Export stoichiometry and contribution of copepod faecal pellets to vertical flux of particulate organic carbon, nitrogen and phosphorus

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ABSTRACT: Sinking of particles is a key mechanism in the transport of organic matter from the ocean's productive surface layer to the deep sea and sediments, but also constitutes a loss of carbon and growth-limiting nutrients to the pelagic food web. Knowledge on export of particulate phosphorus is limited, particularly in high-latitude regions, in spite of its role as a co-limiting factor in many marine systems. We therefore investigated suspended concentrations and vertical export (by means of sediment traps) of particulate organic carbon (POC), nitrogen (PON) and total particulate phosphorus (TPP) at 3 contrasting sites in the Fram Strait and Barents Sea opening and quantified the contribution of zooplankton faecal pellets to POC, PON and TPP export. The TPP fluxes are the first to be reported from this region and probably the first from the entire Arctic Ocean. The suspended and exported C:N ratios were close to the Redfield ratio and did not differ significantly from each other (mean atomic ratios of 6.1 and 6.3, respectively). The mean C:P of suspended particles (91) was below Redfield, whereas the exported mean (117) exceeded Redfield, indicating more efficient retention of phosphorus than of nitrogen in the water column. Copepod faecal pellets had low C:P ratios and contributed a higher proportion to phosphorus export (mean of 17%) than to carbon and nitrogen export (10%). Faecal pellets may therefore be an important loss factor for phosphorus from the water column compared to slower-sinking material, which is retained more efficiently.

KEY WORDS: Vertical flux · Carbon · Nitrogen · Phosphorus · Stoichiometry · Faecal pellets · *Calanus* spp. · Arctic

INTRODUCTION

Vertical export of particulate organic matter constitutes an important part of the biological carbon pump and is the primary food input to organisms inhabiting depths below the ocean's productive surface layer. In oceanic systems, the magnitude and composition of vertical flux is controlled by autochthonous production of organic matter and by consumption and degradation of organic matter in the pelagic food web. Vertical export reduces the availability of carbon and growth-limiting nutrients (nitrogen and phosphorus) in the surface layer, and export of nitrogen and phosphorus may therefore contribute to enhancing nutri-

ent limitation. Knowledge of export stoichiometry and a comprehension of the regulating mechanisms are therefore crucial to understanding carbon and nutrient cycling and export potential in the ocean.

Several studies have documented persistent deviations from the Redfield C:N ratio of 6.6 by atoms (Redfield 1934, Redfield et al. 1963) both for nutrient uptake (Mei et al. 2005), suspended particulate biomass (Sterner et al. 2008) and export production (Körtzinger et al. 2001). C:N ratios of particulate organic matter above Redfield seem to be a common feature in high-latitude systems (Daly et al. 1999, Loh & Bauer 2000, Olli et al. 2002) and have been accounted for in production estimates (Smith et al.

1997, Tremblay et al. 2002) and ecosystem models developed for these regions (Tian et al. 2003, Wassmann et al. 2006). However, more knowledge is needed on the variability and regulation of export stoichiometry in order to correctly construct carbon budgets and models and, hence, improve the understanding of biological productivity and export in marine systems (Boyd & Trull 2007). In particular, the role of the pelagic food web in mediating fluxes of carbon and limiting nutrients needs to be further elucidated. Microbial degradation typically leads to faster dissolution of nitrogen and phosphorus than of carbon, and these elements are therefore retained more efficiently in the water column (reviewed by Boyd & Trull 2007). The role of zooplankton grazing for shaping the export stoichiometry is less well known. Copepods assimilate nitrogen more efficiently than carbon, reflected in carbon enrichment in faecal pellets relative to the diet (Checkley & Entzeroth 1985, Daly et al. 1999). Faecal pellets may temporarily be important for carbon export (Turner 2002, Wexels Riser et al. 2008), but their potential role as a loss factor for nitrogen and phosphorus has not been thoroughly investigated in various marine systems. Excretion by zooplankton at depth during their vertical migration is an important loss factor for phosphorus in tropical regions where passive sinking is relatively small (Hannides et al. 2009). The lack of synchronised diel vertical migration in Arctic zooplankton during the midnight sun period suggests that this pathway is negligible in the Arctic (Blachowiak-Samolyk et al. 2006, Cottier et al. 2006, Wexels Riser et al. 2007). The seasonal descent of ontogenetically migrating copepods to overwintering depths contributes significantly to the biological carbon pump in addition to the passive sinking flux of faecal pellets and carcasses (Steinberg et al. 2008, Sampei et al. 2012).

While most investigations in nitrogen-limited environments have focused on carbon and nitrogen fluxes, phosphorus has the potential to act as a co-limiting nutrient and, hence, contribute to regulating carbon export (Thingstad & Rassoulzadegan 1995). Phosphorus is becoming increasingly recognised as the limiting nutrient in some parts of the ocean (Karl et al. 2001, Vidal et al. 2003, Hannides et al. 2009). Phosphorus limitation may also occur seasonally in primarily nitrogen-limited systems (Tamminen & Seppälä 1999). It is well known that Pacific and Atlantic waters present in the Arctic differ in their inorganic N:P ratio, with Pacific water exhibiting a surplus of phosphorus. Damm et al. (2010) recently showed that the excess phosphorus in the Pacific

water supports methane production by bacteria, which does not take place in the phosphorus-poor Atlantic water. Particle export leads to reduced availability of nutrients in the water column and may, hence, provide a feedback mechanism to methane, which is a strong greenhouse gas. However, export of particulate phosphorus from the water column has not been investigated in these regions.

