Phytoplankton dynamics in the Barents Sea estimated from chlorophyll budget models

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Pigment budgets use chlorophyll *a* and phaeopigment standing stock in combination with their photooxidation and sedimentation rates in the euphotic zone to estimate phytoplankton growth and grazing by micro- and macrozooplankton. Using this approach, average phytoplankton growth in the euphotic zone of the Barents Sea was estimated at 0.17 and 0.14 d^{-1} during spring of 1987 and 0.018 and 0.036 d^{-1} during late- and postbloom conditions in summer of 1988. Spring growth was 65% lower than the estimates from radiocarbon incorporation, supporting a 33% pigment loss during grazing. Macrozooplankton grazing and cell sinking were the main loss terms for phytoplankton during spring while microzooplankton grazing was dominant in summer.

In contrast to tropical and temperate waters, Arctic waters are characterized by a high phaeopigment : chlorophyll *a* ratio in the seston. Photooxidation rates of phaeopigments at in situ temperatures (0 ± 1°C) are lower than in temperate waters and vary by a factor of 2 for individual forms (0.009 to 0.018 $m^{-2}\,mol^{-1}$). The phaeopigment fraction in both the suspended and sedimenting material was composed of seven main compounds that were isolated using high-performance liquid chromatography and characterized by spectral analysis. The most abundant phaeopigment in the sediment traps, a phaeophorbide-like molecule of intermediate polarity (phaeophorbide a_3), peaked in abundance in the water column below the 1% isolume for PAR (60–80 m) and showed the highest rate of photooxidation. This phaeopigment was least abundant in the seston when phytoplankton was dominated by prymnesiophytes but increased its abundance in plankton dominated by diatoms. This distribution suggests that larger grazers feeding on diatoms are the main producers of this phaeopigment.

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Introduction

Estimates of phytoplankton growth and fate of the newly formed carbon are essential to our understanding of the physical and biological processes that govern the distributions and transformations of organic matter in an aquatic ecosystem. Due to its specificity to plants, chlorophyll *a* has been successfully used as a tracer of phytoplankton carbon for the last 40 years (Richards & Thompson 1952) and is one of the best estimators of phytoplankton abundance in marine waters. Chlorophyll *a* degradation products, in particular the fluorescent compounds, are tracers of phytoplankton carbon in processes such as grazing (Currie 1962), sedimentation (Lorenzen et al. 1981; Bathmann & Liebezeit 1986), and diagenesis in sediments (Daley & Brown 1973; Hurley & Amstrong 1990).

Because of their specificity and abundance, photosynthetic pigments have become important tools in phytoplankton identification (Jeffrey 1974; Hooks et al. 1988). Several forms of chlorophyll *a* (Brown 1985; Chisholm et al. 1988) and chlorophyll *c* (Jeffrey & Wright 1987; Nelson & Wakeham 1989) in marine phytoplankton are used as tracers of certain phyla. Fucoxanthin (Stauber & Jeffrey 1988), fucoxanthin derivatives (Wright & Jeffrey 1987; Bjørnland et al. 1988), and xanthophylls (Gieskes & Kraay 1983, 1986; Guillard et al. 1985) are by themselves or in combination with the chlorophylls also used as markers. Although not altogether quantitative, this approach is complementary to other techniques such as microscopy and can give a first approximation to the complexity and composition of the phytoplankton assemblage.

Chlorophyll degradation products are considered quantitative estimators of grazing (Shuman & Lorenzen 1975) and have been used in laboratory (Landry et al. 1984) and field studies (Welschmeyer et al. 1984; Downs & Lorenzen 1985) of herbivory activity. Based on premises of stoichiometric degradation of chlorophyll by

herbivory, Welschmeyer & Lorenzen (1985) developed a pigment budget model to estimate phytoplankton growth and losses. This model uses chlorophyll *a* and phaeopigment standing stock in combination with their photooxidation and sedimentation rates in the euphotic zone to estimate phytoplankton growth and grazing by micro- and macrozooplankton. The model assumes that chlorophyll *a* is only associated with phytoplankton while phaeopigments are product of the stoichiometric degradation of chlorophyll *a* due to grazing (or at least with a known loss fraction).

The usefulness of fluorescent degradation products as quantitative estimation of grazing has been challenged by a number of laboratory studies. Klein et al. (1986), Conover et al. (1986) and Lopez et al. (1988) found high and variable (0–99%) pigment losses in grazing experiments. In contrast, field applications have found low (10–33%) losses (Dagg & Walser 1987; Downs 1989). Laws et al. (1988), assuming a 33% pigment loss, found high correlation between growth rates estimated from the pigment budget model and radiocarbon incorporation. It is clear that more experimentation is needed before we can understand the factors associated with this discrepancy.

In this study, phytoplankton growth and zooplankton grazing in the euphotic zone were estimated by a chlorophyll budget model. Distribution, sedimentation, and photooxidation rates of phytoplankton pigments, in particular chlorophyll *a* and its degradation products, are used as indicators of synthesis and transformation of organic carbon in the Barents Sea. When available, the output of the pigment budget model is compared to other estimates in order to assess the usefulness of this approach for Arctic waters.

Methods

Samples for water column and sedimenting particles were collected during two cruises to the Western Barents Sea. The Pro Mare cruise 11 on R/V G.O. SARS from 15 May to 12 June 1987 visited 2 stations with 2 sediment trap deployments at each station. Pro Mare cruise 15, on Norwegian Coast Guard K/V ANDENES, from 1 to 21 July 1988, visited 2 stations with one trap deployment at each station. Dates, positions, depth, and

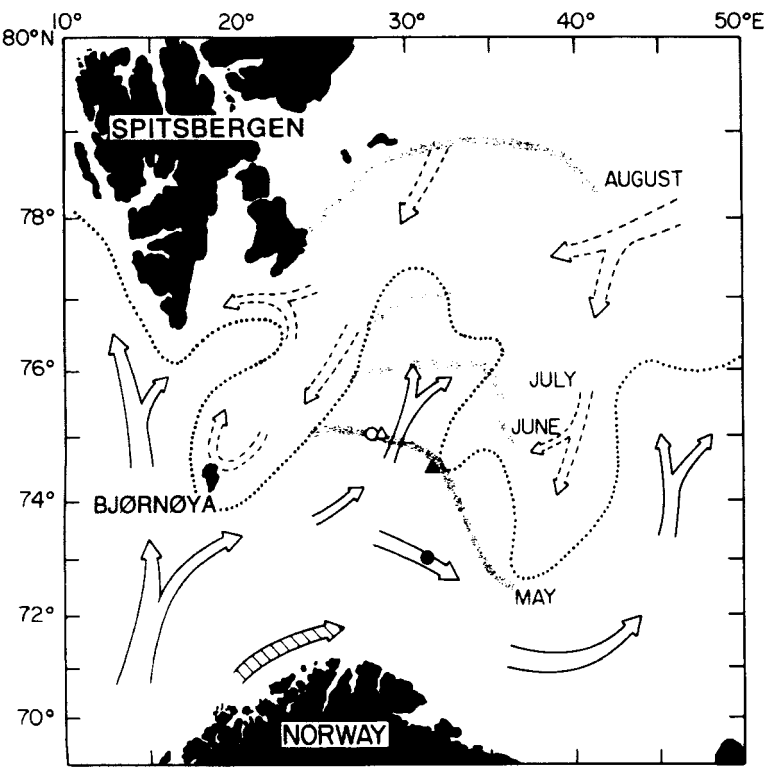


Fig. 1. Water masses of the southwestern Barents Sea: open arrows = Atlantic Water; striped arrow = Coastal Water; dashed arrows = Polar waters. Dotted line = position of Polar Front; shaded lines = average position of ice edge during summer months as ice recedes northwards. Triangles indicate stations visited during spring 1987: open triangle = Stns. 947–987; solid triangle = Stns. 941–994. Circles indicate stations visited during summer 1988: open circle = Stn. 864; solid circle = Stn. 885. Redrawn from Rey & Loeng (1985).

