Biogeochemistry (2007) 83:235–244
DOI 10.1007/s10533-007-9094-2

ORIGINAL PAPER

Vernal sedimentation trends in north Norwegian fjords: temporary anomaly in ^{234}Th particulate fluxes related to *Phaeocystis pouchetii* proliferation

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Received: 23 May 2006 / Accepted: 5 October 2006 / Published online: 8 March 2007

Abstract We report data of a naturally occurring radionuclide, ^{234}Th, an in situ tracer, to investigate vertical export of biogenic matter during a vernal bloom of *Phaeocystis pouchetii* in the fjords of northern Norway. To optimise sampling of different stages of the bloom, three fjords with increasing oceanic influence (Balsfjord, Malangen fjord and Ullsfjord, respectively) were investigated in April 1997. Contrasting situations were encountered between the three fjords: the proliferation of *P. pouchetii* in Ullsfjord surface waters coincided with a drastic reduction of particulate ^{234}Th fluxes in traps, although particulate organic carbon (POC) and dimethylsulphoniopropionate (DMSP) were exported and ^{234}Th was available in surface waters. When large colonies make up a significant fraction of the vertical flux, as observed in Ullsfjord in April 1997, there may be a large and rapid change in the POC/^{234}Th ratio, further complicating the use of ^{234}Th as a tracer for POC export. The results suggest that the proliferation of *Phaeocystis pouchetii* during vernal bloom could temporary increase OC/^{234}Th ratio of particles and delay the particulate export of ^{234}Th, and probably of other particle-reactive species, from surface waters.

Keywords fjord · Northern Norwegian shelf waters · Particle flux · *Phaeocystis* · Sediment trap · ^{234}Th

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Introduction

The microalga genus *Phaeocystis* has a worldwide distribution and is known to develop massive blooms in polar and temperate waters (Riebesell et al. 1995). Spring blooms of *Phaeocystis* often follow diatom blooms, after the decline of dissolved silicate (Lancelot et al. 2005; Wassman et al. 2005). This colony-forming alga is an important source of the volatile organic sulphur compound dimethyl sulphide (DMS) and its

dense blooms can act as a carbon sink (Rousseau et al. 2000; Belviso et al. 2006). Both sulfur and carbon cycles are relevant to climate change studies, sulphur as an important source of cloud condensation nuclei, and carbon being the main contributor to the greenhouse effect. Quantifying the role of *Phaeocystis* blooms in particle fluxes and export is therefore important if we want to understand their potential control on the escape of carbon from the photic zone of coastal waters. Indeed, the community structure determines how much of the primary production settles via the classical food web, via large phytoplankton and their grazers, and how much nutrients are regenerated via the microbial food web (Eppley and Peterson 1979; Verity 2000; Stelfox-Widdicombe et al. 2004). Within the EU funded program Escape (Entangled Sulphur and Carbon cycles in *Phaeocystis* dominated Ecosystems), this study focused upon the vertical export of biogenic material in relation to the plankton community dynamics and structures in north Norwegian fjords.

Thorium-234 (^{234}Th, $t_{1/2}$ = 24.1 days), a naturally occurring radionuclide, was used in this work to explore particle dynamics during the development of a *Phaeocystis* bloom. ^{234}Th is produced in seawater via the decay of its long-lived and highly soluble parent, uranium-238 (^{238}U). Since ^{234}Th is highly particle-reactive, and hence sticks to all particle surfaces, the clearance of ^{234}Th from surface waters is a direct indication of the removal rate of material on sinking particles from the upper ocean. Review papers clearly show the interest in this tracer as a tool for estimating particulate organic carbon export (Buesseler et al. 2006 and references herein). In surface waters, biological activity is the main source of particles and can vary considerably on short time scales. Previous studies have shown the close coupling between dissolved ^{234}Th scavenging and new production in the ocean (Coale and Bruland 1985). The particulate ^{234}Th residence time in oceanic surface waters is of the order of a few days to a few weeks (Moran and Buesseler 1992) and appears to be mainly governed by the classical food web, via the export of detritus (marine snow, aggregates, faecal pellets) (Schmidt et al. 1992; Buesseler et al. 2006).