Earlier vertical flux studies in the Arctic have focused on carbon and nitrogen, and export regulation by the pelagic food web (reviewed by Wassmann et al. 2004, see also Reigstad et al. 2008, Lalande et al. 2009, Forest et al. 2010, Sallon et al. 2011). We investigated the C:N:P stoichiometry of suspended and exported particulate organic matter at 3 hydrographically distinct locations in the European Arctic. Retention efficiencies were determined based on snapshot views of the elemental ratios of contemporaneously sampled suspended and exported biomass, and we hypothesised that the retention of nitrogen and phosphorus in the water column would be equally efficient. We further quantified the contribution of zooplankton faecal pellets to vertical flux of carbon, nitrogen and phosphorus. Large faecal pellets are an important vehicle for organic matter export from the upper water layers due to their fast sinking speed. They are interesting from a stoichiometric standpoint because they derive from consumers whose requirements for elements differ from those of primary producers. This export pathway has previously not been investigated in the Arctic Ocean.

MATERIALS AND METHODS

Sampling

Sampling took place in June 2009 during a cruise with the RV 'GO Sars' to the Greenland Sea, Fram Strait and Barents Sea. Three main stations with sediment trap deployments were located in the Eastern Fram Strait at depths of 1200 m (Stn 65) and 3000 m (Stn 74) and in the Barents Sea opening over the continental shelf at a depth of 470 m (Stn 100, Fig. 1). Stns 65 and 74 were located in open water but were influenced by drift ice, which was still present at Stn 65. Stn 100 was outside the reach of the seasonal ice-cover in the Barents Sea. Zooplankton and suspended organic matter were also sampled at 1 station in the Greenland Sea (Stn B).

CTD profiles and samples for suspended particles were collected with a Seabird CTD and Niskin bot-
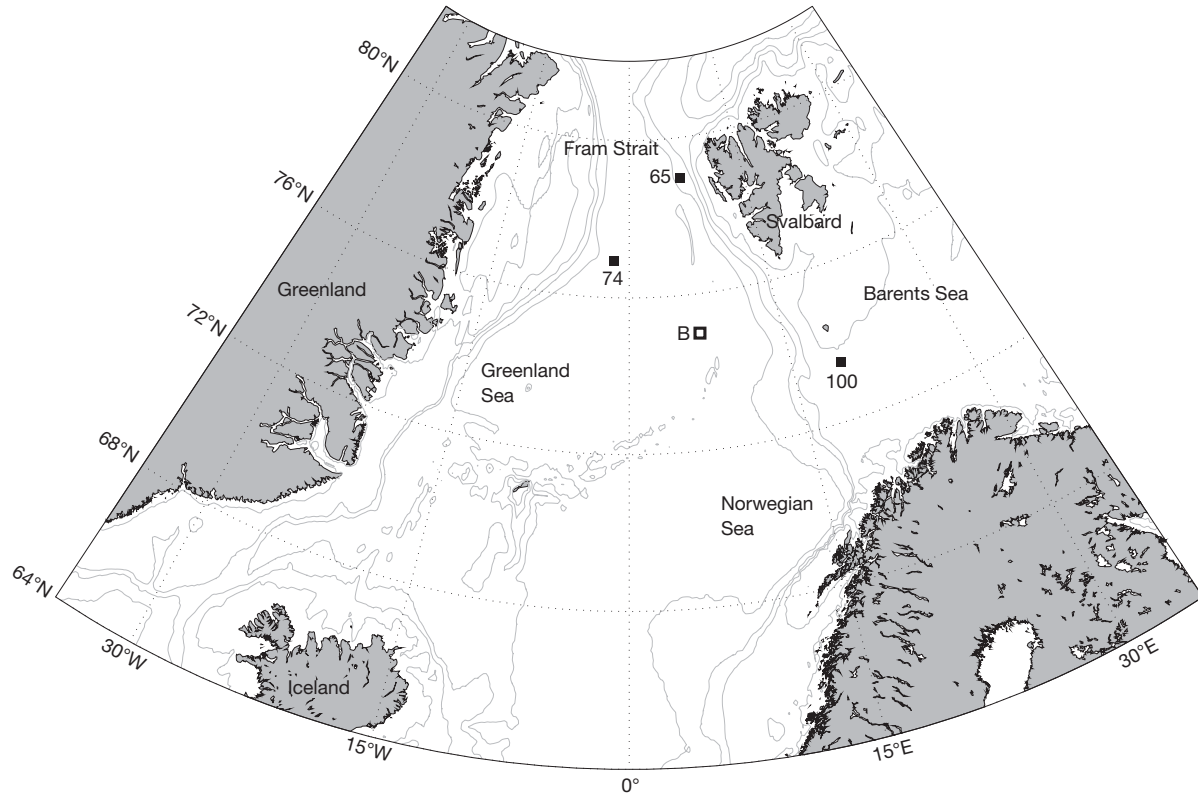
Fig. 1. Study region, with bathymetry (200, 500, 1000 and 2000 m isobaths) and sampling locations indicated. Black squares indicate the main stations (Stns 65, 74 and 100) with sediment trap deployments. Zooplankton and suspended organic matter were also sampled at Stn B

tles mounted on the Rosette from 10 fixed depths (5, 10, 20, 30, 40, 50, 60, 90, 120 and 200 m). Vertically exported particles were collected by means of surface-tethered sediment traps attached to a drifter at 20, 30, 40, 50, 60, 90, 120, 150 and 200 m depth. No fixatives were used in the traps. The samples from 40 and 150 m were used for analyses not covered in this study. The collection time varied between 15 and 24 h. The sediment traps (KC Maskiner og laboratorieudustyr) consisted of parallel cylinders with an inner diameter of 7.2 cm (height:diameter ratio of 6.25) mounted in a gimballed frame equipped with a vane. At moderate current velocities, the cylinders stay vertical and perpendicular to the current direction (Coppola et al. 2002). The trapping efficiency for particulate organic carbon (POC) is 90 to 110%, determined by comparison with the [234]Thorium method (Coppola et al. 2002). The larger discrepancy between fluxes measured by sediment traps and thorium, respectively, observed by Lalande et al. (2008) was due to variations in the [234]Th POC ratio during blooms dominated by *Phaeocystis*. These sediment traps are considered to provide representative estimates of the actual vertical particle flux.

