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Vertical export of biogenic matter in the Chukchi and Barents Seas

Catherine Lalande
University of Tennessee - Knoxville

To the Graduate Council:

I am submitting herewith a dissertation written by Catherine Lalande entitled "Vertical export of biogenic matter in the Chukchi and Barents Seas." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Ecology and Evolutionary Biology.

Jacqueline M. Grebmeier, Major Professor

We have read this dissertation and recommend its acceptance:

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Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Anne Mayhew

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Vertical export of biogenic matter in the Chukchi and Barents Seas

A Dissertation
Presented for the
Doctorate of Philosophy
Degree
The University of Tennessee, Knoxville

Catherine Lalande
August 2006

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Abstract

Drifting sediment traps were deployed in 2004 in the Chukchi Sea to investigate the variability in the vertical flux of biogenic matter in the presence and absence of sea ice. Measurements of chlorophyll-*a*, particulate organic carbon (POC), particulate organic nitrogen, phytoplankton, zooplankton fecal pellets, and the stable carbon isotope composition of the sinking material were accomplished along two shelf-to-basin transects. POC fluxes obtained in ice-covered and ice-free conditions were of different composition but of similar magnitude, indicating that the export fluxes in the presence of ice cover contributed significantly to the annual export of biogenic matter in the Chukchi Sea. These results suggest that a reduction or disappearance of ice cover on the Chukchi continental shelf would not necessarily increase the annual export of POC.

Large-volume sampling of ^{234}Th was conducted simultaneously with drifting sediment trap deployments in the Chukchi Sea. Measurements of ^{234}Th and particulate organic carbon export fluxes obtained with *in situ* pumps and drifting sediments traps agreed to within a factor of 2 for 70% of the measurements. Despite the good agreement between methods, discrepancies in POC export fluxes measured using *in situ* pumps and sediment traps may be reasonably explained by differences in the estimated POC/^{234}Th ratios that arise from differences between the techniques, such as time-scale of measurement and size and composition of the collected particles.

Large-volume sampling of ^{234}Th was conducted to estimate POC export in conjunction with drifting sediment trap deployments in the northern Barents Sea in 2003 and 2005. Although ^{234}Th fluxes measured with both methods agreed within a factor 2 at most stations and depths sampled, sediment trap POC fluxes were much lower than large-volume POC fluxes at almost every station. One possibility is that the offset between the two methods may be due to the prominent presence of the prymnesiophyte *Phaeocystis pouchetii* in the Barents Sea, which could potentially cause the large variation observed in POC/^{234}Th ratios. If this is the case, the use of drifting sediment traps might be a more reliable method to measure the vertical export of biogenic matter in the Barents Sea, in particular during *P. pouchetii* blooms.

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Introduction

I.1 Increase in atmospheric carbon dioxide (CO_2) concentration

During the last 200 years, the atmospheric concentration of CO_2 has significantly increased due to emission of CO_2 from the burning of fossil fuels and deforestation (Fig. 1). The Mauna Loa Observatory recorded a 19.3 % increase in the mean annual concentration of atmospheric CO_2 from 316 parts per million (ppm) in 1959 to 377 ppm in 2004 (Fig. 2; Keeling and Whorf, 2005). Moreover, a sharp rise in atmospheric CO_2 has been recorded since 2004, increasing the current atmospheric CO_2 concentration to 381 ppm (D.A. King, unpublished data). Interestingly, the increasing rate of atmospheric CO_2 is smaller than the rate of anthropogenic CO_2 emissions. During the 1980s and 1990s, despite a large increase in fossil fuel emissions from 5.4 to 6.3 Pg C yr^{-1}, the atmospheric CO_2 increased at a nearly constant rate of 3.3 and 3.2 Pg C yr^{-1} (Le Quéré et al., 2003). This indicates that about half of anthropogenic CO_2 emissions are stored in the terrestrial biosphere and ocean reservoirs and, therefore, do not contribute to the rising of atmospheric CO_2 concentration (Raven and Falkowski, 1999; Battle et al., 2000).

I.2 The role of the ocean in CO_2 drawdown

The global ocean contributes to a net uptake of about 2 Pg C yr^{-1} from the atmosphere and therefore acts as a natural CO_2 sink (Joos et al., 1999; Raven and Falkowski, 1999;

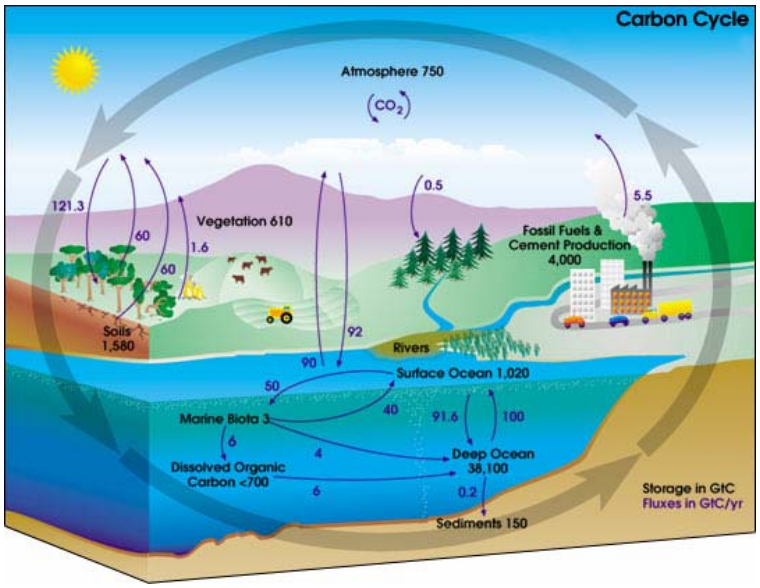

Figure 1. The global carbon cycle; a network of interrelated processes that transport carbon between different reservoirs on Earth. Illustration from NASA Earth Science Enterprise (http://earthobservatory.nasa.gov/Library/CarbonCycle/carbon_cycle4.html)

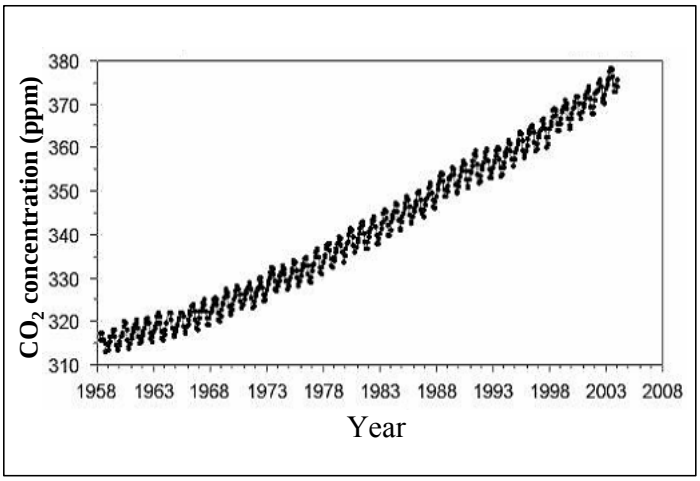

Figure 2. Atmospheric CO_2 concentration measured since 1958 at Mauna Loa Laboratory, Hawaii (http://www.cmdl.noaa.gov/ccgg/trends/co2_data_mlo.php)

Battle et al., 2000; Feely et al., 2001; Orr et al., 2001; Takahashi et al., 2002). An important process contributing to the uptake of carbon by the ocean is the biological utilization of CO_2. CO_2 in the upper ocean is fixed by phytoplankton to produce organic carbon through photosynthesis, a process known as primary production (Fig. 3). Most of the carbon fixed by phytoplankton photosynthesis in the upper ocean is rapidly recycled through grazing by zooplankton or by microbial processes, and only a small fraction exits the surface layer as sinking particles (Eppley and Peterson, 1979; Doney, 1997). Sinking biogenic particles are mainly composed of marine snow (organic aggregates of various origin), phytoplankton, and zooplankton fecal pellets (Turner, 2002). Zooplankton play an important role in the ecosystem by feeding on phytoplankton in surface waters and producing sinking fecal pellets, therefore contributing to both the reduction and increase of the export of particles (Ducklow et al., 2001). Hence, the abundance and composition of phytoplankton and zooplankton may dramatically affect the export of biogenic matter. The export of this organic material from the euphotic zone (zone where light penetrates and photosynthesis occurs) to the ocean's interior returns organic carbon into the deep ocean reservoir of dissolved inorganic carbon where carbon is stored for thousands of years (Fig. 1 and 3; Emerson et al., 1997; Ducklow et al., 2001). This biological pump causes atmospheric CO_2 concentration to be about 150 to 200 ppm lower than what it would be if there was no primary production in the ocean (Sarmiento and Toggweiler, 1984; Maier-Reimer et al., 1996; Falkowski et al., 2000).

