during blooms in coastal waters like those found in Bedford Basin.

Even though mean DOC concentration at the height of the bloom was slightly greater than the mean recorded during the preliminary bloom (Table 3), total and surface active DOC changed very little over time (Fig. 4B). In contrast, low molecular weight and colloidal DOC both increased (Fig. 4C), lagging behind the chlorophyll maximum (Fig. 4A) by 3 to 6 d and 11 to 14 d respectively. The 3 to 6 d gap between the chlorophyll and low molecular weight DOC maxima was not related to the effects of predation on the phytoplankton because zooplankton numbers remained low throughout the bloom (A. Ciotti unpubl.). The 8 d gap between maxima for low molecular weight and colloidal DOC may have been related to the time required to coagulate low molecular weight material into colloid-sized aggregates. However, 8 d is more than enough time to induce coagulation in the mixed layer (Jackson 1990) and the delay between low molecular weight and colloid maxima could equally have been related to the release of colloidal material, e.g. as viruses (Suttle et al. 1990), by ageing, infected phytoplankton. At this point, we cannot distinguish between either of these suggestions; more information on the type of DOC released by phytoplankton is required.

When a carbon to chlorophyll ratio of 40 to 100 (Li et al. 1993, B. Irwin unpubl.) was applied to the approximately 10 μg l^{-1} increase in chl *a* at the height of the bloom (Fig. 4A), the increase in phytoplankton biomass was 30 to 80 μM C. The combined increase in low molecular weight and colloidal DOC was approximately 25 μM C (Fig. 4C, Table 2), i.e. of the same order of magnitude as the increase in phytoplankton carbon. When the uncertainties involved in the application of carbon to chlorophyll ratios (Li et al. 1993) are taken into account, the agreement between accumulated DOC fractions and phytoplankton carbon is fairly close. As a result, the phytoplankton appear to have been the main source of low molecular weight and colloidal DOC at the height of the bloom, when river discharge (Fig. 4A) and surface active DOC (Fig. 4B) were low. To our knowledge, the data in Fig. 4 are the first evidence for phytoplankton as the principle source of specific fractions of DOC. They agree with the results from a number of studies (reviewed by Van Es &

Meyer-Reil 1982, Fogg 1983, 1986) of organic exudate production by ^{14}C-labelled phytoplankton in natural waters. Heterotrophic communities appear to be closely coupled to the production of these exudates and are capable of rapidly turning over the organic carbon released.

At the height of the bloom, coagulation may have been responsible for the small variations in DOC associated with the large increase in chl *a* (Fig. 4). The coagulation of phytoplankton cells during blooms and their rapid settling out as macro-aggregates have been well documented (Billet et al. 1983, Alldredge & Gottschalk 1988, Kranck & Milligan 1988). Our data (Figs. 5 & 6) also indicate that coagulation occurred, with the settling out of SPM and chl *a* from the mixed layer as the bloom declined between 115 and 142 d. During this time, the size spectra of SPM changed (Fig. 7) so that, by 142 d, the spectra were similar in both magnitude and shape at 5 and 20 m. The coagulation of phytoplankton cells (as chlorophyll-rich SPM) could have acted to limit the concentration of colloidal DOC at 5 m by inducing the further coagulation of colloid-sized material (as suggested by Logan & Hunt 1987, Honeyman & Santschi 1989, Logan & Alldredge 1989). The transport of this carbon out of the mixed layer would then lead to the build up of DOC at depth as aggregates continued to age. An increase in total DOC was, in fact, measured at 20 m as the bloom declined (W. Chen unpubl.), reaching a maximum of 140.5 µM C at 142 d.