Upon retrieval, the contents of the 2 parallel cylinders were pooled into 1 sample from each depth. Aliquots were filtered in triplicate on GF/F filters for determination of chlorophyll *a* (chl *a*) and on precombusted (450°C, 4 h) GF/F filters for POC and particulate organic nitrogen (PON) and total particulate phosphorus (TPP) from both water bottle and sediment trap samples. Chl *a* was determined on board, whereas the samples for elemental analyses were stored frozen at –20°C until analysed. Samples for enumeration and size measurements of faecal pellets were fixed with buffered formalin to a final concentration of 2%. Faecal pellets were enumerated in sample aliquots at 100× magnification using an inverted microscope. The lengths and widths of all pellets (43 to 177 per sample) were measured, and the volumes of pellets were calculated assuming a cylindrical shape. Faecal pellet volumes were converted to carbon, nitrogen, and phosphorus based on experimentally determined volumetric conversion factors (see 'Volumetric conversion factors and faecal pellet export' below).

Zooplankton was sampled with a WP-2 plankton net with 180 μm mesh size from 100 m depth to sur-

face. One haul was fixed with buffered formalin to a final concentration of 4% for determination of composition and abundance of zooplankton taxa. The sampling volume was estimated by sampling depth (100 m) times the area of the net opening (0.255 m^2). A second haul was taken with a non-filtering cod-end to collect animals to determine the elemental content of faecal pellets. This sample was gently diluted in 20 l of seawater collected from the ship's water intake at 5 m depth and kept at close to *in situ* temperature.

Analyses

Samples for chl *a* were extracted in methanol overnight in darkness and at room temperature (Holm-Hansen & Riemann 1978). After homogenisation, fluorescence was measured on a Turner AU-10 fluorometer calibrated with pure chl *a* (Sigma S6144) before and after adding 2 drops of 5% HCl.

POC and PON samples were dried at 60°C and exposed to HCl fumes for 24 h in order to remove carbonates. The C and N content was determined on a Leeman Lab CEC 440 CHN analyser and corrected for background contamination determined in blank filters.

TPP analyses followed a slightly modified version of Strickland & Parsons (1965). The dried filters (60°C overnight) were 'dry digested' by burning at 450°C for 4 h prior to digestion in a $K_2S_2O_8$ solution at 125°C for 30 min. Dry digestion has been shown to make particulate phosphorus more soluble and to reduce variability among replicates (Walve & Larsson 1999). The digested material was put in reaction with ascorbic acid and a molybdate solution, after which the absorbance was determined at 880 nm with a Hitachi U-2900 spectrophotometer. Blank filters were carried through the same procedure. Standard curves were prepared for each batch of samples based on a stock phosphate solution of known concentration.

The zooplankton community samples were analysed for the abundance of copepods. Stages were identified in the 3 *Calanus* species and in *Metridia longa* but not in the smaller species which were not sampled quantitatively by the 180 μm mesh WP2 net (Svensen et al. 2011). A minimum of 400 individuals were counted per sample, and successive aliquots were included until at least 150 specimens of the most abundant calanoid species were encountered. Abundance was converted to biomass using published stage-specific individual dry weights (Conover & Huntley 1991, Sabatini & Kiørboe 1994, Karnovsky et al. 2003, Blachowiak-Samolyk et al. 2008).

Volumetric conversion factors and faecal pellet export

Volumetric conversion factors for faecal pellets were determined at Stns B, 65 and 74 to estimate vertical flux of faecal pellet carbon (FPC), nitrogen (FPN) and phosphorus (FPP). Animals in the live zooplankton sample were sorted under magnification (dissecting stereoscope) and transferred to seawater dishes kept on ice using a wide-tip pipette. Batches of 15 to 20 healthy *Calanus finmarchicus* CV individuals (Stns 65 and 74) and *C. hyperboreus* CV (Stn B) were then gently emptied into each of 3 glass beakers (1.8 l) containing water from the depth of maximum fluorescence. After incubation for 17 to 26 h in darkness in a temperature-controlled room at close to *in situ* temperature (2°C at Stn 74 and 5°C elsewhere), the contents of the incubation chambers were gently filtered through a 10 μm mesh. The faecal pellets retained on the mesh were transferred through 3 baths of GF/F-filtered seawater by micropipette to remove algal cells and detritus. A known number of intact *Calanus* pellets were then collected on pre-combusted glass fibre filters for determination of C, N (100–260 pellets per filter, 1–4 filters per station), and P (40–150 pellets per filter, 2–4 filters per station) contents. The volume of pellets was estimated in the sediment trap samples, assuming that cylindrical pellets with a diameter of 50 to 90 μm derived from *Calanus* spp. CVs or adults (Reigstad et al. 2005, Wexels Riser et al. 2008). The volumetric conversion factors (mean ± SD) thus obtained were 63.0 ± 23.7 μg C mm^{-3}, 11.7 ± 2.7 μg N mm^{-3} and 2.4 ± 0.3 μg P mm^{-3}. Since cylindrical pellets from large copepods by far dominated the number of faecal pellets in the sediment traps, we did not attempt to quantify the input from sources other than cylindrical pellets.