The present paper discusses ^{234}Th data in the water column and in settling particles, together with the determination of the stocks of *Phaeocystis pouchetii* and DMSP in surface waters of north Norwegian fjords. The aims of this study are: (i) to describe temporal variability of ^{234}Th activities and fluxes during the progress of a vernal bloom, (ii) to calibrate trap collection efficiencies using ^{234}Th data, and (iii) to assess the impact of *Phaeocystis* proliferation on vertical export of particles.

Material and methods

Study area

To optimize sampling of different stages of the recurrent vernal *Phaeocystis pouchetii* bloom in northern Norway, three fjords with decreasing oceanic influence were investigated in the north Norwegian coastal zone (Fig. 1). The westernmost fjord, Malangen fjord, is relatively open and exposed to shelf waters. Ullsfjord, the northernmost is the most open to coastal waters with a wide entrance. Both fjords are wide and have deep sills. Balsfjord is the least exposed: it is a tapered inland fjord, which is separated from the Malangen fjord and Ullsfjord by three narrow straits. More details on sampling areas including their physical, chemical and biological characteristics can be found in Wassman et al. (1996), Keck and Wassmann (1996), Reigstad et al. (2000) and Archer et al. (2000). The stations were visited sequentially five times, between April 7 and April 25, 1997, aboard the RV Johan Ruud.

Measurements

To sample the settling flux directly, free-floating multiple-sample programmable sediment traps (Pro-Trap) were deployed at all three fjords for about 16 h at each time (trap depth: 60 m). The Pro-Trap system consists of four polyvinyl chloride (PVC) sediment tubes, each of 0.018 square meter exposed area (cylinder height of 80 cm, trap aspect ratio A ¼ 5.3), mounted on a stainless-steel frame. Depth and angle sensors allowed defining the position of the traps in the water