Changes in the efficiency of the biological pump can potentially influence the atmospheric CO_2 concentration and climate on geological time scales. A theory proposed

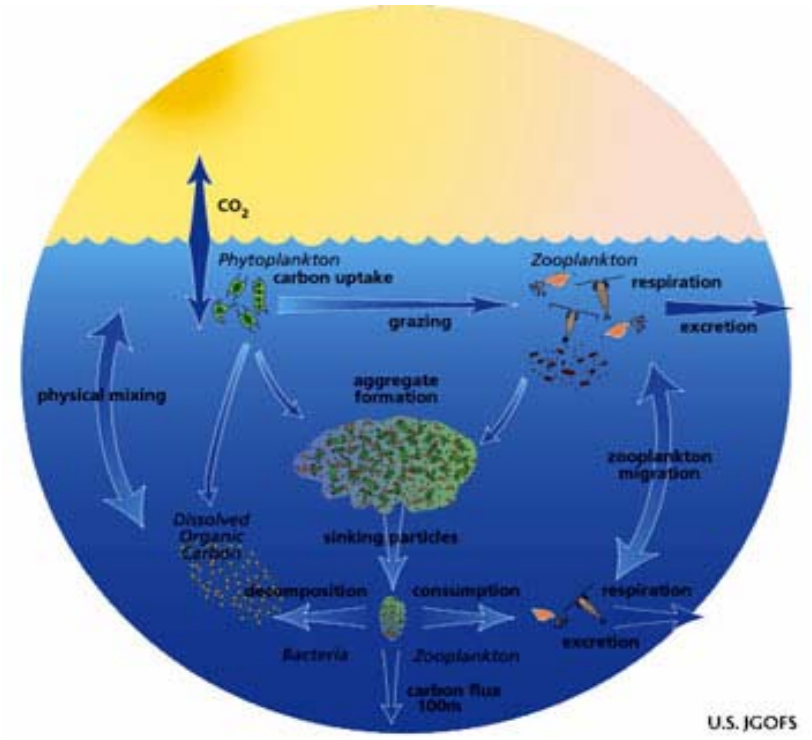

Figure 3. Simplified diagram of the principal components of the biological pump (http://www.uri.edu/news/releases/html/03-0916-01.html)

to explain the low atmospheric CO_2 concentrations recorded during glacial periods relies on the increase in the strength of the biological pump (Sarmiento and Toggweiler, 1984; Raven and Falkowski, 1999; Falkowski et al., 2000; Sigman and Boyle, 2000; Stephens and Kelling, 2000). Therefore, a current increase in primary production could result in an increased efficiency of the biological pump and a possible reduction of the atmospheric CO_2 concentration, similar to what was suggested for glacial periods. The Arctic Ocean is one of the potential regions where an increase in the efficiency of the biological pump could occur in a context of climate warming. Indeed, a decline in sea ice cover could potentially increase primary and export production over the Arctic continental shelves. For this reason, the focus of this study is on the vertical export of biogenic matter in the Arctic Ocean.

I.3 Ice cover, primary production and export production in the Arctic Ocean

A declining trend in seasonal sea ice extent and thickness in the Arctic Ocean has been recorded for the past 120 years (Serreze et al. 2003), with satellite record ice minima observed in September 2002, 2003, 2004 and 2005 (Serreze et al. 2003; Stroeve et al., 2005; Meier et al., 2005). In addition, satellite data obtained from 1978 to 2000 indicated that the Arctic perennial sea ice cover declined at a rate of 8.9 ± 2.0 % per decade, with the largest variations in ice concentrations occurring in the Beaufort and Chukchi Seas (Comiso, 2002). The observed variations in ice cover are very likely to have devastating consequences for polar bears, ice-dependent seals, and indigenous people for whom these animals are a primary food source (ACIA, 2004). Moreover, considerable effects on

primary production and export of sinking particles, also known as export production, are expected in the Arctic Ocean (Wassmann et al., 2004).

Due to the extreme seasonal range in light intensity, from midnight sun to winter darkness, most of the annual primary production on the Arctic continental shelves occurs within a few months (Fig. 4). Phytoplankton blooms develop rapidly when nutrient-rich water is exposed to light following the melting of the snow cover and the break-up of the sea ice (Fortier et al., 2002; Sakshaug, 2004; Wassmann et al., 2004). In areas covered by first-year ice, primary production begins with an ice-edge bloom that forms a 20-100 km wide belt off the ice edge (Sakshaug, 1997). As long as the ice continues breaking up, exposing nutrient-rich water, the bloom will follow the retracting ice edge. The productive season ends in late summer or autumn when the critical light depth for algal growth is reduced to about <20 m or when formation of sea ice begins (Sakshaug, 2004).

Eppley and Peterson (1979) suggested that the amount of biogenic matter exported out of the euphotic zone is equivalent to the new production, i.e. the fraction of the overall net primary production that is supported by external inputs of nutrients, in contrast to nutrient recycled in the surface waters (regenerated production) (Dugdale and Goering, 1967). However, because of the highly episodic nature of primary production on the Arctic shelves, the export of biogenic matter is primarily determined by the match or mismatch between the phytoplankton community productivity and the grazing impact by zooplankton (Peinert et al., 1989; Wassmann et al., 1996; Wassmann, 1998; Sakshaug, 2004; Wassmann et al., 2004; Grebmeier and Barry, 2006). In some Arctic regions, a

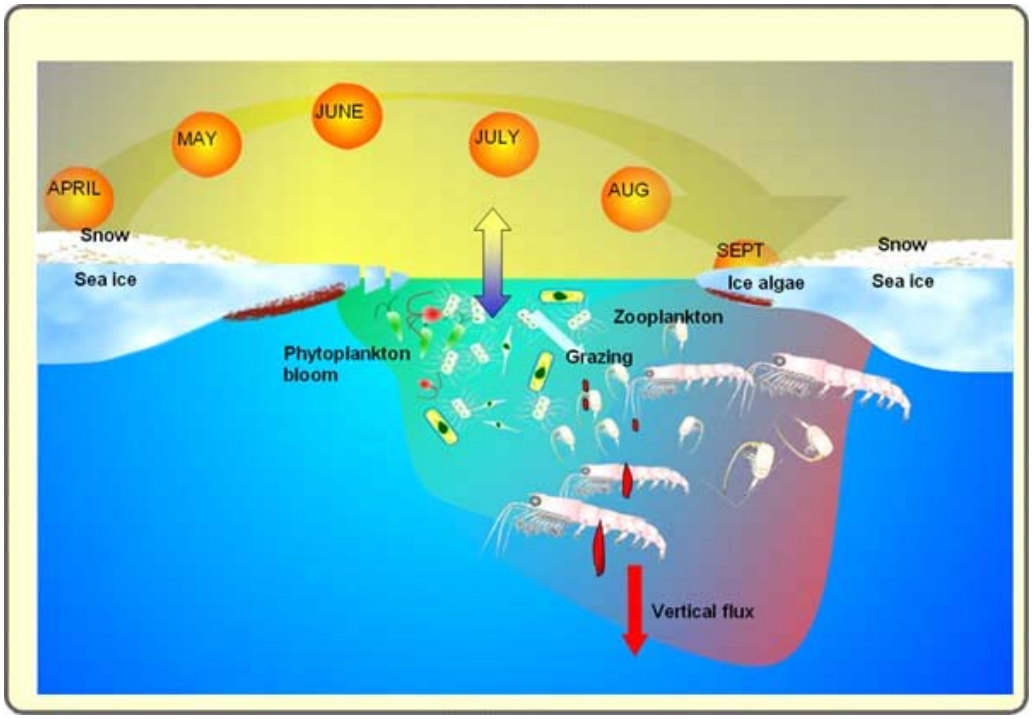

Figure 4. Schematic illustration of principal processes during the productive cycle in the Arctic Ocean (Wassmann et al., 2004)

mismatch between phytoplankton and zooplankton give rise to extensive sedimentation of ungrazed phytoplankton (Fortier et al., 2002; Hargrave et al., 2002; Wasmmann et al., 2004). The tight coupling between pelagic (water column) and benthic (bottom) processes leads to some of the highest benthic biomass concentrations found on the shallow Arctic continental shelves (Grebmeier et al., 1988; Grebmeier et al., 1995; Grebmeier and Barry, 2006).

A few decades of investigations in the Arctic Ocean have shown regional, seasonal, and interannual variations in the magnitude and composition of biogenic matter exported from the upper water column (Wassmann et al., 2004). For example, phytoplankton-derived material dominated the export flux during and after the bloom in early summer in the North Water polynya, while zooplankton fecal pellets were more abundant during late summer months (Hargrave et al., 2002; Sampei et al., 2004). In the Northeast Water polynya, the majority of organic carbon (phytoplankton and ice algae) was probably recycled in the upper water layers or advected away from the polynya (Bauerfeind et al., 1997). In the marginal ice zone of the Greenland Sea, higher export fluxes were observed during ice-rich years than during ice-poor years (Peinert et al., 2001), while the contribution of lithogenic particles (sediments), possibly transported by ice, dominated the total export flux in the permanently ice-covered region (Bauerfeind et al., 2005). In the marginal ice zone of the Barents Sea, the vertical flux of biogenic matter varied with season and water mass, and the food web had a higher recycling capacity in summer than spring (Olli et al., 2002; Wexels Riser et al., 2002). In the Chukchi Sea, particle export exhibited significant seasonal and spatial variability, with a ~4-fold increase in particle

export in the summer relative to the spring (Moran et al., 2005). These results reflect the complexity of factors influencing the vertical export of biogenic matter in the Arctic Ocean.

Under scenarios of global warming, earlier melting of sea ice in spring is likely to enhance annual primary production by extending the growth season on the Arctic continental shelves (Sakshaug, 2004 and references therein). An increase in primary production is expected to subsequently increase the vertical export of biogenic matter on the Arctic continental shelves (Wassmann et al., 2004), which is likely to increase the efficiency of the biological pump and therefore the sequestration of atmospheric CO_2 in the Arctic Ocean (Anderson et al., 1998). However, significant changes in the phytoplankton and zooplankton communities may also affect the vertical flux of biogenic matter on the Arctic continental shelves (Wassmann et al., 2004). Thus, the investigation of processes causing spatial and temporal changes in carbon export, potentially regulating the regional CO_2 cycling, is required in the Arctic Ocean.