RESULTS

Physical environment and chl *a*

The main stations with sediment trap deployments were located in Atlantic water with the core of the upper 200 m exhibiting >0°C temperature and salinity close to 35 (Fig. 2). Stn 74 was cooler, however, with temperatures between –0.3 and 2.7°C. The influence of ice melt was reflected in a cold and relatively fresh surface layer, resulting in stronger and shallower stratification compared to the other stations (Table 1). The homogenous depth distribution
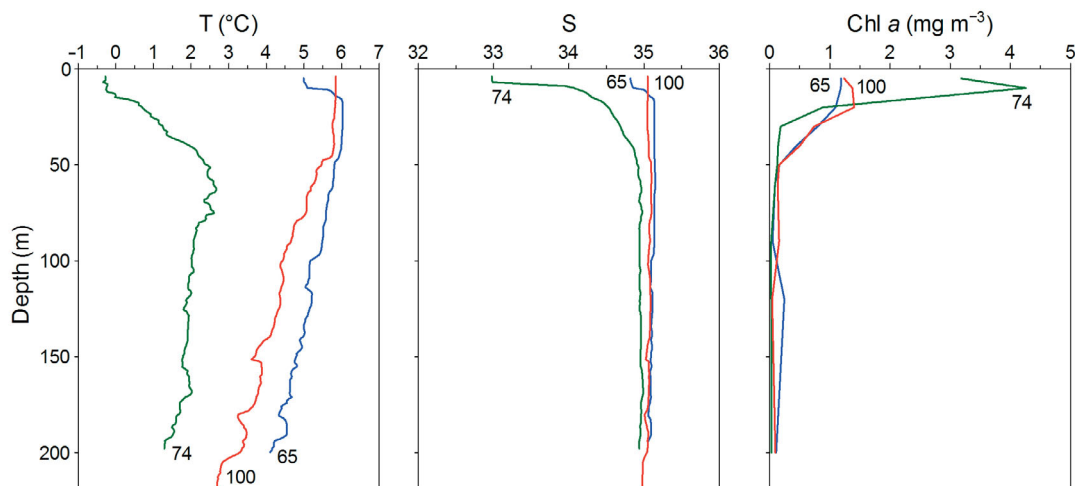
Fig. 2. Vertical distribution of temperature (T), salinity (S) and chlorophyll *a* (chl *a*) in the upper 200 m of the water column at Stns 65 (blue), 74 (green) and 100 (red)

Table 1. Main characteristics of the sediment trap stations. Mixed layer depth (MLD), chlorophyll *a* (chl *a*) biomass, abundance and biomass (dry weight [DW]) of *Calanus* spp. copepods, particulate organic carbon (POC) export and contribution of copepod faecal pellets to POC export (% faecal pellet carbon, FPC)

Station	MLD (m)	Chl a^a (mg m^{-2})	*Calanus* abundance^b (ind. m^{-2})	*Calanus* DW^b (mg m^{-2})	POC export^c (mg m^{-2} d^{-1})	% FPC^c (%)
65	10	64	8458	442	157	8
74	8	77	10375	5269	342	15
100	45	62	9233	179	147	7

^{a}Depth-integrated concentration for the 0–200 m layer
^{b}Depth-integrated abundance for the 0–100 m layer
^{c}Mean of all measurements in the 20–200 m layer

of 4 mg m^{-3}, while it was close to 1 mg m^{-3} at the other stations (Fig. 2). The depth-integrated chl *a* biomass was highest at Stn 74 (Table 1)

Copepod biomass and composition

Total copepod biomass varied by an order of magnitude among stations and was highest at Stn 74 (Fig. 3). *Calanus* spp. dominated the zooplankton biomass at all stations. Among *Calanus* spp., *C. finmarchicus* was the most abundant, but at Stn 74, *C. hyperboreus* dominated in terms of biomass. At this location, *Calanus* spp. accounted for 95% of total zooplankton biomass, whereas this proportion was slightly smaller at the other stations (71–82%; Fig. 3). The stage composition of *Calanus* copepodites differed among stations (not shown). CV dominated the biomass at Stn 65 and CIII at Stn 100. Stn 74 had a higher relative abundance of CVs and
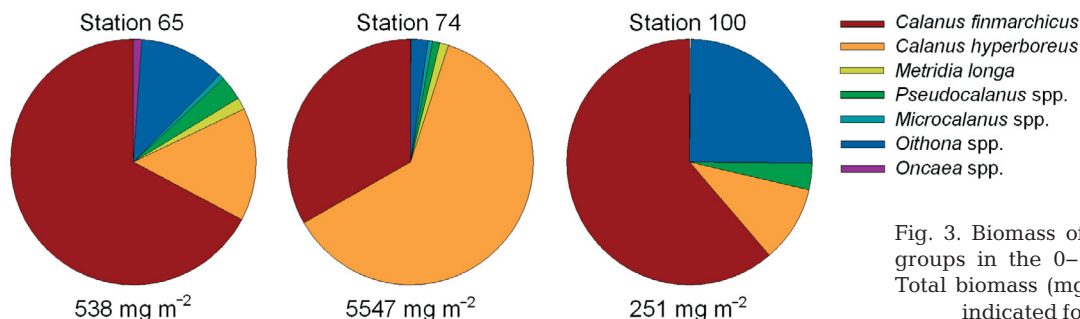
of temperature and salinity at Stn 100 likely resulted from a storm event during the days preceding sampling at this location, causing deep mixing of the water column.