Table 1. Location, sediment trap sampling depth, and water column depth of 4 stations visited in the Barents Sea during this study. The spring bloom was underway in May–June 1987 while summer conditions prevailed in July of 1988.

Date	Station	Latitude	Longitude	Trap depth (m)	Water column depth (m)
27 May–6 June 1987	937–947	75°00′N	28°37′E	50	320
2–7 June 1987	947–987	75°00′N	28°37′E	50	320
21–28 May 1987	894–941	74°29′N	31°31′E	50	230
28 May–8 June 1987	941–994	74°29′N	31°31′E	50	230
13–16 July 1988	864	73°00′N	31°15′E	100	278
4–7 July 1988	885	75°00′N	28°00′E	90	330

length of deployments are presented in Table 1 and Fig. 1.

Hydrographic profiles of temperature, conductivity and depth were obtained with a Neil Brown Mk III CTD-profiler mounted with a General Oceanic Rosette Sampler equipped with ten 10-l Niskin bottles. The sampling depths were 0, 5, 10, 20, 30, 50, 75, 100, 150, 200 and 250 m. Light was measured with a Photosynthetically Active Radiation (PAR) 4π collector placed high on the ship superstructure (Biospherical Instruments model QSL-40). The extinction of light in the water column was estimated with a 4π PAR downwelling irradiance sensor (MER model 1012F optical profiling unit, Biospherical Instruments Inc.).

Sedimentation was measured for a period of 3 to 11 days (see Table 1) using double cylindrical PVC traps with a height of 1.6 m and a diameter of 0.16 m (H/D ratio of 10). In May–June 1987, traps were deployed at 50 and 100 m, while in July 1988 traps were deployed at 60, 100 and 230 m at Stn. 864 and at 40, 90, 150, 200 and 250 m. No poisons were used during the deployments. The rate of carbon decomposition in the sedimenting matter was, on average, not higher than 2% d^{-1} (Wassmann et al. 1991). The contents of each trap were transferred along with about 2 liters. of seawater to a bottle and thoroughly mixed before subsampling. Triplicate samples were taken and filtered for pigments. Pigment sedimentation rates were calculated on basis of the concentration in the trap, length of the deployment, and trap surface area.

Samples were concentrated on Whatman GF/F filters under 50 mbar of differential pressure. Samples for high pressure liquid chromatography (HPLC) were frozen in liquid N_2 and stored at −70°C until analysis. Pigments were extracted overnight at 4°C in the dark with 90% acetone. Extracts were cleared by filtration through Whatman GF/C filters and injected onto the column without further treatment.

Pigments were estimated using the fluorometric technique of Holm-Hansen et al. (1965) on a Turner Designs fluorometer calibrated with chlorophyll *a* (Sigma Chemical Co.) in 90% acetone. This analysis was performed during both cruises. In addition, samples for the summer cruise of 1988 were analyzed for chlorophyll *a* and degradation products (phaeopigments) by high-performance liquid chromatography (HPLC) on a reverse-phase C-18 Brownlee Spherisorb ODS-5 column, 25 cm × 4.6 mm, 5 μm particles. Pigments were eluted in a low-pressure gradient system consisting of a linear gradient from 100% A to 100% B in 10 min and maintaining B for another 15 min. Solvent A consisted of 70:20:10 methanol:water:water + ion pairing agent (v/v), the latter solvent in a concentration of 1.5 g of tetrabutylammonium acetate and 0.96 g of ammonium acetate in 100 ml of water (Mantoura & Llewellyn 1983). Solvent B consisted of 60:40 methanol:ethyl acetate (v/v). Eluting pigments were quantified by fluorescence in a Hitachi F-3000 Fluorescence Spectrophotometer fitted with a flow-through cell, with excitation beam at 410 nm and emission at 680 nm. Pigments were identified by their fluorescence excitation spectra (Table 2). The HPLC column was calibrated with pure pigments prepared as in Vernet & Lorenzen (1987) from a culture of *Thalassiosira nordenskioeldii*, with extinction coefficients as in Lorenzen & Downs (1986) for chlorophyll degradation products, Jeffrey & Humphrey (1975) for chlorophylls *a* and c_{1+2}. Because of a lack of a specific absorption coefficient, chlorophyll c_3 was quantified using the same calibration as for

Table 2. Fluorescence maxima of pigments analysed by reverse-phase high-performance liquid chromatography obtained from their fluorescence excitation spectra. Peak numbers as shown in Fig. 2. Spectra of the pigments were measured in the eluent in a flow-through cell attached to the spectrofluorometer.

Peak number	Pigment	Retention time (min)	Fluorescence maxima (nm)
1	Chlorophyll *c* derivative	6.9	454, 585
2	Chlorophyllide *a*	8.0	437, 624, 665
3	Chlorophyll *c*	8.9	450, 586, 634
4	Phaeophorbide a-like (a_2)	9.5	425, 666
5	Phaeophorbide a-like (a_3)	10.4	414, 614, 662
6	Phaeophorbide a-like (a_{4-5})	12.2	408, 624, 666
7	Chlorophyll *a* + *c* derivatives	14.0	442, 462, 626, 667
8	Chlorophyll *a* derivative	14.6	435, 624, 666
9	Chlorophyll *a*	15.0	435, 626, 667
10	Phaeophytin a-like (a_1)	19.5	417.5, 667
11	Phaeophytin a-like (a_2)	22.0	417.5, 666

chlorophylls c_{1+2} even though a large error might be expected using this approach (Jeffrey & Wright 1987).

Photooxidation estimates of phaeopigments were obtained using material collected in the 100-m traps in June 1987. Samples from the traps were diluted with filtered seawater, shaken to homogenize, and incubated in 250 ml Pyrex bottles. Eight bottles were exposed to sunlight in an incubator placed on deck. Temperature was kept at 0 ± 1°C with running seawater from the ship's water intake. One bottle was wrapped in aluminum foil and kept in the refrigerator, in the dark, at 2°C, as control. The pigment content was measured at 3, 6, 12, 24, 36, and 48 hours of incubation. Photooxidation constants, k_1, were calculated as in Welschmeyer & Lorenzen (1985).

Phytoplankton growth and zooplankton grazing were estimated from pigment budgets. In the summer cruise of 1988, steady state was assumed and the simplified equations presented in Welschmeyer & Lorenzen (1985) were used. Chlorophyll sedimentation from the euphotic zone was not assumed to be zero, and was estimated as $C_f C^{-1}$, where C_f (mg chl *a* m^{-2} d^{-1}) is the chlorophyll flux to the sediment traps and C (mg m^{-2}) is the integrated chlorophyll in the euphotic zone. In the spring of 1987, during the bloom, equations were solved numerically, including chlorophyll sedimentation from the euphotic zone and accounting for changes in the depth of the euphotic zone as expressed in Laws et al. (1988). Pigment concentration was integrated to the depth of 1% incident radiation, defined as the depth of the euphotic zone. Pigment estimated by the Turner Designs fluorometer was used for this analysis because HPLC data for water column phaeopigments were not available for June 1987.