I.4 Estimating export fluxes: Sediment traps and $^{234}Th/^{238}U$ disequilibria

Accurate determination of the export flux is critical for understanding the global carbon cycle and its response to climate change. One of the methods to measure the vertical export of biogenic matter is by using drifting sediment traps collecting material sinking out of the euphotic zone. The drifting traps are usually deployed over 24 h and consist of cylindrical tubes attached to a line with buoys at the surface and a weight at the bottom to

keep it vertical (Fig. 5a). Drifting sediment traps are convenient tools for short-term studies of vertical flux since they are easily deployed, allowing to some extent the tracking of water masses, and are less affected by turbulence than moored traps (Andreassen and Wassmann, 1998). Hence, sediment traps are valuable tools for estimating particle export, although limitations to their design may affect the accuracy of the measurements (Gardner, 2000). Some of the common biases associated with traps include the consumption of the trapped material by zooplankton during deployment, the solubilization of particulate matter to dissolved matter in the trap, and the hydrodynamic effects possibly leading to the undercollection of sinking particles (Gust and Kozerski, 2000; Gardner, 2000; Gustafsson et al., 2004). Nevertheless, drifting sediment traps remain a useful collection technique if precautions are taken to reduce the potential biases. They also have the advantage of providing samples of sinking particles for biological analyses, in contrast to chemical approaches.

Another method commonly used to estimate the export of particulate organic carbon (POC) in the upper ocean is the large-volume filtration of ^{234}Th using *in situ* pumps or CTD rosette (Fig. 5b-c). ^{234}Th ($t_{1/2}$=24.1 days) is produced by the decay of its dissolved conservative parent, ^{238}U. About 40 years ago, the first measurement of ^{234}Th in marine systems indicated that ^{234}Th is depleted relative to ^{238}U in the upper ocean (^{234}Th/^{238}U disequilibrium; Bhat et al., 1969). It was almost 20 years later that the link between ^{234}Th/^{238}U disequilibria and biological activity in the upper ocean was made; due to its particle-reactive property, ^{234}Th is removed from the upper ocean on sinking particles (Coale and Bruland, 1985; Coale and Bruland, 1987). Therefore, ^{234}Th is a useful tracer

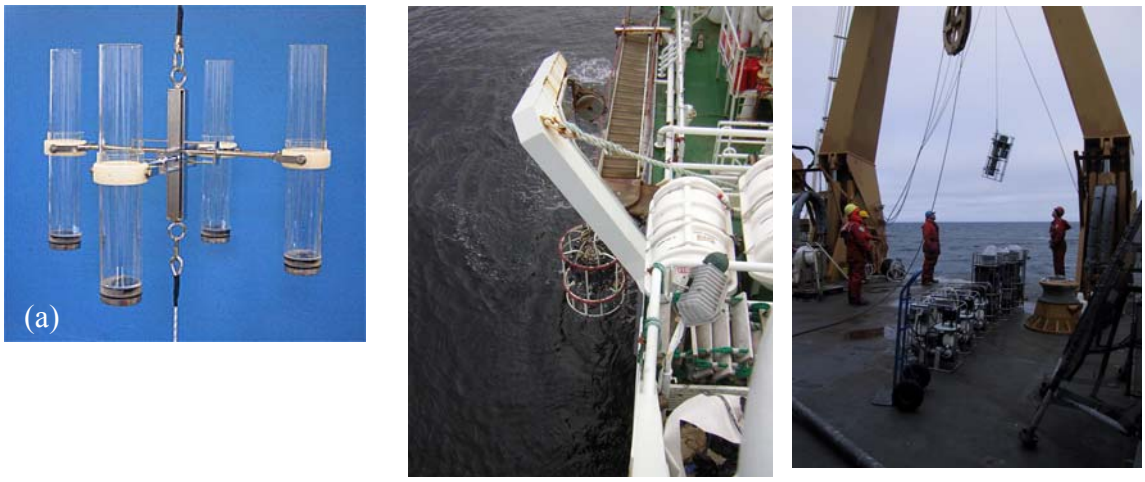

Figure 5.(a) Sediment trap, 4-tubes model, KC Denmark, (b) CTD rosette, (c) *in situ* pumps, Challenger Oceanic Systems and Services, Surrey, U.K.

of scavenging and POC export occurring on a time-scale of days to months because of its short half-life. POC fluxes can be determined by multiplying the ^{234}Th flux by the POC/^{234}Th ratio measured on sinking particles (Buesseler et al., 1992a). ^{234}Th has been increasingly used in the last decades to estimate POC export in the Arctic Ocean, where it exhibited a wide spatial variability of POC fluxes (Moran, 2004 and references therein).

In early years of its use, it was suggested that drifting sediment traps may not provide an accurate record of particle fluxes in the upper ocean after studies indicated that trap-derived POC flux and independent measurements of ^{234}Th-derived POC flux can differ by a factor of ± 3-10 (Buesseler, 1991). While the ^{234}Th technique has the advantage of allowing greater spatial coverage than sediment traps, there is also uncertainty in the ^{234}Th approach as it is difficult to define and measure the depth-integrated ^{234}Th flux and the POC/^{234}Th ratio of sinking particles (Moran et al., 2003). In fact, POC/^{234}Th ratios obtained with the ^{234}Th method might not be as representative of the POC/^{234}Th ratios in sinking particles compared to POC/^{234}Th ratios obtained directly with sediment traps (Murray et al., 1996; Charette et al., 1999; Benitez-Nelson et al., 2001; Amiel et al., 2002; Coppola et al., 2002; Moran et al., 2003; Moran, 2004; Buesseler et al., 2006). Nonetheless, ^{234}Th was identified as the most promising independent tracer of particle export for trap calibration studies in the upper ocean, and it is strongly recommended that measurements be made of the ^{234}Th deficit in conjunction with short-term sediment trap deployments (Gardner, 2000).

I.5 Key questions and objectives

This doctoral dissertation was conducted as part of the Western Arctic Shelf-Basin Interactions (SBI) Project and the Carbon flux and ecosystem feedback in the northern Barents Sea in an era of climate change (CABANERA) Project. Samples were taken during two SBI cruises from May-June and July-August 2004 in the Chukchi Sea on board *USCGC Healy* and during two CABANERA cruises in July 2003 and in May 2005 in the northern Barents Sea on board *R/V Jan Mayen* (Fig. 6). In the context of the current decline in sea ice cover observed in the Arctic Ocean and of uncertainties associated with export production measurements, some key questions addressed as part of this doctoral dissertation were:

- Does the vertical export of biogenic matter increase in the absence of ice cover in the Chukchi Sea?
- How does the composition of the export fluxes change from ice-covered to ice-free conditions in the Chukchi Sea?
- What is the degree of agreement between export fluxes measured with sediment traps relative to large-volume filtration of ^{234}Th in the Barents and Chukchi Seas?

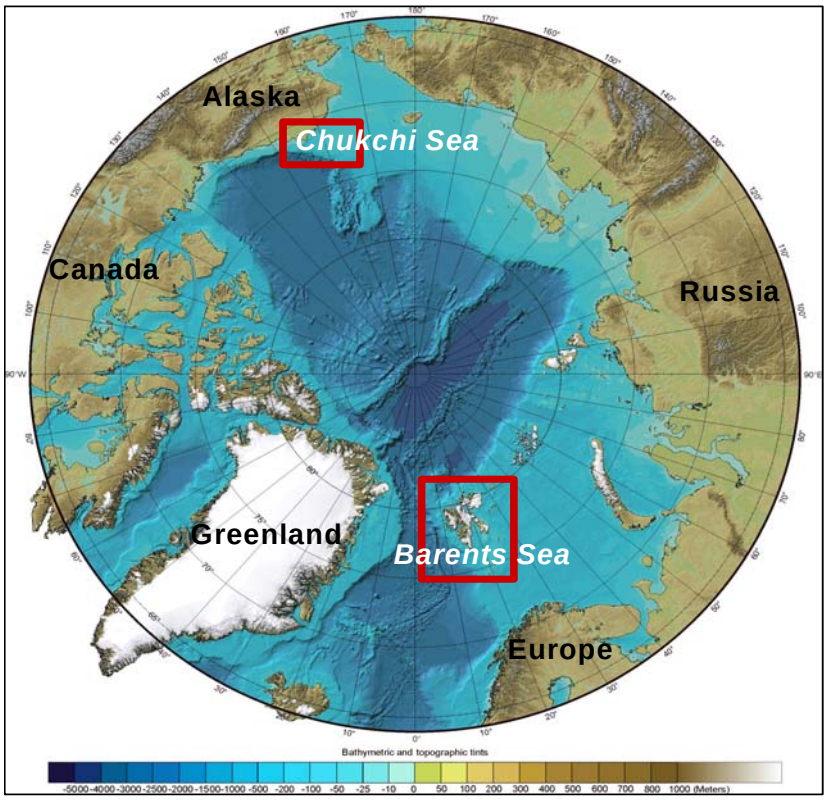

Figure 6. Study areas in the Chukchi Sea (SBI Project - USA) and northern Barents Sea (CABANERA Project - Norway)

In order to answer these questions, the objectives of this doctoral dissertation were:

1- Compare the magnitude and the composition of the export fluxes obtained from drifting sediment trap deployments in the presence and absence of ice cover in the Chukchi Sea
2- Compare ^{234}Th-derived and sediment trap-derived POC export fluxes obtained in the Chukchi Sea
3- Estimate POC export fluxes using ^{234}Th in the marginal ice zone of the Barents Sea and compare these fluxes with direct POC export obtained from drifting sediment trap deployments

Each objective corresponds to one of the following chapters, which were written in the form of manuscripts to be submitted to peer-reviewed journals.