All stations revealed an accumulation of chl *a* in the upper 50 m, with maximum concentration between 0 and 20 m. Stn 74 had a maximum chl *a* concentration

Fig. 3. Biomass of the main copepod groups in the 0–100 m depth layer. Total biomass (mg dry weight m^{-2}) is indicated for each station

adult females of both *C. finmarchicus* and *C. hyperboreus* which contributed to higher zooplankton biomass at this station. The biomass of *Metridia longa*, *Pseudocalanus* spp. and smaller copepods such as *Oithona* spp., *Microcalanus* spp. and *Oncaea* spp. differed among stations, but the proportion of these species together never exceeded 30% of the total biomass. However, the abundance and biomass of these taxa were probably underestimated since zooplankton was sampled with a 180 µm mesh.

Vertical flux of POC, PON, TPP and faecal pellets

Vertical flux was highest at Stn 74, with 265 to 430 mg POC m^{-2} d^{-1}, 48 to 83 mg PON m^{-2} d^{-1} and 5 to 10 mg TPP m^{-2} d^{-1}. The fluxes were slightly higher at Stn 65 than at Stn 100, but clearly lower than at Stn 74 (Fig. 4). At Stns 65 and 74, the vertical flux of all constituents declined with depth, being lowest at 200 m. At Stn 65, the POC flux decreased most sharply below 120 m depth, whereas a decrease
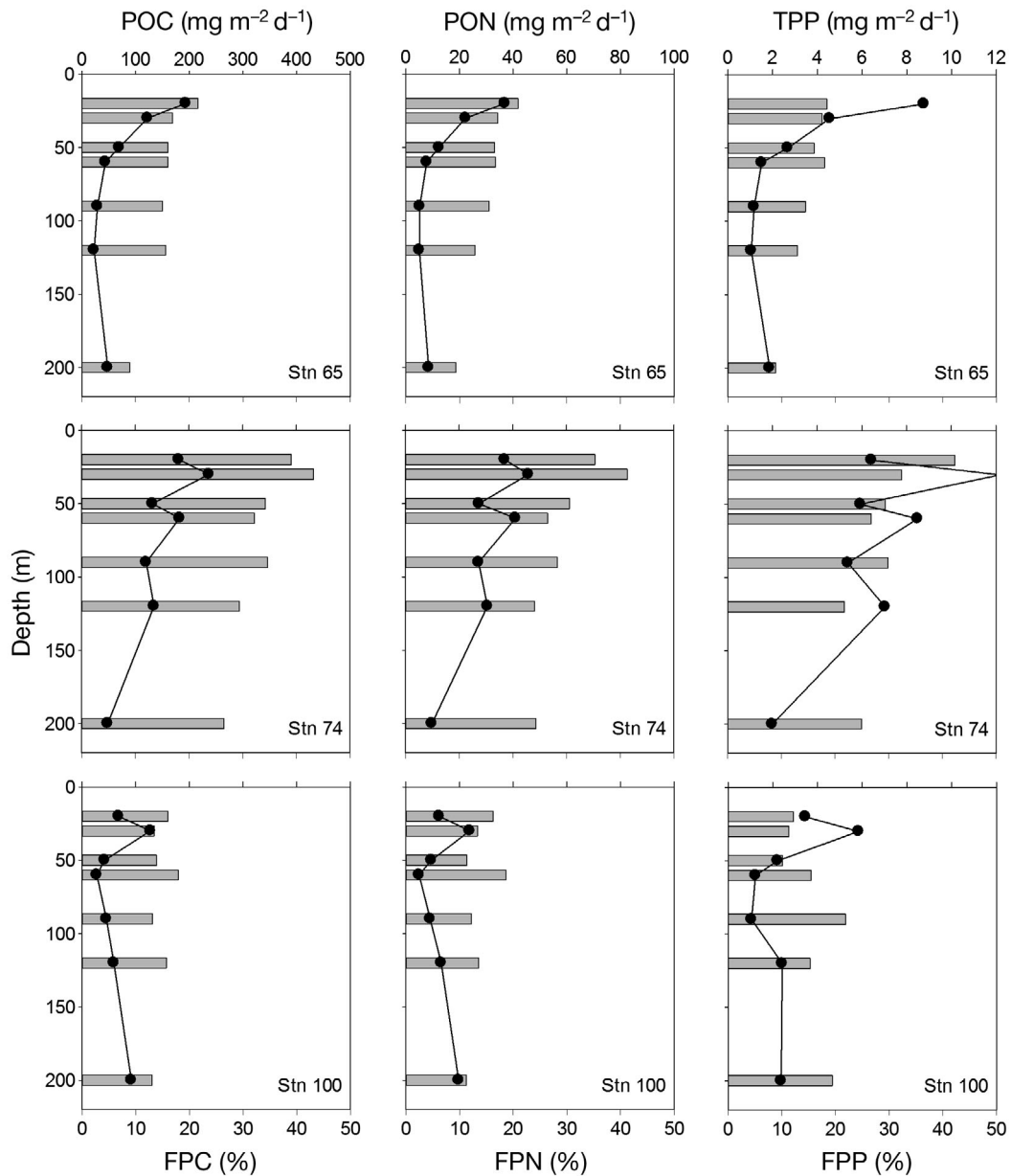