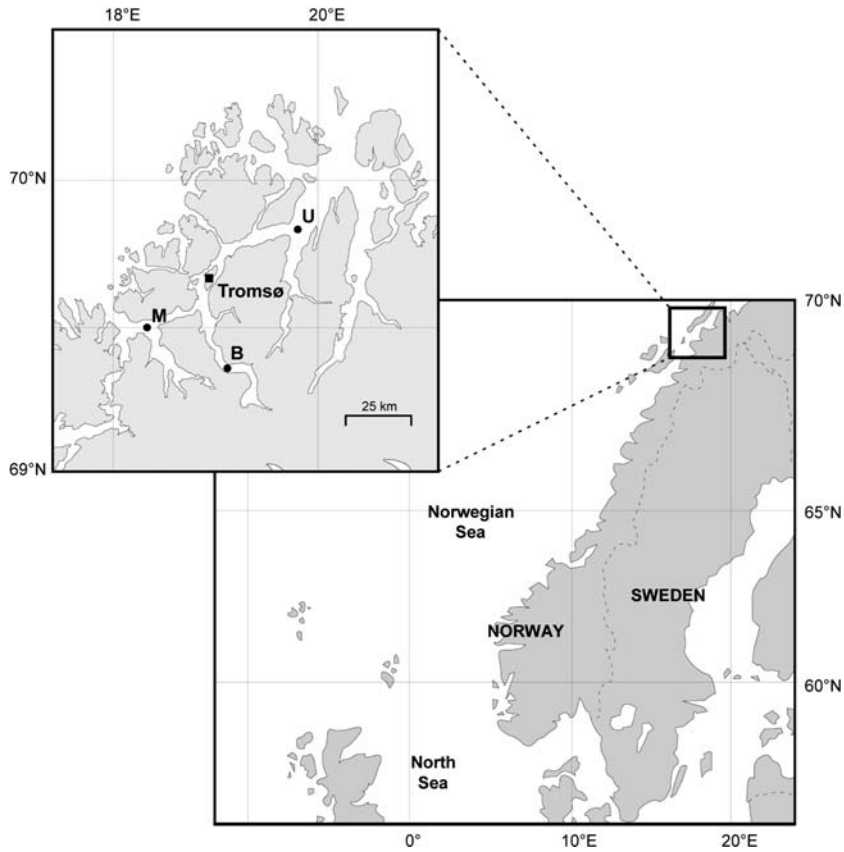

Fig. 1 Map of the investigated fjords

column, while light scattering was measured by a Sea Tech LS sensor. A VALEPORT 800-0 series electromagnetic current meter provided 2-axis flow velocity measurements at the trap aperture (see Belviso et al. 2006 for details). Upon recovery, swimmers (living zooplankton) were removed from the samples prior to all analyses, in order to assess properly the passive particulate fluxes. Trap samples were immediately filtered on precombusted and preweighed Whatman GF/F filters of 25 or 47 mm diameter and stored at –20°C until analysis (within six months). All carbon and nitrogen analyses were performed on a Carlo Erba NC 2500 gas chromatography analyzer. The difference-on-ignition (DOI) method was used to separate organic and inorganic carbon (Majeed 1987). Details on the determination of DMSP stocks and fluxes are given in Belviso et al. (2006).

One sediment tube, devoted to the determination of ^{234}Th, took a single sample for the entire duration of each deployment. On recovery of the traps, trapped particles were filtered on GF/F; ^{234}Th activities were measured with a low-background high-efficiency γ detector. ^{234}Th activities were measured from its 63.2 and 92.4–92.8 keV - gamma rays, and decay corrected to the time of sample collection (Schmidt and Reyss, 2000). The standards used for the calibration of the γ detector are: (1) a mock-up of sediment and U and Th US standards from National Bureau of Standards (NBS) at 1,000 ppm, and (2) a known amount of ^{238}U deposited on an aluminum disk checked by α-counting using a grid chamber of a known efficiency. Counting efficiencies and backgrounds for ^{234}Th are detailed in Schmidt and Reyss (2000) and Schmidt (2006).

During the fifth (and last) sampling date, a profile of ^{234}Th was sampled between the surface and the trap depth (60 m) at each station. Immediately after sampling, the 20 l of seawater was passed through a 0.45 μm pore size filter to separate dissolved from particulate phases. Within one month after the collection, particulate

^{234}Th (^{234}Th^{P}) was directly measured on the filter as trapped particles. After acidification to pH 2, pre-weighed 50 mBq ^{229}Th chemistry yield tracer and 120 mg Fe (as $FeCl_3$) were added to the dissolved sample. After spike equilibration, $Fe(OH)_3$ was precipitated by adding NH_4OH to pH 7. After recovery of the precipitate, the purification of ^{234}Th was obtained by anionic exchange. After elution, Th was extracted with 1-(2thenoyl)-3,3,3-trifluoracetone in toluene at pH 3 and then evaporated onto an aluminum foil. The first α counting of this foil allowed the determination of ^{229}Th for chemical yield (between 20% and 60%); the following γ-counting allowed the measurement of ^{234}Th. Due to the short half-life of ^{234}Th, the separation of ^{234}Th from its parent was done within 24 h. Calculations of dissolved ^{234}Th activities consider ingrowth corrections for time elapsed between sampling and chemistry (Schmidt and Reyss 2000; Schmidt et al. 2002).

The U–salinity relationship (Chen et al. 1986) is appropriate for estimating dissolved ^{238}U in the open ocean; in other regimes, i.e., continental shelves, estuaries or marginal seas, the U concentration must be measured (Schmidt and Reyss 1991; Rutgers van der Loeff et al. 2006). Seawater samples were collected at each station for ^{238}U determination. Uranium was concentrated from 2 l seawater, as previously described for ^{234}Th, in the presence of a known amount of ^{232}U spike and 20 mg Fe. Then uranium activities were determined by α-counting (Schmidt 2004).

Phytoplankton abundance was determined in samples from depth profiles taken at dawn as described by Archer et al. (2000). Data on *Phaeocystis* abundance provided here are means from the 1, 4 and 8 m depth samples. Phytoplankton carbon is calculated from biovolume measurements as described by Archer et al. (2000).