Results

Hydrography. Spring conditions

Two stations were visited during the spring of 1987 (Fig. 1). Stns. 947–987 were situated in Atlantic waters during a bloom of *Phaeocystis pouchetii*, with chlorophyll *a* concentrations of 4 to 6 mg m^{-3} from the surface to a depth of 60 to 80 m. At this station stratification was very weak, nitrate was detectable through the mixed layer, and the euphotic zone (1% isolume PAR) extended to 18 m (Wassmann et al. 1991). Stns. 941–994 were located in an area under the influence of the Polar Front (Rey & Loeng 1985) and close to the ice edge. Stn. 941 was similar to Stn. 947 but with only 1.3 mg chl *a* m^{-3} in the top 20 m of the water column. Ten days later, at Stn. 994, a strong subsurface chlorophyll *a* maximum had developed at 43–45 m, at the depth of a strong halocline, due to surface meltwater. Nitrate was depleted in the mixed layer and the depth of 1% isolume (PAR) was 41 m. Chlorophyll *a* concentrations averaged 0.5 mg m^{-3} in the mixed layer and peaked at 12 mg m^{-3} at the maximum. This temporal variability in the chlorophyll profile

suggests strong advection in the area (Wassmann et al. 1990), precluding the use of the pigment budget model at this station.

Summer conditions

The stations visited in July 1988 were located in Atlantic waters (Fig. 1) and had already experienced the spring bloom. Of the two, Stn. 885 had a deeper mixed layer (30 m), and a lower density gradient at the pycnocline (Wassmann et al. 1991). Nitrate concentrations were undetectable throughout the mixed layer and a nutricline was established between 20 and 75 m. Chlorophyll *a* concentrations were 0.9 mg m^{-3} in the mixed layer and had a subsurface maximum of 1.6 mg m^{-3} at the top the nutricline, at a depth of 30 m, with a secondary maximum at 60 m (Fig. 2D). This station presents characteristics of late bloom conditions in the Barents Sea when phytoplankton distribution changes from high concentration in the mixed layer to a deep chlorophyll maximum at the nutricline (Thingstad & Martinussen 1991 this volume). Station 864, further north, had a shallower mixed layer (20 m) and a stronger density gradient than Stn. 885. Temperature profiles revealed a warming of surface waters (5°C) over colder water (2.7°C). Nitrate concentrations were also undetectable at the mixed layer. A nutricline was present from 50 to 100 m (Wassmann et al. 1991). Chlorophyll *a* concentrations were low in the mixed layer (0.2 mg m^{-3}) and peaked at about 75 m with a concentration of 1.2 mg m^{-3} at the depth of maximum nutrient gradient (Fig. 2D). This station represents summer, or postbloom, conditions in the Barents Sea (Thingstad & Martinussen 1991).

The euphotic zone, calculated as the depth of 1% isoline for PAR, extended to 37 and 25 m for Stns. 864 and 885, respectively. While the chlorophyll maximum during the late bloom was at the bottom of the euphotic zone (Stn. 885), the chlorophyll maximum in the postbloom (Stn. 864) was well below the 1% isolume for PAR (Fig. 2A and D). Although the exact position of the chlorophyll *a* maximum might have been lost due to low resolution in the sampling (depths sampled were only 50, 75 and 100 m), it was situated below the 0.1% isolume for PAR (55 m).

Phaeopigment diversity

Five phaeophorbide-like and three phaeophytin-like pigments were found consistently in the water column and sediment traps (Fig. 3). The nomenclature corresponds to Vernet & Lorenzen (1987) also used by Downs (1989) and Hurley & Armstrong (1990). Two phaeopigments, not named in Vernet & Lorenzen (1987), less polar than phaeophorbide a_3, were named a_4 and a_5, as in Downs (1989). Phaeophorbide a_5 was not always well resolved from a_4, the most abundant of the two pigments (peak 6 in Fig. 3). Phaeophytin a_1 and a_2 (peaks 10 and 11 in Fig. 3) were present in all samples. A third minor form eluted after a_1, but was not quantified. I present here quantification of the more abundant phaeophorbide- and phaeophytin-like pigments, a_2, a_3 and a_{4+5} and a_1 and a_2, respectively.

Pigments in seston

The vertical profile of accessory chlorophylls followed that of chlorophyll *a* (Fig. 2A and D). The abundance of chlorophylls c_{1+2} and c_3 at Station 885 during the late bloom suggests a dominance of diatoms over prymnesiophytes (Jeffrey & Wright 1987). The ratio of chlorophyll c_3:chlorophyll c_{1+2} (w/w) integrated over the top 100 m was 0.1. Stn. 864 was dominated by chlorophyll c_3-containing algae, probably prymnesiophytes (Jeffrey & Wright 1987). The ratio of chl c_3:chl c_{1+2} (w/w) in the upper 100 m was 0.91. A ratio of approximately 1.0 is commonly found in cultures of prymnesiophytes, suggesting that most of the chl c_{1+2} is mostly c_2 from the prymnesiophytes. Deeper in the water column, at the depth of the chlorophyll *a* maximum, chlorophyll c_{1+2} become more abundant, suggesting more diatoms at the nutricline.

Vertical distribution of phaeopigments was similar to that of chlorophyll *a*. Maximum concentrations coincided with the chlorophyll *a* maximum at both stations although at Stn. 885 the deep maximum (60 m) was more conspicuous than the shallow one (30 m). Phaeophorbide a_{4+5} was the most abundant phaeopigment in the euphotic zone at both stations, followed by a_2 and a_3. Below the euphotic zone, the stations differed. At Stn. 885 phaeophorbides a_3 and a_2 became more abundant while phaeophorbide a_{4+5} stayed dominant in the postbloom situation (Stn. 864). Phaeophytins presented a similar distribution to that of the phaeophorbides (Fig. 2C and F) but were more abundant during post-bloom con-

ditions (Stn. 864). Phaeophytin a_1 was generally more abundant than phaeophytin a_2.

Pigment sedimentation

The two stations in July of 1988 presented different patterns of sedimentation for chlorophylls and phaeopigments (Table 3). Phaeopigment sedimentation (all forms of phaeophorbide and phaeophytin combined) was always higher than chlorophyll *a* sedimentation for any given depth sampled. During the late bloom (Stn. 885) chlorophyll *a* sedimentation was maximum at 40 and 90 m and decreased at larger depths. Phaeopigment sedimentation was lower at 40 m and was higher at 90 m and deeper. At Stn. 864, during postbloom conditions, sedimentation of all pigments increased 5-fold from 60 to 100 m. The similar pattern of both chlorophyll *a* and phaeopigments suggests that the chlorophyll *a* maximum at about 75 m was the main source of sedimenting matter at this station.

Sedimentation rates of phaeopigments showed different patterns among pigment forms and stations (Table 3). Phaeophorbide a_3 was the most abundant degradation product in sediment traps. The only exception was at 60 m at Stn. 864 where phaeophorbide a_{4+5} showed the highest sedimentation rate. Phaeophorbide a_2 had maximum sedimentation rates in the top 100 m during late-bloom conditions, with decreased sedimentation rates with depth, while the opposite was observed in postbloom conditions (Stn. 864). Phaeophorbide a_3 had maximum rates of sedimentation at 90 or 100 m. At greater depths, the pattern of sedimentation differed for both stations, remain-