Fig. 4. Vertical flux (bars, upper *x*-axes) of particulate organic carbon, nitrogen, and total particulate phosphorus (POC, PON and TPP, respectively) at Stns 65, 74 and 100. Percentages of copepod faecal pellet C, N and P (FPC, FPN, FPP, respectively) of the total POC, PON and TPP fluxes are indicated by points and lines (lower *x*-axes)
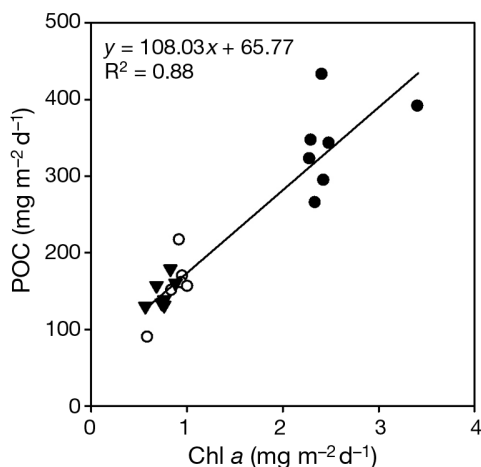
Fig. 5. Relationship between vertical flux of particulate organic carbon (POC) and chlorophyll *a* (chl *a*) across all observations (Stn 65: O, Stn 74: ●, Stn 100: ▼)

90 μm produced by older stages of *Calanus* spp. were the most abundant. The vertical flux of FPC and its contribution to POC export was highest at Stn 74 and was progressively lower at Stns 65 and 100 (Table 1, Fig. 6). Stns 65 and 74 revealed a decrease in FPC flux with depth, whereas this was not apparent at Stn 100. The attenuation of the FPC flux took place in the upper 60 m at Stn 65, while the flux decreased more gradually throughout the 0 to 200 m depth range at Stn 74.

The proportion of faecal pellets to vertical flux of POC, PON and TPP decreased with depth at Stns 65 and 74. At Stn 100, there was a reduction between 20 and 60 m, followed by an increase in the deeper traps (Fig. 4). Faecal pellets contributed equal proportions to POC and PON flux, with averages of 8, 15 and 7% at Stns 65, 74 and 100, respectively. The FPP contribution to TPP flux was higher, with 13, 28 and 11% at respective stations. While faecal pellets never accounted for more than 24% of exported POC and PON, their maximum contribution to TPP flux was 51%. Their mean contribution to vertical flux across all depths and stations was 10% of POC and PON and 17% of TPP.

in PON and TPP was already evident below 60 m. At Stn 74, the fluxes did not decrease monotonously, but there appeared to be a decline in all constituents between 30 and 60 m. At Stn 100, fluxes hardly decreased even below 120 m depth. The PON fluxes generally revealed the same depth variation as the POC fluxes. TPP fluxes increased between 120 and 200 m at 2 stations, but otherwise revealed the same trends as the POC and PON fluxes (Fig. 4). A linear regression of the vertical flux of POC on chl *a* across all stations and depths revealed a strong positive relationship, with a mean POC:chl *a* ratio of 108 for the exported organic matter ($R^2 = 0.88$, p < 0.0001, df = 20, Fig. 5).

Cylindrical copepod faecal pellets comprised the largest fraction of the faecal material found in the sediment traps, on average accounting for 90% of total FPC. Of these, pellets with a diameter of 50 to

Stoichiometry of suspended and exported organic particles

The C:N and C:P ratios revealed no consistent variation with depth in either suspended or exported material (not shown). The mean of all depths for suspended C:N varied from 5.0 (Stns B, 65 and 100) to 7.8 (Stn 74; Table 2). The mean C:N of exported particles (5.9–6.7) was closer to Redfield, and the variation among stations was smaller than in suspended particles (Table 2).
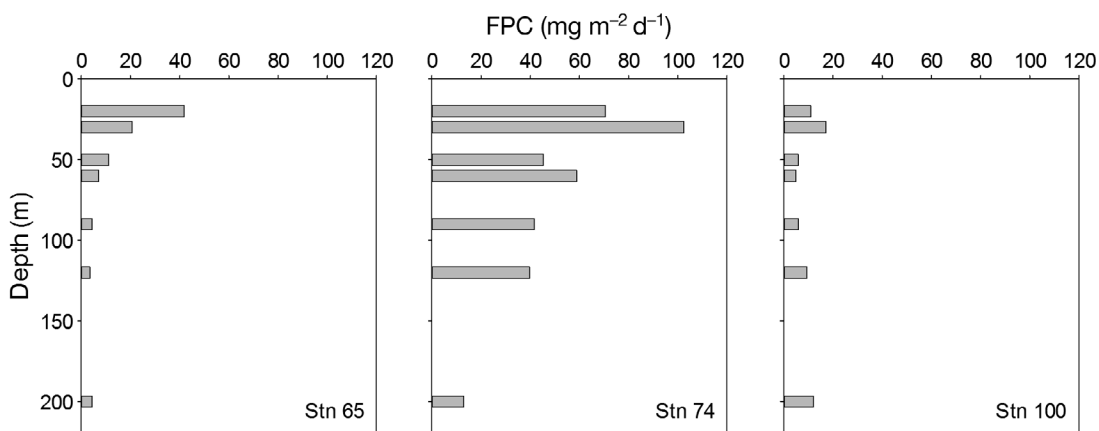

Fig. 6. Vertical flux of faecal pellet carbon (FPC) by copepod faecal pellets at 3 stations

Table 2. Stoichiometric ratios (mean ± SD of all depths) of suspended and exported particles and copepod faecal pellets (FP). a:a: atomic ratios; ND: no data

Station	C:N (a:a)			C:P (a:a)		
	Suspended	Exported	FP	Suspended	Exported	FP
B	5.2 ± 0.2	ND	7.1	101 ± 12	ND	89.8
65	5.0 ± 0.3	5.9 ± 0.5	6.6	90 ± 26	112 ± 12	54.0
74	7.8 ± 2.3	6.7 ± 0.4	5.0	85 ± 29	126 ± 16	55.0
100	5.4 ± 0.6	6.3 ± 0.6	ND	97 ± 23	113 ± 33	ND

The mean suspended C:P ratio was below Redfield (106) at all stations, and lowest at Stn 74. Conversely, the C:P of exported particles exceeded the Redfield ratio at all stations and was highest at Stn 74 (Table 2). The mean C:P of exported particles was significantly higher than the suspended C:P (t-test, $p < 0.001$, df = 41). The variability was higher in suspended than in exported C:P ratios, consistent with the patterns in C:N.