Irreversible scavenging model of ^{234}Th

^{234}Th as a tracer is widely used and critical for two tasks: to quantify fluxes and residences time of particles, and to calibrate trap efficiency by comparing estimated water-column ^{234}Th fluxes with those measured by traps (Cochran et al. 2000). In surface waters, ^{234}Th activities are the result of a balance between its continuous production from ^{238}U, its decay, removal onto rapidly sinking particles, and advection/diffusion. The temporal change in total ^{234}Th is expressed by the classical transport equation:

$$\delta A^{\mathrm{Th}}/\delta t = \lambda A^{\mathrm{U}} - \lambda A^{\mathrm{Th}} - P + V \qquad (1)$$

where A^{U} is the ^{238}U activity, A^{Th} is the total ^{234}Th activity, λ is the decay constant of ^{234}Th (=0.0288 day^{-1}), P is the net removal flux of ^{234}Th^{P}, and V is the sum of the advective/diffusive fluxes (Savoye et al. 2006 and references therein). Measurements of both dissolved and particulate ^{234}Th allow us to calculate rates of exchange between dissolved and particulate phases, removal fluxes and particle residence times. By assuming steady state and negligible advective/diffusive terms, particulate ^{234}Th flux, P, must balance the measured deficit relative to A^{U}. Particle residence times with respect to removal from surface layer are given by the ratio ^{234}Th^{P}/P.

Results

Hydrography, *Phaeocystis* and DMSP distribution in the three fjords

The differences in temperature, salinity and density indicated no major exchange of water masses throughout the cruise. Salinity was lowest in Balsfjord (33.5–33.7), and highest in Ullsfjord (34.2–34.5) (Reigstad et al. 2000).

The development of the *Phaeocystis* bloom was different between the three fjords (Fig. 2). The lowest cell numbers were observed in Balsfjord, with contributions of *Phaeocystis* cells to total phytoplankton cells of less than 12% throughout the study period; diatoms dominated in Balsfjord. On the other hand, Ullsfjord, with open access to coastal waters, presented a well-developed vernal bloom, with the highest *Phaeocystis* abundances; this alga dominated the phytoplankton community (in numbers of cells) in April. The abundance of *Phaeocystis* in Malangen fjord waters was relatively low and intermediate between the two other fjords.

DMSP in surface waters, produced primarily by *Phaeocystis*, paralleled the distribution of this