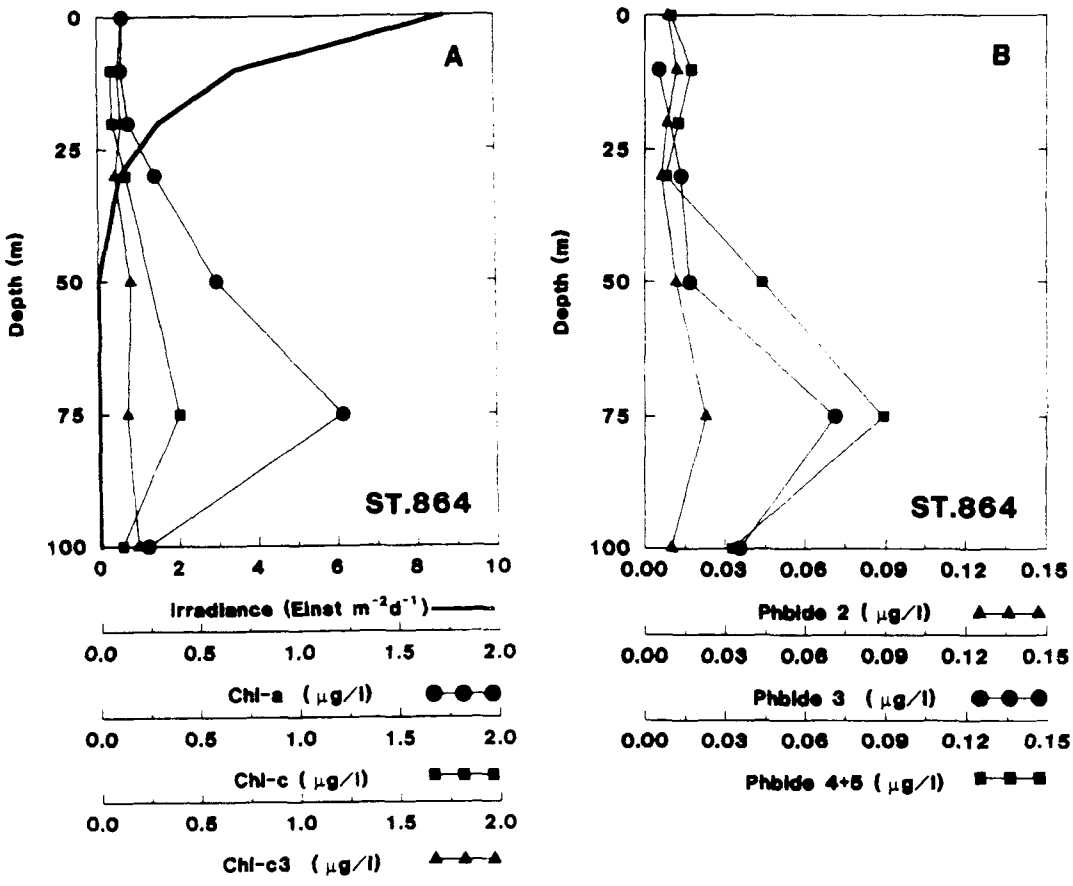
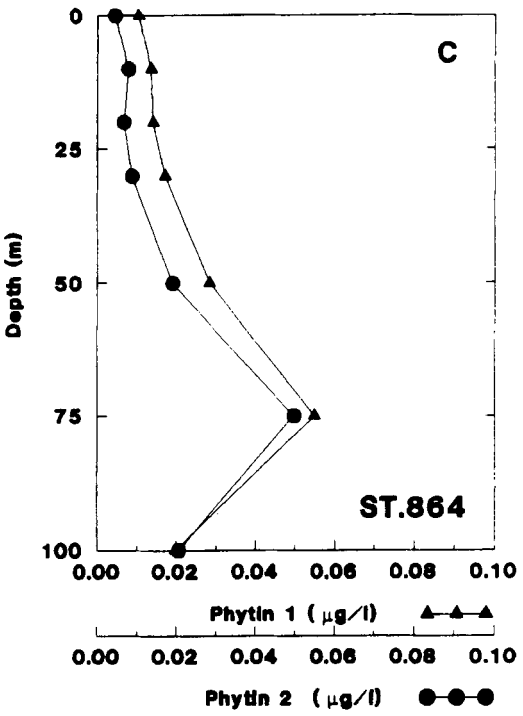
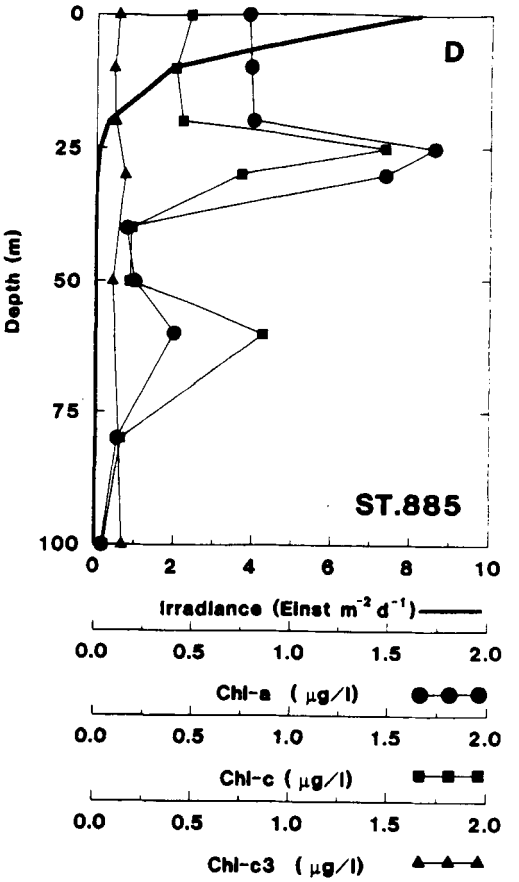
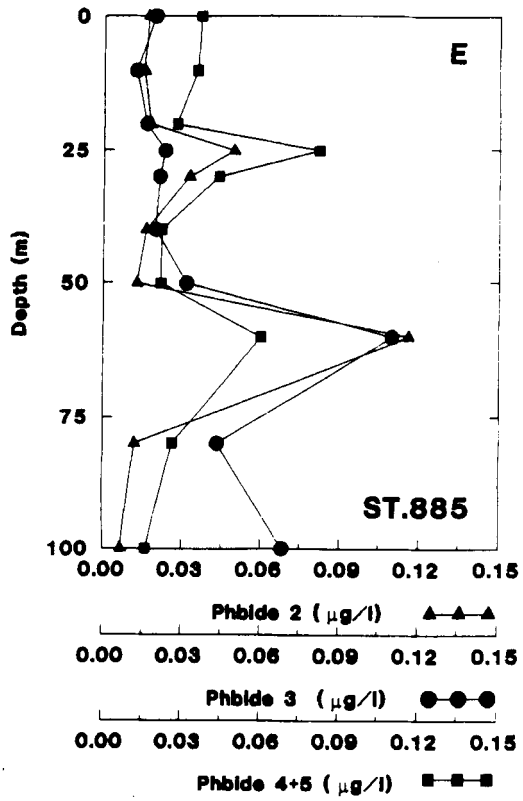
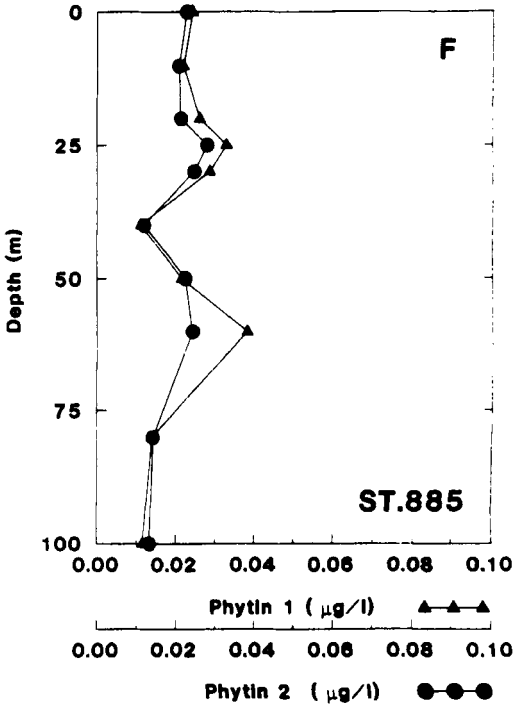


Fig. 2. Vertical profiles of pigments from 0 to 100 m at two stations in the Barents Sea visited during July 1988. Pigments were analysed by HPLC. Irradiance (thick line) is shown for each station in (A) and (D).