DISCUSSION

Environmental and ecological settings

This study is based on 3 discrete observations from different parts of the Fram Strait and the Barents Sea. All sampling locations were dominated by Atlantic water, but differed in terms of water column stratification and biological conditions. Stn 74, located in the central Fram Strait, represents a cold-water spring bloom scenario with strong stratification and high abundance of algal pigments, and dominance of the Arctic zooplankton species *Calanus hyperboreus*. Stn 65 was characterised by early-bloom conditions with lower abundance of algal pigments, mainly concentrated at the surface. Stn 100 represents a mixing scenario during an ongoing bloom. The mesozooplankton communities at Stns 65 and 100 were dominated by *C. finmarchicus* typical of Atlantic water masses. The Barents Sea station was characteristic of a mixing scenario following a storm. These conditions were important for the observed patterns in vertical flux and for the zooplankton mediation of organic matter export, which will be discussed in the following sections.

Patterns in vertical export and regulating factors

The vertical flux of POC and PON were within the ranges observed in the Barents Sea and Svalbard region during summer (Andreassen et al. 1996, Olli et al. 2002, Reigstad et al. 2008), and higher than in the adjacent Northeast Water Polynya (Bauerfeind et al. 1997). The TPP fluxes are the first to be reported from this region and probably the first from the entire Arctic Ocean. Comparisons to other regions will therefore focus on stoichiometry and retention. The strong positive relationship between vertical flux of POC and chl *a* indicates that organic matter derived from phytoplankton production was the principal source of exported POC. The high exported POC:chl *a* ratio (108) suggests a more degraded composition of the exported material than in e.g. Arctic waters of the Barents Sea, where the corresponding ratio was lower (54; Reigstad et al. 2008).

The higher contribution of zooplankton faecal pellets to vertical flux at Stn 74 than elsewhere was likely a consequence of higher zooplankton biomass due to the greater abundance of *Calanus hyperboreus* and older stages (CV and females) of both *C. finmarchicus* and *C. hyperboreus*. *C. hyperboreus* is the largest of the 3 Arctic calanoid species, approximately twice as large as *C. finmarchicus* by prosome length (Karnovsky et al. 2003, Swalethorp et al. 2011) and produces lager faecal pellets (Wexels Riser et al. 2008). Hence, this species has a strong impact both on zooplankton biomass and faecal pellet export. Furthermore, since faecal pellets typically are recycled in the upper part of the water column (Wexels Riser et al. 2007), we hypothesise that the strong and well-defined pycnocline at Stn 74 allowed a high proportion of faecal pellets to be exported because the distance relevant to grazing and pellet degradation was reduced. This is in agreement with observations from the Barents Sea shelf, showing more efficient recycling of faecal pellets in the less stratified Atlantic section compared to the strongly stratified Arctic section (Wexels Riser et al. 2002). In contrast, smaller, slower-sinking particles (algal cells and aggregates) would be retained more efficiently in the water column under stratified conditions. At the other stations, the lower phytoplankton biomass was reflected in lower vertical flux. The smaller proportion of faecal pellets at Stns 65 and 100 was likely due to a combination of the lower biomass of *Calanus* spp. at these stations and stronger retention of faecal pellets in the water column.

Without sustained production of new autotrophic biomass below the euphotic zone, consumption and

degradation of organic matter by the pelagic food web reduces the vertical flux with increasing depth. The vertical distance over which elemental fluxes are attenuated varies significantly among geographical regions (Wassmann et al. 2003, Buesseler et al. 2007, Buesseler & Boyd 2009). In stratified regions such as large parts of the Arctic Ocean and coastal waters, the POC flux typically diminishes strongly in the upper 100 m and in close proximity to the pycnocline (Wassmann et al. 2003, Reigstad et al. 2008). In the present study, POC fluxes decreased with depth at the 2 stations characterised by stratification in the upper 10 m (Stns 65 and 100; Table 1). Mixing of the water column at Stn 100 likely caused a redistribution of biomass, resulting in a diffuse pattern of vertical flux and weak reduction with depth. Deep mixing during the productive season caused by atmospheric forcing therefore sets up an active and fast transport of fresh organic matter to deep-water layers and sediments (Reigstad et al. 2008, Renaud et al. 2008). As a consequence, the vertical flux of POC at 200 m depth was higher at the deeply-mixed Stn 100 than at the stratified Stn 65 although fluxes closer to the surface were lower (Fig. 4). Mixing events related to the cyclic pattern of atmospheric low-pressure systems are a common feature in the Barents Sea during summer and contribute to higher primary production and carbon fluxes to the seabed in the weakly stratified open Barents Sea south of the extent of the seasonal ice cover (Reigstad et al. 2011).