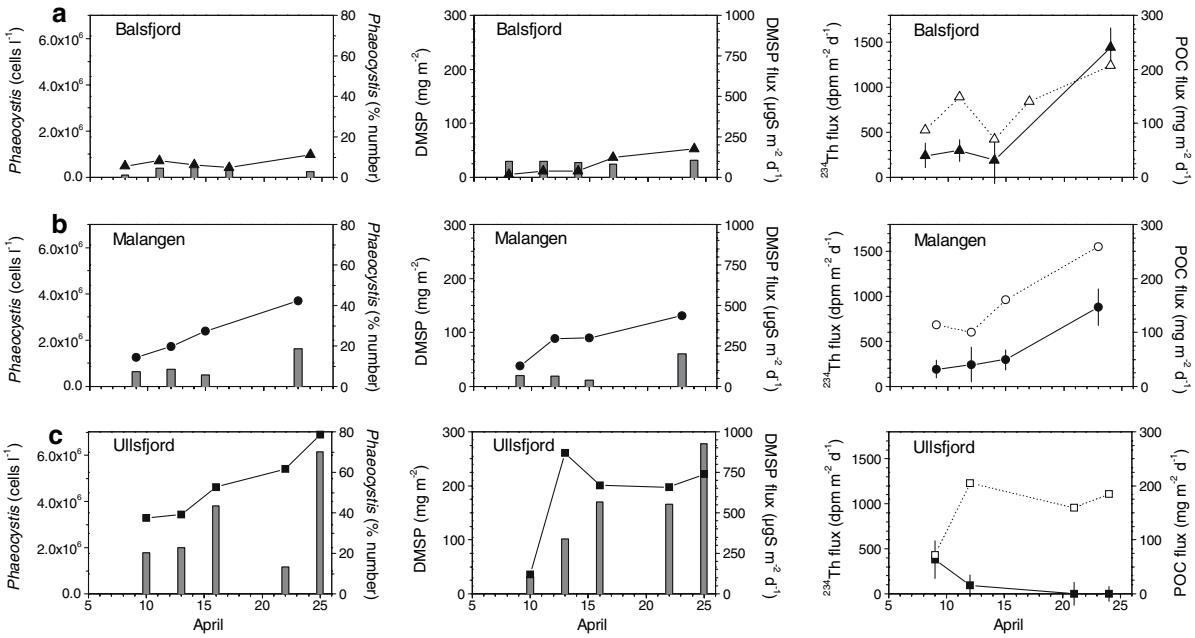

Fig. 2 Summary of changes in the stocks of *Phaeocystis* (left; bars: number of cells; closed symbols: % of *Phaeocystis* cells to total cell number) and DMSP (middle; bars: total water column standing stock; closed symbols: export fluxes) and particulate ^{234}Th flux (right, closed symbols) and POC flux (right, open symbols) for the three fjords studied in April 1997. The measured DMSP, POC and ^{234}Th fluxes are from sediment trap samples collected at 60 m depth on the same cruises as the profiles

alga, with increasing stocks from Balsfjord Malangen to Ullsfjord (Fig. 2). Fluxes and standing stock of DMSP were positively correlated in the three fjords, but the slope of the relationship was different from one fjord to the other. Measured POC fluxes in the same trap mimic temporal evolution in DMSP fluxes, although DMSP to POC ratios in the settled material differed between fjords. This is related to the difference in phytoplankton community composition between the three fjords: *Phaeocystis*-dominated phytoplankton in Ullsfjord being richer in DMSP than diatom-dominated phytoplankton in Balsfjord.

Vertical distribution of ^{234}Th

One profile of particulate and dissolved ^{234}Th between surface and 60 m depth was taken at each station in late April (Table 1). ^{238}U activities increased with oceanic influence, in association with the salinity, from 2.10 dpm l^{-1} (Balsfjord) to 2.38 dpm l^{-1} (Ullsfjord; Table 2). Particulate ^{234}Th was extremely variable from negligible to 0.64 dpm l^{-1} and represented up to 62% of the total ^{234}Th. The mean 0–40 m ^{234}Th^{P} to total ^{234}Th ratio was lowest in Ullsfjord (20%). Total ^{234}Th activities varied both with depth and with fjords, ranging from 0.73 dpm l^{-1} to 1.96 dpm l^{-1}. These values were always lower than ^{238}U activities (2.10–2.38 dpm l^{-1}). Marked deficits (33–65%) were observed in all three fjords at the end of April (33–65%). Equilibrium state (^{234}Th/^{238}U = 1) was only observed at 60 m depth in Balsfjord. These trends are consistent with a common pattern of increasing scavenging in shallow waters (Gustafsson et al. 1998). As the ^{234}Th deficit is due to exported particles, these large deficits may indicate that efficient particle export had occurred during the sampling period or few weeks before. Such deficits are comparable to the range of values reported in other Arctic regions (Coppola et al. 2002; Trimble and Baskaran, 2005).

The calculated mean particulate ^{234}Th residence times for the upper 60 m were about

Table 1 Particulate, dissolved and total ^{234}Th activities

Site	Depth (m)	$^{234}Th^{p}$ dpm l^{-1}	$^{234}Th^{d}$ dpm l^{-1}	$^{234}Th^{T}$ dpm l^{-1}
Balsfjord April, 24, 1997	0	0.32 ± 0.06	0.41 ± 0.06	0.73 ± 0.08
	20	0.40 ± 0.05	0.88 ± 0.09	1.28 ± 0.10
	40	0.64 ± 0.09	0.77 ± 0.17	1.40 ± 0.19
	60	0.61 ± 0.09	1.35 ± 0.28	1.96 ± 0.29
Malangen April, 23, 1997	0	0.57 ± 0.14	0.34 ± 0.34	0.92 ± 0.37
	20	0.38 ± 0.08		
	60	0.10 ± 0.10	1.21 ± 0.36	1.31 ± 0.27
Ullsfjord April, 25, 1997	0	0.24 ± 0.08	0.77 ± 0.14	1.00 ± 0.17
	40	0.22 ± 0.10	1.11 ± 0.13	1.33 ± 0.17
	60	0.55 ± 0.10		