Chapter 1

Export fluxes of biogenic matter in the presence and absence of seasonal sea ice cover in the Chukchi Sea

This chapter is a paper that will soon be submitted for publication by C. Lalande, J.M. Grebmeier, P. Wassmann, L.W. Cooper, M.V. Flint and V.M. Sergeeva. My contributions to this paper include: responsibility of the sediment trap deployments, sample analyses (except for the phytoplankton analyses done in Moscow by V.M Sergeeva and M.V. Flint), interpretation of data and preparation of the manuscript.

1.1 Introduction

The Chukchi Sea is one of the most productive Arctic shelf when the ice edge recedes, with an estimated annual production >400 g C m^{-2} yr^{-1} (Sakshaug, 2004; Hill and Cota, 2005). Since there is a constant input of nutrient-rich waters through the Bering Strait, the major factor constraining primary production on the Chukchi Sea shallow continental shelf and slope, when incident radiation is sufficient, is the seasonal variation in ice cover (Springer and McRoy, 1993; Gosselin et al., 1997; Hill and Cota, 2005). A declining trend in seasonal sea ice extent is currently ongoing in the Arctic, with record ice minima observed in September 2002, 2003, 2004 and 2005 (Serreze et al. 2003; Stroeve et al., 2005; Meier et al., 2005). In addition, satellite data obtained from 1978 to 2000 indicated that the Arctic perennial sea ice cover declined at a rate of 8.9 ± 2.0% per decade, with the largest variations in ice concentrations occurring in the Beaufort and Chukchi Seas (Comiso, 2002). Since the timing and magnitude of primary production depend largely on light conditions and thereby on ice cover in the Chukchi Sea, an earlier melting of sea ice following the increase in light irradiation in spring is likely to enhance annual primary

production by extending the growth season (Sakshaug, 2004). Increased primary production in scenarios of reduced ice cover is expected to subsequently increase the vertical export of biogenic matter on the Arctic continental shelves (Wassmann et al., 2004).

The vertical export of organic matter from the euphotic zone is assumed to be equivalent to new production (Dugdale and Goering, 1967; Eppley and Peterson, 1979). However, because of the highly seasonal and episodic nature of primary production on the Arctic shelves, the retention or export of biogenic matter is determined by the match or mismatch between the seasonal dynamics of phytoplankton community and the grazing impact by zooplankton (Peinert et al., 1989; Wassmann et al., 1996; Wassmann, 1998; Sakshaug, 2004; Wassmann et al., 2004; Grebmeier and Barry, 2006). Significant changes in bloom development and thus phytoplankton production, standing stock, and composition may therefore affect the vertical flux of biogenic matter through changes in the food web structure (Wassmann et al., 2004).

Various investigations of vertical flux of biogenic matter using either short-term or long-term moored sediment traps have been conducted in the Arctic Ocean (e.g. Wassmann et al., 2004 and references therein), however the work presented here is the first one conducted in the Chukchi Sea using short-term drifting sediment traps. A previous study of export fluxes derived from $^{234}Th/^{238}U$ disequilibria over the Chukchi Sea shelf indicated that high primary production rates in the absence of ice cover contributed to elevated POC export fluxes, with POC fluxes increasing approximately 4-fold between

ice-covered and ice-free conditions (Moran et al. 2005). In addition to the estimation of the magnitude and seasonal variability of POC export fluxes, the deployment of sediment traps over the Chukchi Sea shelf and slope allowed the determination of the composition of the export fluxes, which may vary considerably as a result of a reduction in seasonal ice cover. Drifting sediment trap POC fluxes were within a factor of 2 of POC export fluxes obtained from simultaneous ^{234}Th-derived POC fluxes, indicating a reasonable agreement between both methods in the Chukchi Sea (Lalande et al., accepted). The objective of this study was to compare the magnitude and the composition of the export fluxes in the presence and absence of ice cover to provide insight on the processes affecting the vertical flux of biogenic matter over the Chukchi Sea shelf.

1.2 Material and methods

1.2.1 Sampling

Drifting sediment traps were deployed at 5 stations in May-June (ice cover) and at 4 stations in July-August (ice-free) 2004 as part of the Western Arctic Shelf-Basin Interactions (SBI) process cruises on board the *USCGC Healy*. Stations sampled were located along shelf-to-basin transects both in and outside a submarine canyon. The East Hanna Shoal (EHS) line was a non-canyon transect and Barrow Canyon (BC) was the in-canyon transect (Fig. 7). A drifting array of sediment traps deployed at five depths (30, 40, 50, 60, and 100 m) was anchored to an ice floe for deployments in the ice cover in spring and drifted during open water deployments in the summer for periods ranging from 11 to 20 hours (Table 1). The sediment traps (KC Denmark, Silkeborg, Denmark)

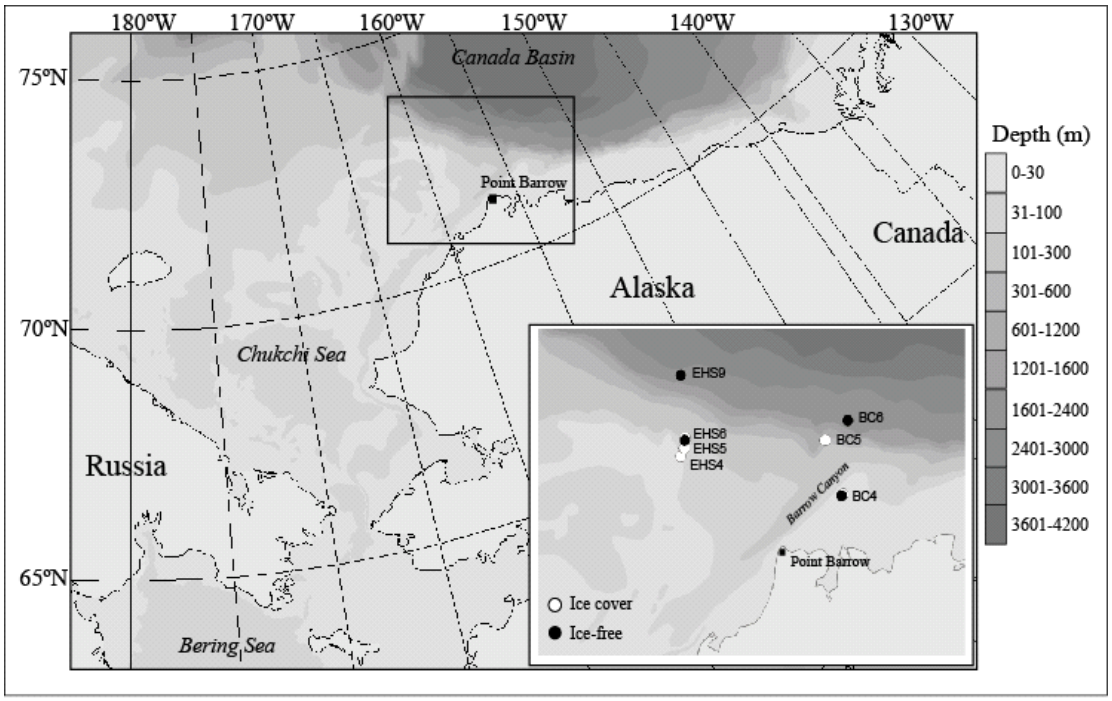

Figure 7. Sediment traps deployment stations in the Chukchi Sea. Stations are designated as BC (Barrow Canyon) and EHS (East Hanna Shoal)

Table 1. Sediment traps deployment stations, times, locations, water column depth, and deployment times in 2004 in the Chukchi Sea

	Station	Date	Latitude (ºN)	Longitude (ºW)	Water depth (m)	Deployment time (hours)
Ice cover	EHS4	May 30	72 38.5	158 41.2	153	16.0
Ice cover	EHS5	May 31	72 43.3	158 24.2	247	11.0
Ice cover	EHS6	June 2	72 51.2	158 12.8	689	20.3
Ice cover	BC5	June 13	72 03.3	154 37.1	1184	15.3
Ice cover	BC4	June 16	71 55.3	154 51.6	545	17.9
Ice-free	BC4	July 25	71 54.5	154 57.9	326	19.8
Ice-free	BC6	August 6	72 10.6	153 55.3	2061	14.9
Ice-free	EHS6	August 12	72 49.1	158 15.4	398	16.6
Ice-free	EHS9	August 14	73 02.7	157 59.2	1938	18.3

consisted of four detachable cylindrical tubes with lead weights at the bottom (7.2 cm x 45 cm; height/diameter ratio: 6.25) mounted in a cross frame to ensure the vertical position of the tubes during deployment. No baffles were used in the tube opening and no poison was applied in the traps due to the short periods of deployments. Upon recovery, contents of the four tubes deployed at each depth (~8 L) were mixed together into Nalgene® containers and kept cold and in the dark until processed over the next few hours. The containers were gently mixed to homogenize samples before subsampling, and aliquots from each depth were taken for measurements of chlorophyll *a* (Chl-*a*), particulate organic carbon (POC), particulate organic nitrogen (PON), phytoplankton, zooplankton fecal pellet, and the bulk stable carbon isotope composition ($\delta^{13}C$) of the sinking material.