C
ST.864
Depth (m)
0
25
50
75
100
0.00 0.02 0.04 0.06 0.08 0.10
Phytin 1 (µg/l)
0.00 0.02 0.04 0.06 0.08 0.10
Phytin 2 (µg/l)


D
ST.885
Depth (m)
0
25
50
75
100
0 2 4 6 8 10
Irradiance (Einst m-2 d-1)
0.0 0.5 1.0 1.5 2.0
Chl-a (µg/l)
0.0 0.5 1.0 1.5 2.0
Chl-c (µg/l)
0.0 0.5 1.0 1.5 2.0
Chl-c3 (µg/l)


E
ST.885
Depth (m)
0
25
50
75
100
0.00 0.03 0.06 0.09 0.12 0.15
Phbide 2 (µg/l)
0.00 0.03 0.06 0.09 0.12 0.15
Phbide 3 (µg/l)
0.00 0.03 0.06 0.09 0.12 0.15
Phbide 4+5 (µg/l)


F
ST.885
Depth (m)
0
25
50
75
100
0.00 0.02 0.04 0.06 0.08 0.10
Phytin 1 (µg/l)
0.00 0.02 0.04 0.06 0.08 0.10
Phytin 2 (µg/l)

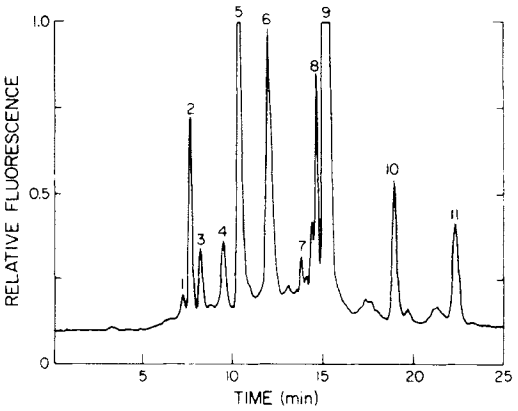


Fig. 3. Chromatogram showing chlorophyll *a* and chlorophyll degradation products from a sediment trap sample collected in July 1988 in the Barents Sea. Pigments were analysed with a reverse-phase HPLC and detected by fluorescence with excitation wave length at 420 nm and emission at 680 nm. Peak identities correspond to those in Table 2.

ing high at Stn. 885 while decreasing at Stn. 864. Phaeophorbide a_{4+5} increased their sedimentation rates with depth, with the exception of 100 m at Stn. 864 where rates peaked. Sedimentation rates of phaeophytin a_2, the form least abundant in the water column, were always equal to or larger than those of phaeophytin a_1. The pattern of sedimentation of the 2 phaeophytins was similar to that of phaeophorbide a_3. In general, maximum rates of sedimentation were found at 90 and 100 m at Stns. 864 and 885 respectively, immediately below the depth of the pigment maxima, where diatoms were more abundant.

Phaeopigment photoxidation rates

The results from the 3 experiments were combined and the resultant first order photooxidation decay constant, k_1 (m^2 mol^{-1}) was computed. Photooxidation rate constants vary among the individual chlorophyll degradation forms by a factor of 2, from 0.009 to 0.015 m^2 mol^{-1} (Fig. 4). The average photooxidation rate constant for all pigment combined (SUM PHAEO) was 0.012 m^2 mol^{-1}.

Pigment model

The estimations of phytoplankton growth rate and zooplankton grazing during spring and summer based on the pigment model of Welschmeyer & Lorenzen (1985) are shown in Table 4. Phytoplankton during the bloom of *Phaeocystis pouchetii* in Atlantic waters, not influenced by the Polar Front, grows at an average rate in the euphotic zone of 0.14–0.17 d^{-1}. Macrozooplankton grazing (0.05–0.06 d^{-1}) dominated over microzooplankton grazing (0.01–0.02 d^{-1}), accounting for approximately 35% of the phytoplankton loss. Sinking of intact cells out of the euphotic zone, estimated from the sedimentation rate of chlorophyll *a*, was 7–8% of the growth. Between 45 to 50% of the newly formed chlorophyll accumulated in the euphotic zone. When compared to growth rates estimated from ^{14}C incorporation, assuming a C:chl*a* ratio of 75 from the POC data (F. Rey, unpubl. data) and growth calculations according to Eppley (1972), the model underestimated phytoplankton growth by 35%. Due to the lack of independent estimates of the phytoplankton C:chl*a* ratio, it is not possible to determine how much pigment might have been lost during grazing (i.e. Lopez et al. 1988). A loss of 33% though is expected during macrolankton grazing (Downs 1989) and seems to be a representative pigment loss term in the spring bloom (Laws et al. 1988).

Estimates of phytoplankton growth rates for the summer were an order of magnitude lower than for spring (Table 4). Macrozooplankton grazing rates were also an order of magnitude lower than in the spring, while microzooplankton grazing rates were about the same. In late bloom conditions (Stn. 885), where diatoms dominated in the water column, micro- and macrozooplankton grazing were comparable. Ten percent of the chlorophyll sank out of the euphotic zone and about 8% still accumulated. In postbloom conditions, where small flagellates were dominant, microzooplankton grazing accounted for 85% of the phytoplankton growth, while 7% sank out of the euphotic zone, and there was almost no net accumulation of phytoplankton in the euphotic zone. No radiocarbon incorporation data are available from this cruise in order to compare growth estimates.

Discussion

Arctic phytoplankton

Phytoplankton growth at the ice edge of polar regions is characterized by an intense growth

Table 3. Biomass and sedimentation rates of chlorophyll *a* and its main degradation products during July 1988. Pigments were analysed and quantified by HPLC. Pigment identification as in Table 2 and Fig. 2. "Sum Phaeo" denotes total phaeopigment. Pigment biomass was integrated from the surface to the depth of the euphotic zone. Sedimentation rates were calculated without correction for daily losses, estimated to be <2% d^{-1} (Wassmann et al. 1991). Percentage loss was estimated as (sedimentation × 100/biomass) in units of d^{-1}.

Station	Pigments	Depth (m)	Biomass (mg m^{-2})	Sedimentation (mg $m^{-2} d^{-1}$) × 10^{-2}	%Loss (d^{-1})
864	Phbide 2	60	0.45	0.1	0.22
	Phbide 3		0.42	0.3	0.71
	Phbide 4 + 5		0.90	1.2	1.33
	Chl *a*		13.67	2.5	0.18
	Phytin 1		0.86	0.2	0.23
	Phytin 2		0.48	0.2	0.42
	Sum Phaeo		3.11	2.0	0.64
	Phbide 2	100	1.29	2.0	1.55
	Phbide 3		2.85	24.3	8.53
	Phbide 4 + 5		4.09	7.0	1.71
	Chl *a*		54.83	15.9	0.29
	Phytin 1		2.83	2.5	0.88
	Phytin 2		2.22	4.5	2.03
	Sum Phaeo		13.28	40.3	303.0
	Phbide 2	230	1.29	1.8	1.40
	Phbide 3		2.85	5.8	2.04
	Phbide 4 + 5		4.09	4.0	0.98
	Chl *a*		54.83	2.5	0.05
	Phytin 1		2.83	1.1	0.39
	Phytin 2		2.22	1.4	0.63
	Sum Phaeo		13.28	21.7	163.0
885	Phbide 2	40	0.94	1.7	1.81
	Phbide 3		0.71	5.5	7.75
	Phbide 4 + 5		1.59	3.2	2.01
	Chl *a*		38.11	7.2	0.19
	Phytin 1		0.97	0.8	0.82
	Phytin 2		0.87	1.7	1.95
	Sum Phaeo		5.08	12.9	253.0
	Phbide 2	90	3.01	1.8	0.60
	Phbide 3		3.20	14.9	4.66
	Phbide 4 + 5		3.08	3.9	1.27
	Chl *a*		47.9	6.8	0.14
	Phytin 1		1.95	1.5	0.77
	Phytin 2		1.66	3.8	2.29
	Sum Phaeo		12.99	25.9	199.0
	Phbide 2	150	3.01	1.0	0.33
	Phbide 3		3.20	13.9	4.34
	Phbide 4 + 5		3.08	6.0	1.95
	Chl *a*		47.95	2.9	0.06
	Phytin 1		1.95	1.1	0.56
	Phytin 2		1.66	1.9	1.14
	Sum Phaeo		12.99	23.9	184.0
	Phbide 2	200	3.01	1.0	0.33
	Phbide 3		3.20	17.6	5.50
	Phbide 4 + 5		3.08	7.8	2.53
	Chl *a*		47.95	2.3	0.05
	Phytin 1		1.95	0.8	0.41
	Phytin 2		1.66	1.4	0.84
	Sum Phaeo		12.99	28.6	220.0
	Phbide 2	250	3.01	0.7	0.23
	Phbide 3		3.20	15.3	4.78
	Phbide 4 + 5		3.08	7.2	2.34
	Chl *a*		47.95	2.5	0.05
	Phytin 1		1.95	0.9	0.46
	Phytin 2		1.66	1.1	0.66
	Sum Phaeo		12.99	25.2	194.0