Table 2 Mean 0–60 m activities of particulate and total ^{234} Th, and ^{238}U; residence time of particulate ^{234}Th ($T(P)$); and ^{234}Th fluxes

Site	$^{234}Th^{p}$ dpm l^{-1}	$^{234}Th^{T}$ dpm l^{-1}	^{238}U dpm l^{-1}	$T(P)$ days	Calculated ^{234}Th fluxes dpm m^2 d^{-1}	Trapped ^{234}Th fluxes dpm m^2 d^{-1}
Balsfjord April, 24, 1997	0.49 ± 0.15	1.34 ± 0.37	2.10 ± 0.15	22.6	1307 ± 93	1444 ± 184
Malangen April, 23, 1997	0.35 ± 0.19	1.06 ± 0.45	2.29 ± 0.12	10.0	2122 ± 127	880 ± 162
Ullsfjord April, 25, 1997	0.34 ± 0.16	1.17 ± 0.23	2.38 ± 0.10	9.6	2097 ± 37	<82

Calculated ^{234}Th fluxes are based on ^{234}Th data using the model described in the method section; trap ^{234}Th fluxes correspond to measurements on trap samples for the corresponding period

10 days for the Ullsfjord and Malangen stations and 23 days for the Balsfjord station. These residence times are comparable to the mean values calculated for the Barents Sea (15 days, Coppola et al. 2002).

Particulate fluxes of ^{234}Th

^{234}Th fluxes presented a more confusing signal (Fig. 2). Like the DMSP fluxes, the ^{234}Th fluxes increased throughout April in both the Balsfjord and Malangen fjords. In contrast, ^{234}Th fluxes dropped dramatically (from moderate to negligible values) in Ullsfjord after mid April. This trend was rather unexpected in spring when fluxes are usually increasing during the development of the spring bloom (Buesseler et al. 1992). Profiles in the upper 60 m of the three fjords showed that total ^{234}Th activities ranged from 0.7 to 1.9 dpm l^{-1}. There were no large differences in ^{234}Th availability between the fjords. This result would signify that the rapid decrease in ^{234}Th fluxes at Ullsfjord was not related to a complete depletion of this radionuclide. In such coastal systems, it is not possible to exclude exchange with adjacent coastal waters, especially for Ullsfjord, the most open fjord. Nevertheless hydrological data do not indicate major exchange of water masses during the sampling period (Reigstad et al. 2000). In addition such exchanges, if occurring, would be likely to convey ^{234}Th, as coastal waters have higher salinity and consequently higher ^{234}Th.

Discussion

^{234}Th fluxes and trap collection efficiencies

During ESCAPE, integrating ^{234}Th profiles down to 60 m (to get a particulate ^{234}Th flux) provided a meaningful comparison with the sediment trap,

which collected particulate ^{234}Th flux passing the depth horizon of 60 m. Steady-state fluxes ranged between 1300 and 2100 dpm m^{-2} d^{-1} (Table 2). For Balsfjord, measured and calculated fluxes compared rather well, which indicates a high efficiency of the trap.