1.2.2 Sample processing

Aliquots were filtered on precombusted Whatman GF/F filters for analyses of Chl-*a* (2 x 100 ml), POC and PON (200 ml), and $\delta^{13}C$ (~3 L). When present, larger zooplankton (swimmers) were carefully removed from the GF/F filters using forceps. Filters for measurements of POC, PON and $\delta^{13}C$ were dried for 24 h at 60°C, while Chl-*a* was extracted in 90 % acetone for 24 h at 4ºC in the dark and measured shipboard on a Turner Designs AU-10 fluorometer (Welschmeyer, 1994). POC and PON were measured using an Exeter Analytical CE 440 elemental analyzer (University of California, Santa Barbara, USA) after removal of inorganic carbon by exposing the GF/F filters to fumes of concentrated HCl in a dessicator for 24 h. Blank filters exposed to 200 ml of GF/F-

filtered seawater were used to account for DOC adsorption and POC fluxes were corrected using the average blank value of 57.4 ± 16.3 μg C. Filters for isotopic composition measurements of the sinking material were combusted *in vacuo* within sealed Vycor® glass in the presence of cupric oxide, copper metal and silver foil at 850ºC following the methods outlined in Cooper et al. (2002). Carbon dioxide that was generated was separated cryogenically and measured by mass spectrometry using a VG SIRA Series II stable isotope mass spectrometer (University of Tennessee, Knoxville, USA). Analytical precision was ± 0.3 ‰ based upon replicate analyses of 6 samples, and the data are reported as $\delta^{13}C$ values relative to the international V-PDB standard.

Aliquots of trap samples were preserved in Lugol solution for subsequent microscopic examination of phytoplankton (100 ml) and in 4% buffered formaldehyde to preserve zooplankton fecal pellets (100 ml). Phytoplankton samples were decanted to a volume of 1.5-2.0 ml. The final volume was processed using Nauman (0.5 ml), Nojeotte (0.09 ml) and Goryaev ($9x10^{-4}$ ml) counting chambers. Phytoplankton cells were identified to genus or species level, counted, and the average cell size of each taxonomic group was measured and the cells biovolume was calculated using appropriate geometrical formulas. The phytoplankton biovolumes were then converted to phytoplankton carbon (PPC) according to the conversion factors of Strathmann (1967) for diatoms and dinoflagellates and Menden-Deuer and Lessard (2000) for flagellates and coccolithophorids. Zooplankton fecal pellet samples were left to settle for at least 12 h after which the water was siphoned off the surface until a few ml remained. The remaining material was placed in a Petri dish and fecal pellets were counted for the whole sub-sample under a

dissecting scope (~40x magnification). The length and width of the fecal pellets were measured, and pellet volumes were calculated based on the cylindrical or ellipsoidal shape of the pellets. Fecal pellet volumes were converted to fecal pellet carbon (FPC) using volumetric carbon conversion factors of 0.042 mg C mm^{-3} for cylindrical copepod pellets and 0.057 mg C mm^{-3} for ellipsoidal appendicularian pellets (González and Smetacek, 1994; Fortier et al., 2002).

Chl-*a* and POC fluxes were related to the standing stocks of Chl-*a* (D. Stockwell, unpublished data) and suspended POC (N. Bates, unpublished data) to calculate the daily sedimentation loss rate (%) of Chl-*a* and POC out of the euphotic zone. The standing stock of suspended Chl-*a* as well as POC was estimated by vertically integrating the water column measurements from the upper 50 m.

1.3 Results

1.3.1 Chl-a and POC fluxes

Chl-*a* fluxes measured under ice cover were on average ~4 times higher than in ice-free water at the EHS stations, with values ranging from 0.38 to 2.50 mg m^{-2} d^{-1} under ice cover and 0.07 to 0.64 mg m^{-2} d^{-1} in ice-free water, and 2 times higher at the BC stations with values ranging from 0.84 to 2.04 mg m^{-2} d^{-1} under ice cover and 0.47 to 1.08 mg m^{-2} d^{-1} in ice-free water (Fig. 8). The vertical profiles of Chl-*a* flux measured under ice cover decreased with depth at the EHS stations and increased with depth at the BC stations, while there were little variation of Chl-*a* fluxes with depth at all stations in ice-free water

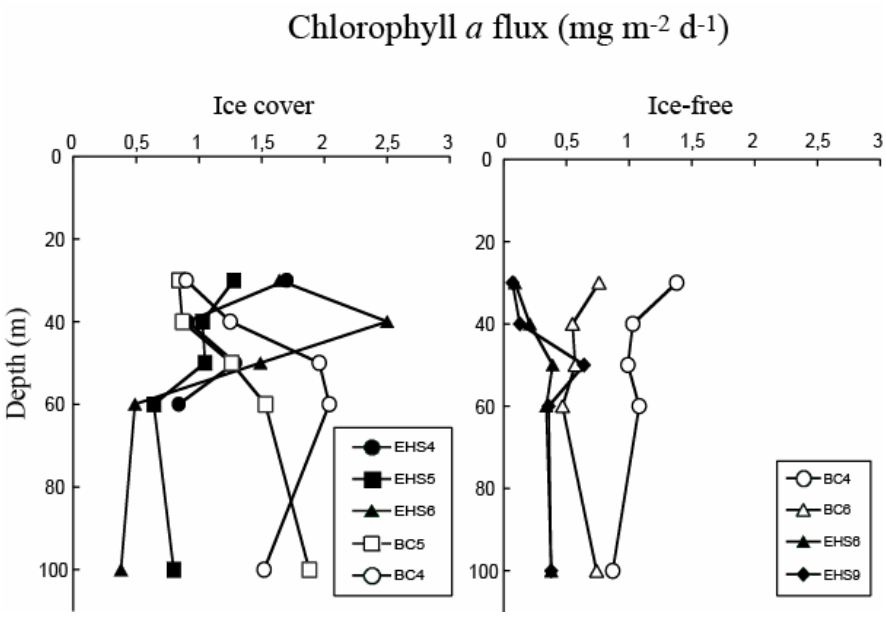

Figure 8. Chlorophyll-*a* fluxes (mg m^{-2} d^{-1}) at the EHS and BC stations in ice-covered and ice-free conditions

(Fig. 8). In contrast to Chl-*a* fluxes, POC fluxes increased from ice- covered to ice-free conditions, with POC fluxes on average 3 times higher in ice-free conditions than under ice cover at the EHS stations, with fluxes ranging from 4 to 90 mg C m^{-2} d^{-1} under ice cover and 42 to 367 mg C m^{-2} d^{-1} in ice-free water (Fig. 9). However, POC fluxes were similar at the BC stations, with ice-free fluxes on average 1.2 times higher than ice-covered fluxes, ranging from 156 to 508 mg C m^{-2} d^{-1} under ice cover and 176 to 796 mg C m^{-2} d^{-1} in ice-free water (Fig. 9). Also, POC fluxes were on average ~7 times and 2.5 times higher at the BC stations than at the EHS stations under ice cover and in ice-free water, respectively (Fig. 9). Under ice cover, the POC flux decreased with depth at the EHS stations, whereas the fluxes slightly increased with depth at the BC stations, although variations were fairly large. In ice-free water, POC fluxes were mostly constant with depth at the EHS stations, while the POC fluxes decreased with depth at the BC stations (Fig. 9). The Chl-*a*: POC ratios of the sinking particles were the highest under ice cover at the EHS stations, ranging from 0.011 to 0.172, while the ratios at the BC stations ranged from 0.002 to 0.005. In ice-free water, the Chl-*a*: POC ratios were similar at all stations, with values ranging from 0.001 to 0.006 at the EHS stations and from 0.001 to 0.003 at the BC stations.

1.3.2 PPC and FPC fluxes

Vertical fluxes of PPC under ice cover at the EHS stations were on average ~5 times lower than at the BC stations, with values ranging from 2.0 to 11.7 mg C m^{-2} d^{-1} at the EHS stations and from 12.9 to 55.0 mg C m^{-2} d^{-1} at the BC stations (Fig. 10). PPC fluxes

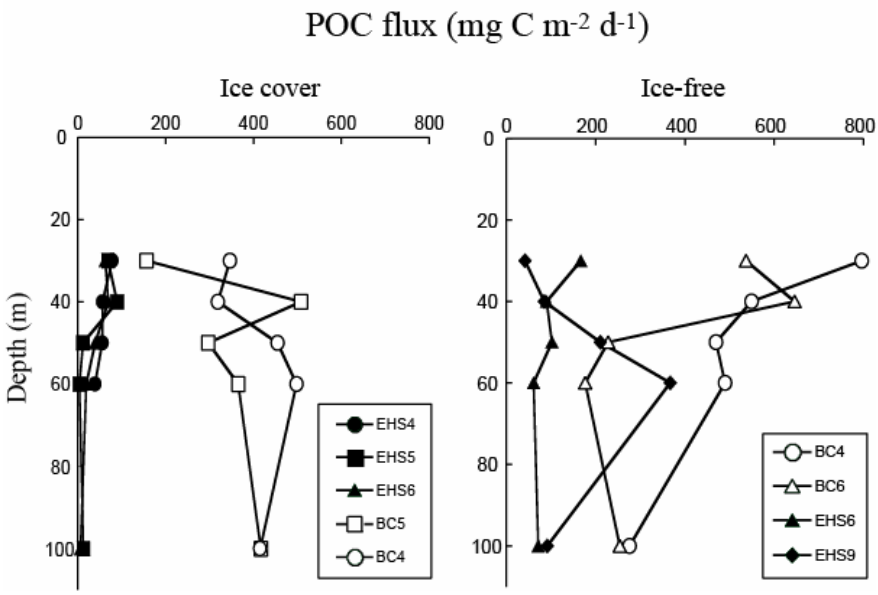

Figure 9. Particulate organic carbon fluxes (mg m^{-2} d^{-1}) at the EHS and BC stations in ice-covered and ice-free conditions