Export stoichiometry and retention efficiency of C, N and P

In the present study, the C:N ratios of suspended and exported material were below Redfield at Stns 65 and 100, whereas they were slightly elevated at the peak-bloom Stn 74. The C:N ratios suggest that ice-rafted or terrestrial organic matter which typically has C:N ratios above 10 (Grebmeier et al. 1988, Andreassen et al. 1996, Tamelander et al. 2009) was not an important source to vertical export. Stoichiometric ratios are also influenced by the species composition of primary producers, revealed in higher C:N ratios of exported organic matter in the diatom-dominated Arctic section of the Barents Sea compared to the *Phaeocystis*-dominated Atlantic section (Olli et al. 2002). Information on the species composition of phytoplankton is not available, and therefore we cannot evaluate this source of variation.

The mean C:N ratio of exported particles was the same as in suspended particles, indicating that carbon and nitrogen were exported in the same proportions. This is supported by the lack of change in C:N ratios with depth, both in suspended and exported particles. In reviewing remineralisation rates, Boyd & Trull (2007) found nitrogen to be remineralised faster than carbon in most areas investigated, but not in all. Their compilation of data did not include observations from the Arctic or other strongly stratified regions, however. The present results agree with earlier studies in the European Arctic showing that carbon and nitrogen are exported from the upper 200 m in the same proportions during summer (Olli et al. 2002, Reigstad et al. 2008).

There are few reports on C:P stoichiometry of exported organic matter from primarily nitrogen-limited regions such as the Arctic Ocean. In the primarily nitrogen-limited Baltic Sea, the retention efficiencies of carbon, nitrogen, and phosphorus vary both spatially and seasonally, with phosphorus being retained up to 5 times more efficiently than carbon in the upper water column during spring (Heiskanen et al. 1998, Reigstad et al. 1999). In large parts of the ocean, phosphorus appears to be mineralised faster than carbon and approximately at the same rate as nitrogen (Loh & Bauer 2000, Boyd & Trull 2007). The consistently higher C:P of exported particles compared to suspended ones in the present study indicates that phosphorus remineralises faster than carbon and nitrogen and that carbon and nitrogen were exported in equal proportions. Phosphorus lost from senescent phytoplankton is remineralised within hours and recycling is faster than for carbon and nitrogen (Garber 1984). Phosphorus-starved phytoplankton and bacteria also solubilise phosphorus enzymatically from complex molecules by alkaline phosphatase, thereby contributing to its retention in the water column (Thingstad et al. 1998). Based on the average suspended and exported C:P ratios, phosphorus was retained 1.2 to 1.4 times more efficiently than carbon, with the highest retention efficiency at Stn 74, which was characterised by peak-bloom conditions. These inferred retention efficiencies are 2 orders of magnitude below those observed in the P-limited subtropical North Pacific (Hannides et al. 2009). The lack of significant changes in the C:N and C:P ratios of exported particles with depth suggests that phosphorus is derived from particles close to the surface (i.e. above 20 m) and that sinking particles retain their properties at least within the depth range of 200 m considered in this study.

Potential for P export through copepod faecal pellets

Although zooplankton faecal pellets generally are efficiently recycled in the water column, the small but variable fraction escaping destruction and degradation contributes to vertical export of organic matter from the water column (Viitasalo et al. 1999, Wexels Riser et al. 2007). Turner (2002) estimated that faecal pellets on average contribute 20% of exported POC where this proportion has been determined. Their potential as loss factors for nitrogen and phosphorus from the water column has received less attention, however. This study suggests that faecal pellets are a phosphorus-rich source of organic matter, contributing to a relatively higher proportional export of phosphorus than of carbon and nitrogen. The elemental composition of faecal pellets mainly varied in terms of carbon content among stations, possibly relating to the variation in the composition of suspended particulate organic matter that was used as a diet (Daly 1997). Taking the variation in faecal pellet carbon content into account would have increased the C:P ratio of faecal pellets to 104 at the most. This is below the C:P of the exported organic matter, which corroborates our finding that faecal pellets are a stronger loss factor for phosphorus than for carbon and nitrogen from the water column. Our estimates of a 17% contribution of faecal pellets to TPP export and 10% to PON should be considered conservative since the nitrogen and phosphorus contents were only determined in copepod pellets. However, these estimates should be representative of Arctic marine systems since copepods typically dominate the mesozooplankton communities in these regions. Pellets from appendicularians and krill are temporarily abundant in sediment trap samples (Wexels Riser et al. 2008), but without knowledge of their phosphorus content, their contribution to phosphorus export cannot be quantified.

The results suggest that leaching of phosphorus from senescent phytoplankton to the surrounding water is delayed when cells are packed in faecal pellets. The larger volume:surface ratio of aggregates and pellets compared to single cells or algal colonies also means that less substrate is exposed to alkaline phosphatase present in the environment, and the solubilisation of phosphorus from these particles may thus be reduced. Although their average contribution to phosphorus export was only 7% higher than to carbon and nitrogen export, faecal pellets may nevertheless provide a mechanism for fast removal of phosphorus from the water column under conditions favouring retention of slower-sinking detritus. Given the low C:P ratio of faecal pellets, the high faecal pellet flux at Stn 74 seems to disagree with the C:P ratio of total exported particulate organic matter being highest at this station. Another unidentified fraction of the sinking material must therefore have been enriched in carbon in order to produce this pattern.

This study shows that sinking of large zooplankton faecal pellets provides an important mechanism for removal of phosphorus from the water column. The relative importance of this pathway is likely augmented under strongly stratified conditions when smaller, slower-sinking detritus is recycled. Increasing the number of observations in a future study to include scenarios where faecal pellets are more abundant would be important in order to further evaluate their role for phosphorus export.

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