In contrast, measured particulate ^{234}Th fluxes in Malangen and Ullsfjord were far below the calculated ones (Table 2). A rapid interpretation of these results would lead to the conclusion that recovery efficiencies of the sediment trap were low, even negligible, for Ullsfjord. This is, however, unlikely since temporal evolution of biological parameters in trap collections (DMSP, POC) were in good correlation to their standing stocks (Fig. 2). Another explanation may be related to the ^{234}Th calibration method. In the present work, ^{234}Th fluxes are calculated from a single profile of ^{234}Th assuming steady state and neglecting advection. Although the use of non-steady-state modeling is more accurate (Buesseler et al. 1992; van der Loeff et al. 1997), steady-state models have been shown to provide adequate estimations of ^{234}Th fluxes (Benitez-Nelson et al. 2000), except when sampling occurs just after a high export event that depleted the ^{234}Th stock (Tanaka et al. 1983). To test the pertinence of the steady-state model used in the present work, we reconstructed the depletion levels of ^{234}Th during the sampling period using measured data and fluxes from the traps (with the assumption of optimal recovery; Fig. 3). The results clearly show that the situation is different between the three fjords. The reconstructed ^{234}Th activities are always present at significant levels in Balsfjord, but in the two other fjords, high deficiencies occurred in early April. The deficits of ^{234}Th measured in Malangen fjord and Ullsfjord indicate a memory effect of an export event in early April. Consequently, ^{234}Th cannot be used to calculate trap efficiencies in theses cases.

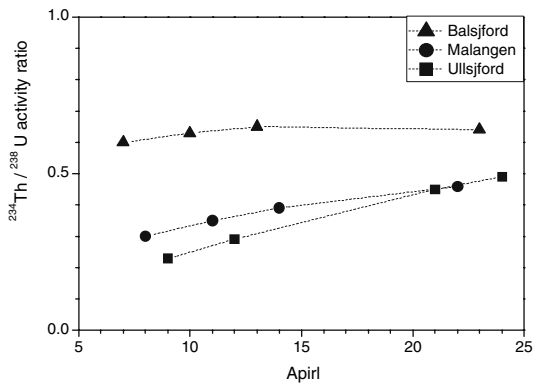

Fig. 3 Reconstruction of the temporal evolution of ^{234}Th: ^{238}U activity ratio in the upper 0–60 m. Total ^{234}Th for the layer 0–60 m was calculated from the values of late April, taking into account the production rate from ^{238}U, the measured fluxes in trap and the decay of ^{234}Th

Impact of *Phaeocystis* proliferation on settling flux

The most striking feature in the temporal evolution of particulate fluxes throughout April 1997 was the differences between its components (Fig. 2). The relationship between particulate organic carbon, DMSP and ^{234}Th were clearly different between fjords. POC fluxes showed a wide range (70–260 mg m^{-2} d^{-1}), with the highest values observed after mid April. DMSP fluxes exhibited the same trend, although DMSP:POC ratios varied between the fjords (Fig. 2) while ^{234}Th fluxes presented a very unusual pattern in Ullsfjord, decreasing to negligible levels at the end of April. This cannot be fully explained with a ^{234}Th deficiency due to an earlier export event, since ^{234}Th is always available in surface waters and activities were increasing during April (Fig. 3).

The major difference among the three fjords was the timing of the vernal bloom. In April 1997, Balsfjord and Malangen were diatom-dominated ecosystem, whereas Ullsfjord was *Phaeocystis*-dominated (Reigstad et al. 2000). DMSP fluxes were positively related to the proliferation of *Phaeocystis*, while ^{234}Th fluxes showed an inverse pattern (Fig. 4). Hence the question was raised what mechanism could lead to a system exporting DMSP and POC but not ^{234}Th.

We hypothesize therefore that the observed low ^{234}Th flux in traps is associated to the composition of settling material. Faecal pellets did not dominate the vertical export in April 1997: in fact phytoplankton, mainly diatoms and *Phaeocystis*, comprised a major fraction of the sinking particles (Reigstad et al. 2000). The high PPC (total phytoplankton carbon)/POC ratios