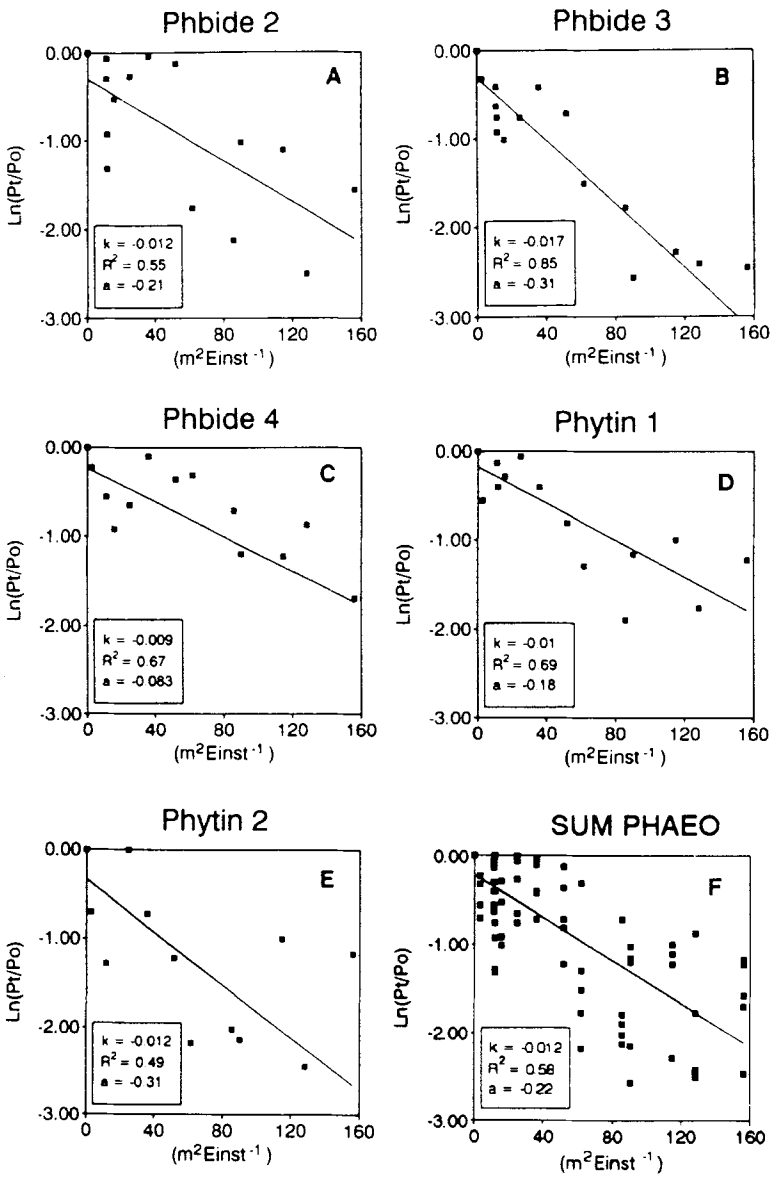


Fig. 4. Estimation of photooxidation rate constants for the chlorophyll degradation products abundant in the water column and sediment trap matter. Data include three experiments incubated on deck in June 1987 from material collected in 100-m traps at Stns. 941–994 and 947–987. Temperature was maintained at 0 ± 1°C with running seawater from the ship's intake. Peak 4 is a mixture of phaeophorbide a_{1+5}. SUM PHAEO (F) is the average photooxidation rate constant for all the phaeopigments combined.

period during the spring due to increased stabilization of the water column, sun angle and daylength (Dunbar 1981; Rey et al. 1987; Niebauer & Alexander 1989; Sakshaug 1989). In the Arctic, and in particular in the northern part of the Barents Sea, the bloom crashes after nitrate has been stripped from the mixed layer and marks the onset of the summer period which is characterized by a subsurface chlorophyll *a* maximum near the nutricline. The stratification of water is either due to ice melting at the ice edge or to warming of surface layers, as in the case of Atlantic waters in the southwestern area of the Barents Sea (Skjoldal et al. 1987; Loeng 1989). Winter and summer are generally dominated by small flagellates while spring blooms are due to either diatoms and/or *Phaeocystis pouchetii* (Rey et al. 1987). While diatoms are generally present in the Atlantic waters of the Barents Sea, *P. pouchetii* is dominant in ice edge blooms (Wassmann et al.

Table 4. Results from pigment model as in Welschmeyer & Lorenzen (1985). Stations during May/June 1987 were solved numerically, accounting for changes in mixed layer depth and accumulation of biomass in the euphotic zone, as in Laws et al. (1988). Stations in July 1988 were assumed to be in steady state and solved as in Welschmeyer & Lorenzen (1985). Primary production measurements were used to estimate phytoplankton growth rate according to Eppley (1972) and using the Carbon:chlorophyll ratio estimated from particulate (POC) data*. Stations 896/941/994 in May/June 1987 were not considered due to lateral advection present at the stations. *Macro* and *micro* refer to macrozooplankton and microzooplankton; *sinking* is an estimate of sinking rate of intact cells as indicated by the sedimentation rate of chlorophyll *a*; *accum* refers to the fraction of phytoplankton growth that remains in the euphotic zone.

	Station	Zooplankton grazing (d^{-1})		Phytoplankton growth (d^{-1})	Mass balance				*Phytoplankton growth (d^{-1})
		Macro	Micro		Macro	Micro	Sinking	Accum	
July 1988	864	0.0024	0.0309	0.036	7%	85%	7%	1%	—
	885	0.0059	0.0087	0.018	33%	49%	10%	8%	—
May 1987	947 (t1)	0.06	0.02	0.17	34%	13%	8%	45%	0.2
	987 (t2)	0.05	0.01	0.14	36%	7%	7%	50%	0.18

1990), either after a diatom bloom, when silicate becomes limiting for diatoms, or from the onset of the bloom. Similar observations have been made in the Greenland Sea (Cota et al. 1990) and in the waters around Iceland (Stefansson & Olafsson 1990).