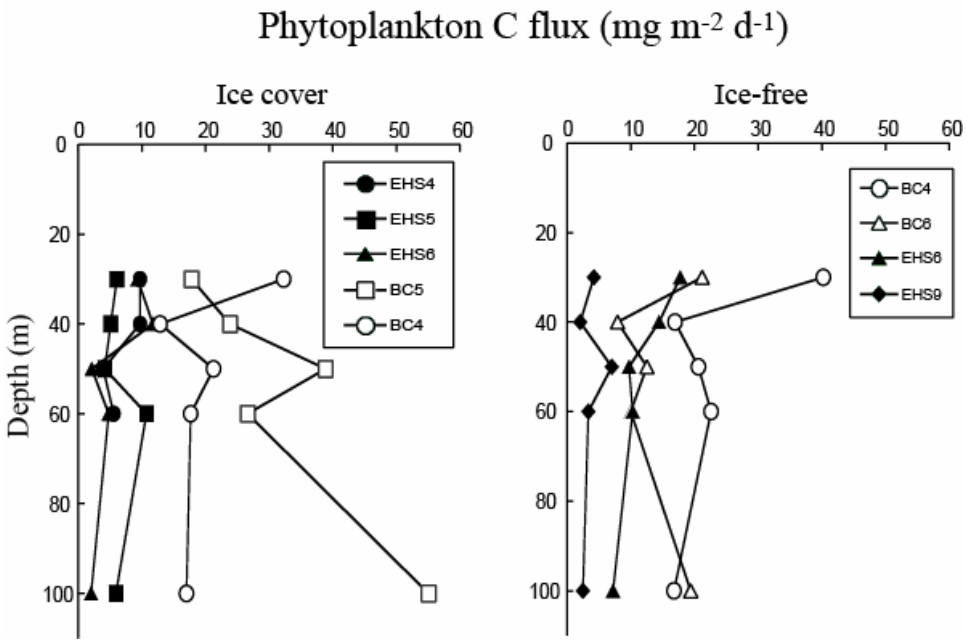

Figure 10. Phytoplankton carbon fluxes (mg m^{-2} d^{-1}) at the EHS and BC stations in ice-covered and ice-free conditions

were also higher on average at the BC stations in ice-free water, with fluxes ranging from 2.1 to 17.8 mg C m^{-2} d^{-1} at the EHS stations and from 7.9 to 40.2 mg C m^{-2} d^{-1} at the BC stations (Fig. 10). PPC fluxes were largely dominated by diatoms at all stations and depths under ice cover, except at a depth of 60 m at station EHS5 where *Phaeocystis sp.* dominated the flux by 44% (Fig. 11). Diatoms also dominated the PPC flux at station BC4 in ice-free water, while dinoflagellates and diatoms contributed almost equally to the PPC flux at station BC6 (Fig. 11). Dinoflagellates largely dominated the PPC flux at both stations along the EHS transect in ice-free water (Fig. 11). Under ice cover, PPC fluxes corresponded, on average, to a higher proportion of the POC fluxes at the EHS stations (36.1%) than at the BC stations (7.5%). The opposite trend was observed in ice-free waters, with a higher proportion of PPC contributing to the POC fluxes at the BC stations (58.3%) than at the EHS stations (8.3%) (Table 2). The vertical fluxes of FPC, dominated by copepod fecal pellets, were generally <25 mg C m^{-2} d^{-1} under ice cover and were higher in ice-free conditions with values ranging from 2 to 79 mg C m^{-2} d^{-1}, except at a single depth where the FPC flux reached up to 264 mg C m^{-2} d^{-1}, probably reflecting a patchiness event (60 m, station BC4, ice-free; Fig. 12). The fluxes of FPC contributed on average to a higher proportion of the POC fluxes at the EHS stations (38.7%) than at the BC stations (3.7%) under ice cover, and to a similar proportion of the POC fluxes at the EHS (17.8%) and BC (20.2%) stations in ice-free conditions (Table 2).

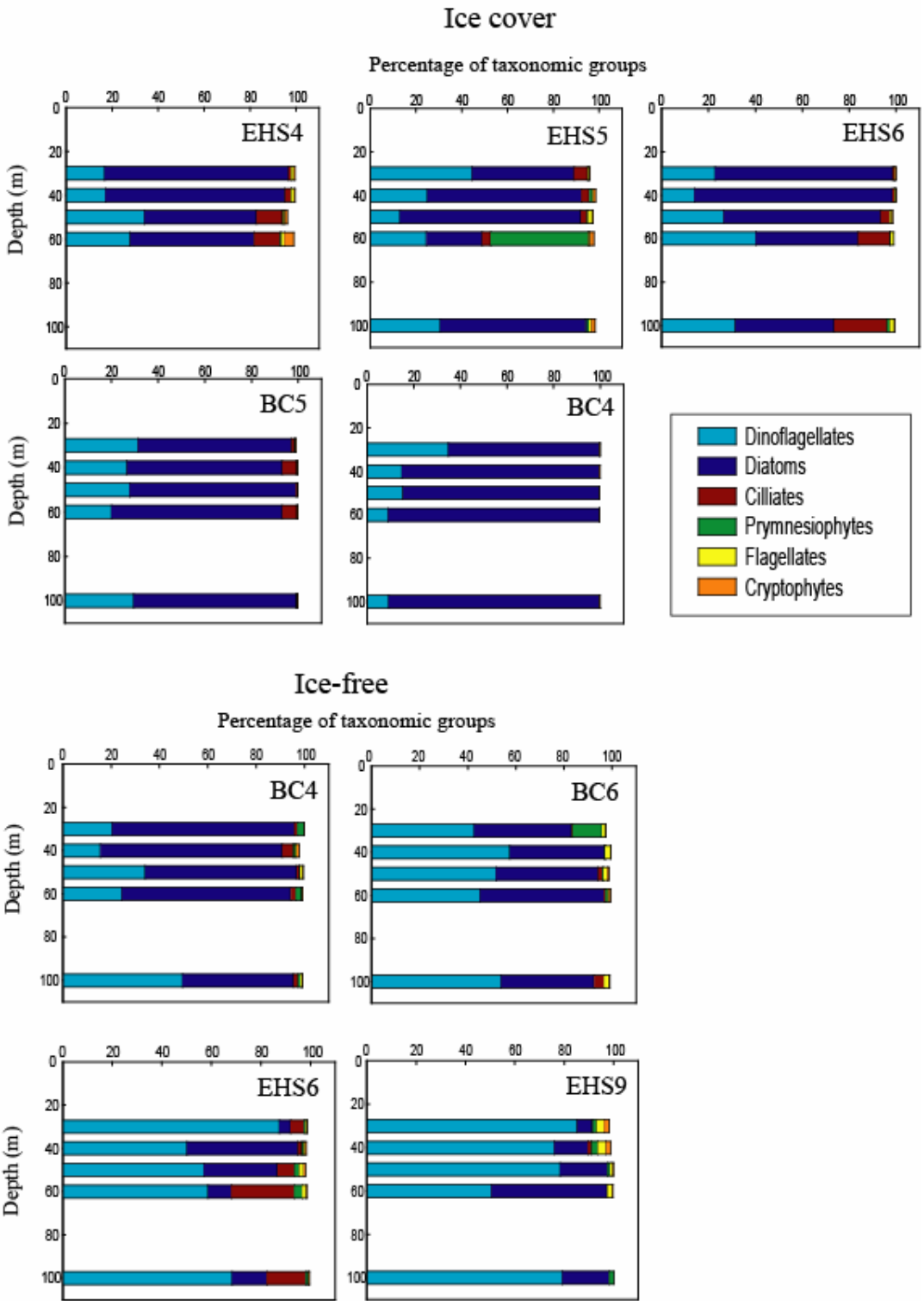

Figure 11. Phytoplankton carbon taxonomic composition (%) at the EHS and BC stations in ice-covered and ice-free conditions

Table 2. Fraction (%) of the POC fluxes associated with phytoplankton carbon (PPC) and fecal pellet carbon (FPC), and daily loss rates (%) of chlorophyll *a* (Chl-*a*) and particulate organic carbon (POC) from the upper 50 m of the water column at the EHS and BC stations

		Fraction of POC fluxes		Daily loss rates	
		% PPC	% FPC	% Chl-*a*	% POC
Ice cover	EHS	36.1	38.7	2.6	1.8
Ice cover	BC	7.5	3.7	1.7	5.8
Ice-free	EHS	8.3	17.8	3.1	4.0
Ice-free	BC	58.3	20.2	1.8	5.4