Jackson's (1990) model of aggregate dynamics can be used to verify our contention that coagulation was in operation at the height of the bloom. His model treats an algal bloom as a 2-state system in which coagulation is either not important when phytoplankton numbers are low or is dominant when phytoplankton exceed a critical cell number (C_{cr}) determined by cell physiology and the hydrodynamic environment. The predominant species of phytoplankton during the bloom was *Chaetoceros socialis* (S. R. Durvasula unpubl.) which had a cell diameter of about 10 µm. If the rate of turbulent energy dissipation (ε) at 5 m was 0.04 $cm^2\ s^{-3}$ (Oakey & Elliot 1982, Soloviev et al. 1988), the specific growth rate (μ) of cells was 1.0 d^{-1} and the probability of cells sticking together on collision (α) was 0.25, the C_{cr} estimated from Jackson's (1990) plots was 29×10^3 cells ml^{-1} The actual number of cells recorded at the height of the bloom was between 17 and 24×10^3 cells ml^{-1} at 115 d (S. R. Durvasula unpubl.). Given the uncertainties involved in defining cell diameter, cell shape and cell stickiness (Jackson 1990), and Oakey & Elliot's (1982) conclusion that individual estimates of ε are known to within a factor of 2, the measured number of cells was in reasonable agreement with the C_{cr} predicted by Jackson (1990).

On the basis of data obtained by gel permeation chromatography, Sugimura & Suzuki (1988) suggested that high molecular weight or colloidal material is a major component of DOC in seawater. Data obtained by ultrafiltration (Benner et al. 1992, Ogawa & Ogura 1992) suggest the opposite, that low molecular weight fractions predominate, accounting for 65 to 80 % of total DOC. We found that low molecular weight DOC, i.e. organic carbon less than 0.001 µm in diameter (or a molecular weight of 10000) was between 55 and 91 % of total DOC during the bloom in Bedford Basin (Tables 1 & 2). At its maximum colloidal DOC, i.e. carbon between 0.001 and 0.2 µm in diameter, was only 16 % of the total (Table 2). Benner et al. (1992) have suggested that, even though their contribution to the oceanic DOC budget is small, colloids may still be the most important component of labile DOC due to their carbohydrate content. However, to obtain any quantitative idea of the lability of colloidal DOC, a clear relationship must be established between this important fraction of the DOC pool and phytoplankton as its source. In our data set, the relationship between colloidal DOC, total DOC and phytoplankton biomass (expressed as chl *a*) is not entirely clear for 3 reasons: (1) a direct link between total and colloidal DOC could not be established because surface active DOC (associated with river discharge) was found in the mixed layer (Figs. 3 & 4); (2) the increase in colloidal DOC that we observed was almost 2 wk after the chlorophyll maximum (Fig. 4); and (3) the effects of coagulation at the height of the bloom could have removed colloidal DOC, transporting it to greater depths.

We certainly did not find the linear correlations between total DOC and chl *a* that Kepkay & Wells (1992) found in the mixed layer on the Scotian Shelf and Slope. On the contrary, total DOC remained almost invariant as chl *a* increased at the height of the bloom and then decreased (Fig. 4). Linear correlations of DOC with chl *a* or apparent oxygen utilization (AOU) could be considered as strong evidence for phytoplankton as a source and heterotrophic oxidation as a sink of DOC. At this point, however, it is important to note that Kepkay & Wells (1992) and Tanoue (1992) have both stated that these relationships may be more casual than systematic and cannot be applied ocean wide. It has not been possible to establish a consistent and reproducible relationship between DOC and AOU or phytoplankton biomass.

In conclusion, the production and size fractionation of DOC during the bloom in Bedford Basin was controlled by a number of factors, including river discharge (Fig. 3) and the onset of the chlorophyll maximum (Fig. 4). Low molecular weight and colloidal DOC accumulated in the mixed layer (Fig. 4), but only after a critical number of phytoplankton cells had been

reached at the height of the bloom. In addition, the accumulation of colloidal DOC accounted for a maximum of only 16 % of total DOC (Table 2), but this relatively small pool of DOC could have been the most labile, turning over rapidly in response to heterotrophic degradation. It is also important to remember that all of the colloidal DOC produced during the bloom did not necessarily accumulate in the mixed layer. Instead, it may have coagulated with phytoplankton aggregates and been transported downward, contributing to the eventual release of DOC in deeper water. The downward transport of DOC has been advanced as a key issue in the transport of carbon to the deep ocean (Toggweiler 1990, Bacastow & Maier-Reimer 1991). Accurate definitions of this transport must now include the production and transport of both low molecular weight and colloidal fractions, and also include colloidal DOC that has coagulated with aggregates.

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