Diatoms were dominant in the blooms of Atlantic waters in June of 1987 (Vernet unpubl. data) and during late-bloom conditions in July of 1988 (Stn. 885). Single cell prymnesiophytes (i.e. *Emiliana huxleyi*) were present in pre-bloom conditions in May 1987 (Vernet unpubl. data) and increasingly dominant from late-bloom to postbloom in July 1988 (Stn. 864). At the ice edge in May–June 1987, more than 95% of the plankton consisted of *P. pouchetii* cells (C. Hewes, pers. comm.). The distribution of accessory pigments gave a good approximation to characterizing these phytoplankton assemblages in the Barents Sea (Fig. 2). Plankton dominated by diatoms were rich in chl c_{1+2} (Stauber & Jeffrey 1988), while those with prymnesiophytes such as *E. huxleyi* and *P. pouchetii* had chl c_3 in addition to chl c_2 (Jeffrey & Wright 1987). With respect to carotenoids, *E. huxleyi* has 19′ hexanoyloxyfucoxanthin as the main carotenoid (Vernet 1989). Diatoms and *P. pouchetii* have focuxanthin (Wassmann et al. 1990). The difference in dominant carotenoid within the prymnesiophytes makes it possible to differentiate them.

Large cells such as diatoms and the colonial form of *P. pouchetii* dominate the spring bloom, at which time there are shallow mixed layers, nitrate is present in measurable concentrations, and the density stratification is weak. On the other hand, small flagellates characterize deep or nutrient-depleted mixed layers, encountered in either pre- or postbloom conditions. In this study, large diatoms were abundant in late spring (Stn. 885) but were displaced by prymnesiophytes in the mixed layer as nitrogen became low. These diatoms still grew at the depth of chlorophyll maximum in summer conditions (Stn. 864), when irradiance was low but rates of nutrient supply were probably high. This scenario supports the hypothesis that large cells can grow in environments where there is an increase in the rate of nutrient supply (Thingstad & Sakshaug 1990).

Chlorophyll degradation

The more abundant forms of chlorophyll *a* degradation found in seston and sedimenting particles of the Barents Sea (see Fig. 2) are similar to the forms found in temperate coastal marine waters (Klein & Sournia 1987; Vernet & Lorenzen 1987; Downs 1989; Roy & Poulet 1990), lakes (Carpenter et al. 1986; Hurley & Armstrong 1990) and sediments (Brown et al. 1977). The uniformity of components suggests common catabolic pathways in aquatic environments (Hendry et al. 1987). In Arctic waters, as in other areas of the ocean, the main pathways of chlorophyll degradation involve biotic and abiotic factors. Oxidizing and non-oxidizing enzymes from either the alga itself or a grazer that has ingested it, light, bacterial activity, and oxygen are the main degradative agents (Hendry et al. 1987). The last two sources can be

considered secondary in short periods of time (Downs 1989; Roy & Poulet 1990), particularly in polar waters (Wassmann et al. 1991). In the euphotic zone, light plays a main role in the degradation of chlorophyll and phaeopigments associated to detritus. Pigments are degraded to colorless compounds (Struck et al. 1990), the main product of photooxidation (SooHoo & Kiefer 1982; Welschmeyer & Lorenzen 1985; Vernet & Lorenzen 1987; Downs 1989). In the absence of light, below the euphotic zone, enzymatic activity resulting from zooplankton grazing may be the main factor of chlorophyll degradation. Activity from cellular enzymes, such as chlorophyllase, dephytylizes chlorophyll *a* in diatoms (Jeffrey & Hallegraeff 1987). From chlorophyllide further enzymatic activity has been found to produce pyropheophorbide via phaeophorbide in cultures of *Chlorella fusca*. Pyrophaeophorbide, the end product, was found to be very stable in the dark and thus accumulated (Ziegler et al. 1988). It is clear that further studies are needed in order to characterize the different forms of phaeophorbide-like molecules and other degradative forms (Matile et al. 1989). The constancy of the molecules analyzed, common to so many environments, justify the effort.

Photooxidation rates of chlorophyll degradation seem to follow first-order kinetics (SooHoo & Kiefer 1982; Welschmeyer & Lorenzen 1985). At 0°C, photooxidation rates of individual phaeopigments vary by a factor of 2 (Fig. 4A–D). In the Barents Sea, phaeophorbide a_3 had the highest rate of photooxidation, followed by phaeophorbide a_2 and phaeophorbide a_1. The lowest rates are associated with the less polar forms, phaeophorbides a_{4+5}. Both forms of phaeophytins also had lower rates than the more polar phaeophorbides. Downs (1989) found the same differences among phaeophorbides a_2 and a_3, although the constants were, on the average, 3 to 5 times higher. An important corollary of the difference in photooxidation rates of phaeopigments is that the distribution of phaeopigments in the euphotic zone has to be interpreted in light of these differences, where the abundance is a function of the balance between production and loss rates. Distributions depicted in Fig. 2 and photooxidation rates in Fig. 4 suggest that phaeophorbide a_{4+5} can accumulate twice as fast as phaeophorbide a_3 for a similar production rate, and may account in part for their abundance in the euphotic zone. Total photooxidation rate can be calculated as the decay rate of the combined pigments (Fig. 4F). For a more accurate calculation of the photooxidation rate of the whole phaeopigment assemblage we should include the relative contribution of each individual component.

Photooxidation rates measured in this study at 0°C are lower than previously published data for temperate waters (SooHoo & Kiefer 1982; Welschmeyer & Lorenzen 1985; Downs 1989) and support the hypothesis of temperature dependence. Welschmeyer & Lorenzen (1985) and Downs (1989) found photooxidation rates to be independent of temperature. The authors suggest that the source and type of phaeopigment are a probable cause of the variability observed. The rates measured in this study suggest otherwise. Individual rates of phaeopigments measured by HPLC and the combined photooxidation constant show lower degradation rates at lower temperatures. Fig. 5 shows an Arrhenius plot including all the published k_l values from marine environments where temperature has been measured. They have been converted to units of $m^2\ mol^{-1}$ (Table 5). The regression obtained is similar to the one by SooHoo & Kiefer (1982). About 35% of the variance is still unexplained suggesting that other variables, such as type of light sensor, type of dominant form of phaeopigment, calibration of the fluorometer, incident

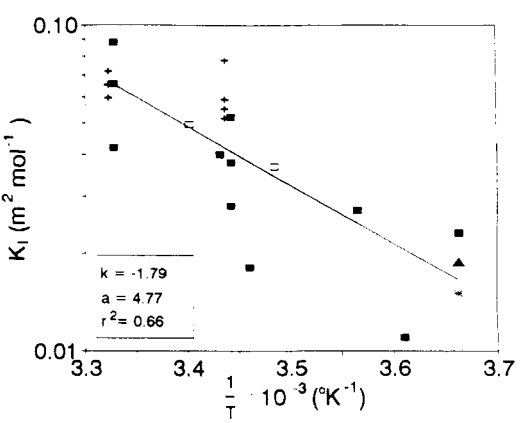


Fig. 5. Arrhenius plot of the photooxidation rate constant as a function of temperature. Estimates from marine waters have been pooled: (solid square) SooHoo & Kiefer (1982); (cross) Welschmeyer & Lorenzen (1985); (open square) Downs (1989); (triangle) Vernet & Mitchell (1990); (asterisk) this study. Temperature range from −0° to 28°C (see Table 4). Statistics and variance explained are similar to those obtained by SooHoo & Kiefer (1982).

Table 5. Summary of the first order photooxidation decay constant of phaeopigments.

Source	$k_i \cdot 10^{-2}$ (m^2/Einst)	Substrate	Temperature
SooHoo & Kiefer (1982)	1.1–8.8	Seston fecal pellets	0–28°C
Welschmeyer & Lorenzen (1985)	6.75	Seston	~9–26°C
Barents Sea (this study)	1.20	Sediment trap	−1–+2°C
Vernet & Mitchell (1990)	1.87	Sediment trap	−1–+2°C
Downs (1989)	3.69–4.9	Sediment trap	14–21°C

spectral irradiance, and probably size of the particles containing phaeopigments, can introduce uncertainty in this type of measurement. The lack of a significant temperature dependence in photooxidation rates in Welschmeyer and Lorenzen (1985) and Downs (1989) studies may be due to the narrower range of temperatures studied and the logarithmic relationship between these 2 variables.