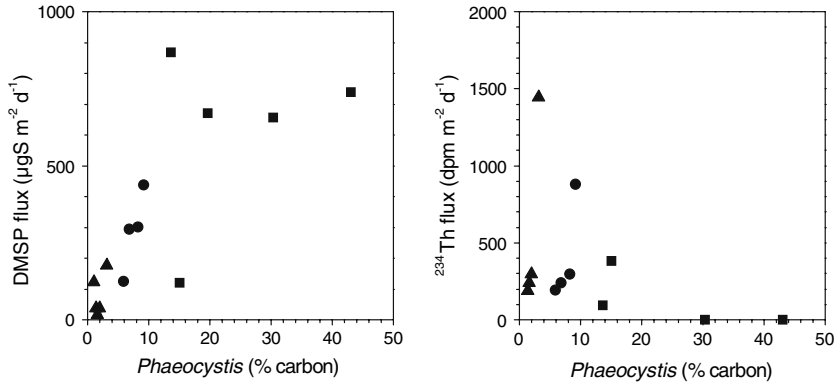

Fig. 4 DMSP (left) and particulate ^{234}Th fluxes (right) as a function of *Phaeocystis* content of the surface waters (expressed as a percentage of total phytoplankton carbon; same symbols as in Fig. 3)

(0.37, 0.39 and 0.29 for Ullsfjord, Balsfjord and Malangen, respectively) suggest that much of the spring bloom in these three fjords in April 1997 was vertically exported as ungrazed phytoplankton. Moreover, during this experiment, it was observed that the vertical export of *Phaeocystis pouchetii* cells (free and colonial) was negligible in Balsfjord, rather low in Malangen Fjord and highest in Ullsfjord (1.2, 8.0 and 25.3% of phytoplankton-carbon export; Reigstad et al. 2000).

The application of the ^{234}Th method for investigating particle dynamics is based on the assumption that ^{234}Th is scavenged onto fine particles that can be aggregated into larger particles able to settle, either due to grazing or bloom senescence and aggregate formation (Buesseler et al. 2006; Savoye et al. 2006). However several recent works point out intricate relationship between ^{234}Th and particles depending on their nature (phytoplankton cells, flocs, lithogenic material) and the occurrence of transparent exopolymer particles (TEP) (Passow et al. 2006; Waite and Hill, 2006). Passow et al. (2006) investigated the affinity of TEP and inorganic clays to ^{234}Th and concluded that POC/^{234}Th ratios depend largely on the types of particles presents (Passow et al. 2006). Buesseler et al. (1995) already postulated that fresh biological particles are likely to have a higher POC:^{234}Th ratio. In Ullsfjord after mid April $^{234}Th^{P}$ activities are the lowest and trap POC/^{234}Th ratios (>120 µmol dpm^{-1}) far exceeded values in Balsfjord and Malangen (12–30 and 25–49 µmol dpm^{-1}, respectively) and all published values (<70 µmol dpm^{-1}) in the review of Buesseler et al. (2006), except a data set from the low-salinity Baltic (up to 800 µmol dpm^{-1}).

In Ullfjord, *Phaeocystis* comprised a major fraction of the sinking particles (Reigstad et al. 2000). Sedimentation of these cells may account for the high DMSP and POC fluxes and low POC/^{234}Th ratio measured in the traps with the highest rates in Ullsfjord.

Conclusions

The main objective of this study was to assess the impact of *Phaeocystis* proliferation on vertical export of particles based on ^{234}Th data in water column and in sediment traps. A specific task was to calibrate the trap collection efficiencies. From our present investigation, we conclude the following:

(1) Special care must be taken when using ^{234}Th measurements for estimating particle fluxes and trap efficiencies in coastal systems. During the early stage of large cells bloom, like *Phaeocystis* proliferation, a complete data set will be require: high-frequency three-dimensional (3D) sampling, determination of $^{234}Th^{P}$ and POC/^{234}Th ratios on suspended and sinking particles, properties of flocs, and the use of a non-steady-state model.

(2) We hypothesize that the proliferation of large, fresh and unflocculated cells and their direct settling temporally affect the partitioning of ^{234}Th within the in situ particles (high POC-to-^{234}Th ratios) and delay, even prevent, the export, via grazing or aggregate

formation, of ^{234}Th and probably of similar particle-reactive elements.

Acknowledgments This work was partly supported by the European Union MAST programme ESCAPE (contract MAS3-CT96-0050) and the Centre National de la Recherche Scientifique. We are grateful to the crew of RV Johan Ruud for their strong support in field work.

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