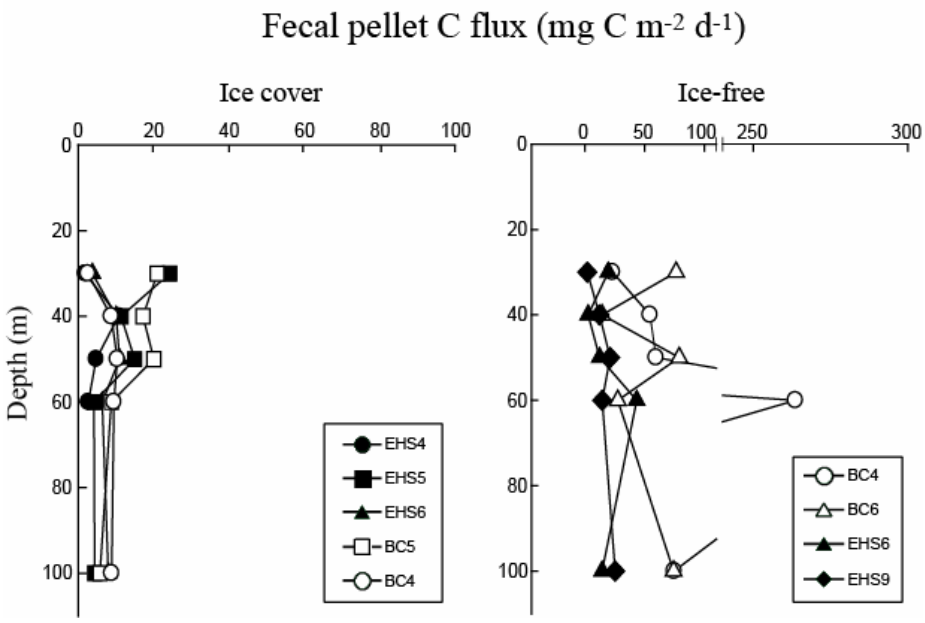

Figure 12. Zooplankton fecal pellet carbon fluxes (mg m^{-2} d^{-1}) at the EHS and BC stations in ice-covered and ice-free conditions

1.3.3 Biochemical composition of the sinking particles

Under ice cover, the C/N ratios (wt/wt) of the sinking particles were more refractory at the EHS stations (from 9.7 to 17.4; mean: 13.1) than at the BC stations (from 5.5 to 9.6; mean: 8.2) (Fig. 13). The C/N ratios increased with depth at the EHS stations while there was little variation with depth at the BC stations. In ice-free water, the C/N ratios showed less variation between EHS and BC stations and among depths, with fluxes ranging from 7.0 to 10.2 (mean: 8.6) at the EHS stations and from 7.7 to 10.9 (mean: 9.5) at the BC stations (Fig. 13). Stable carbon isotope measurements also indicated more refractory sinking material under ice cover at the EHS stations than at the BC stations, with $\delta^{13}C$ values ranging from -28.2 to -25.3 ‰ at the EHS stations and from -24.7 to -22.4 ‰ at the BC stations (Fig. 14). In ice-free conditions, $\delta^{13}C$ values were less variable than under ice cover and ranged from -27.4 to -23.2 ‰ at the EHS stations and from -25.8 to -22.4 ‰ at the BC stations (Fig. 14). In summary, sinking material at the EHS stations had higher C/N ratios and lower $\delta^{13}C$ values than the BC stations under ice cover, while no major difference in the quality of the sinking material was observed between EHS and BC stations in ice-free conditions (Fig. 13, 14 and 15).

1.3.4 Daily loss rates

Daily loss rates of Chl-*a* corresponded to a few percent of the standing stock in the upper 50 m, ranging from 1.2 % to 4.3 % (mean EHS: 2.6 %; BC: 1.7 %) under ice cover and from 1.2 % to 4.0 % (mean EHS: 3.1 %; BC: 1.8 %) in ice-free water (Table 2). The

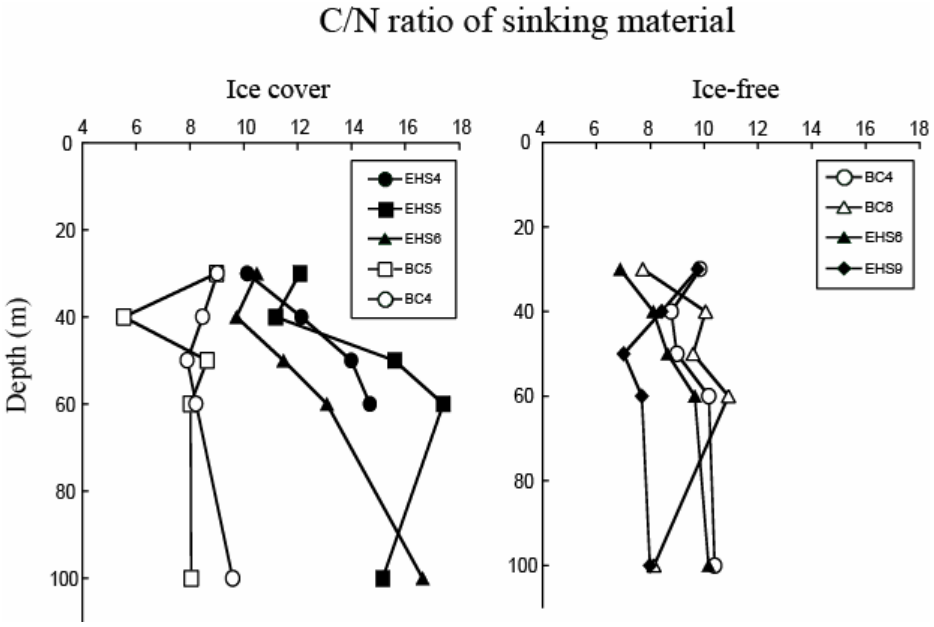

Figure 13. C/N ratios (wt/wt) of sinking material collected at the EHS and BC stations in ice-covered and ice-free conditions

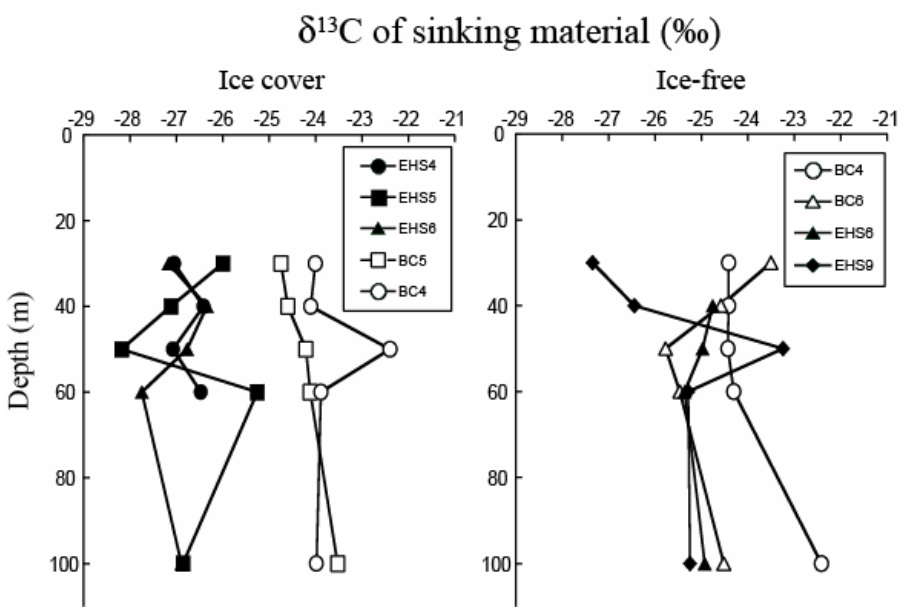

Figure 14. Stable isotopic composition ($\delta^{13}C$) of sinking material collected at the EHS and BC stations in ice-covered and ice-free conditions

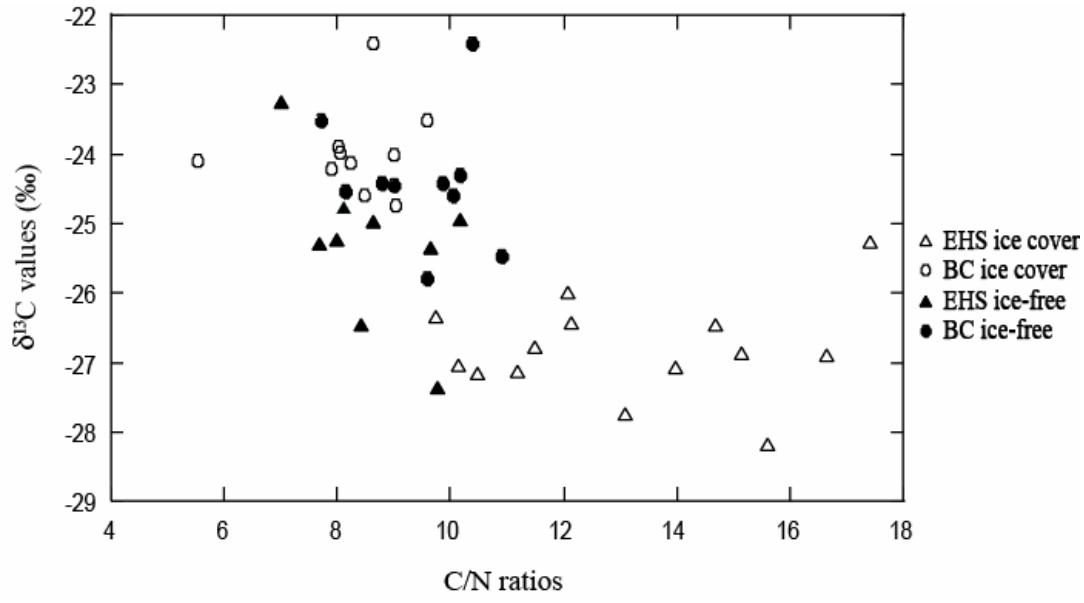

Figure 15. Stable carbon isotopic composition of sinking particles plotted against C/N ratios of sinking material collected at the EHS and BC stations in ice-covered and ice-free conditions

daily loss rates of POC ranged from 0.8 % to 7.7 % (mean EHS: 1.8 %; BC: 5.8 %) under ice cover and from 3.9 % to 6.2 % (mean EHS: 4.0 %; BC: 5.4 %) in ice-free water (Table 2). Both under ice cover and in open water, the highest daily loss rates of POC were observed at the BC stations, while the highest daily loss rates of Chl-*a* were observed at the EHS stations (Table 2).