Accurate values of photooxidation rate constants become increasingly important at lower temperatures. A sensitivity analysis showed that the total contribution of microzooplankton grazing to total grazing in the pigment model decreases rapidly at lower values of k_l (Fig. 6). The model is then most sensitive for low photooxidation rate constants, in the range of values measured for Arctic waters.

Specific forms of chlorophyll degradation seem to be quantitatively related to the type of phyto-

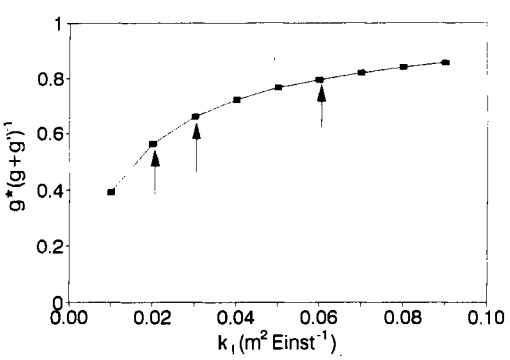


Fig. 6. Temperature dependence of photooxidation rate constant in the pigment budget model (Welschmeyeer & Lorenzen 1985): sensitivity analysis of the contribution of microzooplankton grazing (g) to total grazing ($g + g'$) as a function of the photooxidation rate constant (k_l). Arrows indicate three photooxidation rate constants: this study (0.012 m^2Einst^{-1}), SooHoo & Kiefer (1982) (0.037 m^2Einst^{-1}) and Welschmeyer & Lorenzen (0.0675 m^2Einst^{-1}).

plankton present. Phaeophorbide a_{4+5} was more abundant in the station dominated by prymnesiophytes while phaeophorbide a_3 was produced by degradation of diatoms. It is not possible to differentiate with the present sampling design if the degradation is originated by enzymes in the phytoplankton or in the grazers if we assume a close coupling between phytoplankton groups and types of grazers. The dominant form of phaeophorbide related to the pair alga-grazer is present not only in the seston but also in the large particles that sink out of the surface and are caught by the sediment traps. If, as hypothesized by Shuman (1978) and Welschmeyer & Lorenzen (1985), phaeopigments in the seston are mainly due to microzooplankton grazing while sinking faecal pellets originate mainly from macrozooplankton, the dominance of the same phaeopigment both in the water column and sediment trap suggest that the pathway of chlorophyll degradation is related more to the alga than to the grazer. Sedimentation of the most abundant phaeophorbide *a* in lakes was due to the presence of large grazers (Laevitt & Carpenter 1990) presumably feeding on large algae.

Pigment sedimentation

Pigment sediment out of the euphotic zone by either direct sinking of phytoplankton cells, phytodetritus, or through zooplankton fecal pellets. Intact phytoplankton cells contain almost exclusively non-degraded chlorophyll *a* pigments while the pigments of faecal pellets are mostly phaeopigments (but see Wassmann et al. 1990). Nevertheless some undegraded chlorophyll *a* in the sediment traps could originate from faecal pellets (Vernet & Lorenzen 1987). In this way, estimates of cell sinking based on chlorophyll *a* sedimentation rates would be maximum.

Maximum sedimentation rates of phaeopig-

ment measured below the chlorophyll maximum at both stations suggest that most of the defecation of pigments occurred while zooplankton were feeding at the chlorophyll maximum, as shown by Welschmeyer et al. (1984) and Dagg et al. (1989) in coastal areas. If the active transport of pigments by zooplankton to depth through vertical migration is minimum (Dagg et al. 1989), sedimentation rates at depth are dependent mostly of the remineralization or reingestion of pigments by other plankton at mid-depth. The higher changes observed from 100 to 230 m at Stn. 864 suggest higher recycling of sinking organic matter in the summer with respect to late spring (from 90 m to 250 m at Stn. 885). The constant sedimentation rate of pigments below 150 m at both stations (except phaeophorbide a_3) indicate that most of the transformation may occur immediately below the maximum pigment flux.

Although all forms of phaeopigment were found at all stations, there seems to be a quantitative relationship between some phaeophorbides and the type of phytoplankton. Phaeophorbide a_3, with high and constant sedimentation rates below 100 m, seems to be associated to large particles that sink fast and are not recycled at mid depths. These results agree with higher presence of this pigment in seston associated with larger cells, i.e. diatoms, at the chlorophyll *a* maxima at both stations. Phaeophorbide a_{4+5} is proportionally more abundant where prymnesiophytes dominate, at Stn. 864, but it is also related to fast sinking particles, particularly at Stn. 885. In general, mid-water recycling seems to be more important at Stn. 864, during summer conditions, although a lack of sampling at intermediate depths makes these conclusions tentative.

Phytoplankton population dynamics

The rate of phytoplankton growth estimated by the pigment budget model during the spring (Stns. 947 and 987) is about 65% of the estimate using radiocarbon incorporation. These numbers are within what is expected if we assume a pigment conversion efficiency of about 65% from a large phytoplankton to a large grazer (Shuman & Lorenzen 1975; Welschmeyer & Lorenzen 1985; Laws et al. 1988; Downs 1989). These numbers seem to indicate that chlorophyll budgets are good indicators of phytoplankton dynamics during spring bloom. On the other hand, phytoplankton growth rate estimates for summer stations at the Barents Sea (Stns. 864 and 885) are lower than might be expected for phytoplankton growing at high irradiance in stratified waters. Growth rates estimated from primary production measured in the same area in June–July 1979 (Ellertsen et al. 1982), and assuming a C:chl*a* ratio of 100, are in the order of 0.06–0.1 d^{-1}, 2 to 10 times higher than the estimated rates (Table 4). Similar discrepancies are observed in tropical environments. Laws et al. (1988) suggest that phytoplankton growth rates in the Central Pacific might be underestimated by 66% if we compare data from the pigment model (Welschmeyer & Lorenzen 1985) to the direct measurements of growth rate (Laws et al. 1987). Both tropical and Arctic data indicate that where nutrient recycling is important and where small algae and small grazers are dominant, there is a higher loss factor in the conversion of chlorophyll to phaeopigments. An alternative scenario could be that the observed phaeopigment:chlorophyll ratio would be averaged over a longer food web each of them with a 35% loss in each step of the food web. Independent of the reason, summer situations in the Arctic seem more similar to tropical stations with an average conversion factor larger than 66%. These results are thus in agreement with studies where pigments were useful tracers of macrozooplankton grazing (Dagg et al. 1987) while the opposite is true for microzooplankton (Klein et al. 1986; Strom 1988).

During the spring bloom, phytoplankton grew at maximum growth rates for the ambient light and temperature present at that time of year. Growth rate estimates of 0.14–0.17 d^{-1} in 1987 were calculated based on a mean irradiance in the euphotic zone of 1.66 mol m^{-2} d^{-1}. Planktonic diatoms isolated from the Barents Sea, grown at 18 μmol m^{-2} s^{-1} of continuous light (total daily mean irradiance of 1.55 mol m^{-2} d^{-1}), had an average growth rate of 0.17 d^{-1} (Gilstad & Sakshaug 1990), in good agreement with the model estimates.

In conclusion, estimates of phytoplankton dynamics based on chlorophyll budgets can be used with reliability during ice edge blooms of Arctic waters. During summer conditions the model seems to underestimate phytoplankton growth. Mass balances of C are within expected values during both seasons, although the magnitude of any given pool must be underestimated during the summer. The model parameters used

for temperate and tropical waters cannot be directly applied to polar areas, in particular the photooxidation rate constant for phaeopigments. A close look at the individual phaeopigments in the water column and sedimenting matter can give insight into phytoplankton-grazer interactions. Furthermore, information on phytoplankton composition based on distribution and abundance of accessory pigments can relate grazing to food availability.

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