1.4 Discussion

Although seasonal variation in ice cover is a major factor constraining primary production and subsequent export on the Chukchi Sea shelf and slope, the different oceanographic conditions along the EHS and BC transects can also affect the magnitude and composition of the export fluxes. Barrow Canyon is one of the four main pathways through which nutrient-rich water flowing from Bering Strait exits the Chukchi Sea into the Arctic Ocean (Woodgate et al., 2005). Due to higher input of nutrients, Barrow Canyon exhibits high productivity rates (Hill and Cota, 2005; Bates et al., 2005) and enhanced particle export from shelf to basin (Ashjian et al., 2005; Moran et al., 2005). In 2004, primary production rates measured along the BC transect were approximately 2 and 5 times higher than that of the EHS transect under ice cover and in ice-free conditions, respectively (V. Hill, personal communication). The different hydrographic conditions of each transect were reflected in the export fluxes obtained within each season, as export flux profiles were highly similar at stations located on the same transect, although these stations were on the shelf and on the slope. Export fluxes also reflected different periods in seasonal stage of the pelagic ecosystem due to the time lag

between sediment trap deployments between transects. Therefore, to better assess the impact of ice cover on export fluxes, results are discussed for stations within each transect in chronological order of sampling.

1.4.1 Export fluxes of biogenic matter in the presence of ice cover

1.4.1.1 East Hanna Shoal

The ice cover at the EHS stations was 1.5 to 2 m thick first-year ice with continuous snow cover up to 30 cm thick, and no melting, ice algae or sediments were observed in the ice (R. Gradinger, unpublished data). POC fluxes measured at the EHS stations were low (<90 mg C m^{-2} d^{-1}) and similar to the winter values measured in the Barents Sea (30-70 mg C m^{-2} d^{-1}; Olli et al., 2002). Despite the thick ice and snow cover, the average Chl-*a* flux was higher than the Chl-*a* flux measured in ice-free conditions, up to 2.5 mg m^{-2} d^{-1}, which is consistent with the elevated suspended Chl-*a* concentrations measured along the EHS transect (D. Stockwell, unpublished data). It is unlikely that the thick ice and snow cover allowed sufficient light penetration to sustain the observed Chl-*a* fluxes; however, the elevated Chl-*a*: POC ratios of the sinking material suggest algae growth in weak light and/or large nutrient supply possibly occurring on the underside of the sea ice (Sakshaug, 2004). The removal of snow cover can trigger an under-ice phytoplankton bloom as well as the release of ice algae, resulting in elevated under-ice Chl-*a* and POC fluxes (Peinert et al., 2001; Fortier et al., 2002). However, no melt ponds were observed at the EHS stations and no sympagic algae were observed in the sediment traps. Instead, the dominant phytoplankton cells collected in the traps were the pelagic diatoms

Thalassiosira sp. and *Navicula vanhoeffenii*, which are known to be quantitatively important during the spring bloom in the Arctic Ocean (Quillfeldt, 2000). Therefore, the Chl-*a* fluxes observed could be due to an early under-ice growth, but it is more likely that they reflect the advection of phytoplankton from more productive up-stream regions. Indeed, an area with relatively high phytoplankton abundance was located over the Chukchi shelf up-stream from the EHS transect stations in May-June of 2002 (I. Sukhanova and M. Flint, unpublished data).

FPC fluxes were relatively low at the EHS stations (<25 mg C m^{-2} d^{-1}), but due to the low POC fluxes corresponded on average to 38.7% of the POC fluxes. The majority of fecal pellets recovered at the EHS stations were produced by copepods of the genus *Calanus* spp., which are dominant zooplankton in the Chukchi Sea (Thibault et al., 1999; Plourde et al., 2005). Copepod fecal pellets have specific sinking rates ranging from 5 to >100 m d^{-1} (Turner, 2002; Sampei et al., 2004). These high sinking rates, and thereby short residence times in the water column, indicate that fecal pellets were produced locally, possibly by copepods that overwintered or were advected into the region (Wassmann et al., 1996; Plourde et al., 2005).

High C/N ratios (mean: 13.1) and low $\delta^{13}C$ values (-28.2 to -25.3‰) observed at the EHS stations are consistent with refractory sinking material, even though a large proportion (36.1 %) of the POC fluxes was attributed to PPC. The refractory signature of the sinking material may be due to the large proportion (38.7 %) of fecal pellets contributing to the POC fluxes, as copepod fecal pellets have been shown to be strongly depleted in

^{13}C (5 to 16 ‰) relative to the diet (Breteler et al., 2002; Tamelander et al., 2006). Also, previous evaluation of isotopic end members in the northern Bering and Chukchi Seas indicated distinctly different $\delta^{13}C$ signatures for marine (-21.2 ‰) and terrigenous (-27.0 ‰) material (Naidu et al., 2004). Therefore, it is possible that low $\delta^{13}C$ values of sinking material reflect an input of terrestrial material in the region. Ice-transported particles of lithogenic origin can contribute significantly to the particle flux, as observed in the Greenland Sea where lithogenic matter released from the ice dominated the particle flux (Bauerfeind et al., 2005). In the Chukchi Sea, the ubiquity and high concentration of sediments in the lower layers of sea ice (Eicken et al., 2005) may result in a potentially significant contribution of refractory lithogenic material to the POC fluxes. However, since no melting was observed at the EHS stations, the low $\delta^{13}C$ values of the sinking material was likely due to the advection of terrestrial matter from up-stream locations. Moreover, EHS stations were still under the influence of high winter vertical mixing and active brine formation that kept the water column relatively well-mixed, thus increasing the potential for sediment to be collected into traps.

1.4.1.2 Barrow Canyon

The ice cover at the BC stations was 1 to 1.5 m thick first-year ice, with leads and snowmelt ponds covering up to 70% of the ice cover at the time of sampling (R. Gradinger, unpublished data). POC fluxes were high and within a similar range (4 - 800 mg C m^{-2} d^{-1}) as previously measured in the Barents Sea (Olli et al., 2002), northern Bering Sea (Sasaki and Fukuchi, 2004), and Canadian Archipelago (Fortier, 2004). High

POC and Chl-*a* fluxes observed at the BC stations suggest an under-ice phytoplankton bloom triggered by snowmelt, which is supported by the elevated suspended integrated Chl-*a* concentrations (D. Stockwell, unpublished data). Release of ice algae and under-ice phytoplankton blooms have been observed previously as nutrient-rich waters are exposed to light during ice break-up, and melt water formation gives rise to strongly stratified surface water (Peinert et al., 2001; Fortier et al., 2002; Sakshaug, 2004). The large biomass of the pennate diatom *Fragilariopsis oceanica* recovered at many depths at the BC stations supports the rapid release of algae and the phytoplankton bloom following the ice break-up since *F. oceanica* is known to grow as well in and underneath the ice as in the water column in the loose ice pack (Quillfeldt, 2000). Low Chl-*a*: POC ratios measured on sinking material, associated with the growth of algae acclimated to strong light in stable, shallow surface layers and meltponds (Sakshaug, 2004), are in agreement with the conditions observed at the BC stations. The high Chl-*a* and POC fluxes observed at the BC stations may also in part be due to up-stream production advected from the open lead that form annually along the Alaska coastline. Since Barrow Canyon is an area of enhanced particle export from shelf to basin, the export fluxes measured at BC stations are likely constantly composed of material advected in the region, as well as locally produced.

Nevertheless, PPC fluxes at the BC stations were low and contributed to a surprisingly small fraction (7.5 %) of the POC fluxes, considering the elevated Chl-*a* fluxes, the potential release of ice algae, and the apparent under-ice phytoplankton bloom. Furthermore, FPC fluxes were also low and contributed to only a small proportion of the

POC fluxes (3.7 %), likely due to low abundances of copepods at the BC stations (<200 individuals m^{-3} at BC4; C. Ashjian, unpublished data). These low contributions of PPC and FPC to the POC fluxes raise the question of the large unidentified fraction (88.8 %) of the POC fluxes. Significant proportions of the particle flux may be attributed to unidentified components, as observed in the North Water polynya where the unidentified fraction of the export fluxes ranged from 37 to 96 % over 2 years (Sampei et al., 2004). In this case, the low C/N ratios (mean: 8.5) and high $\delta^{13}C$ values (-24.7 to -22.4 ‰) indicated labile sinking material, similar to $\delta^{13}C$ measurements made in the Barents Sea which revealed average $\delta^{13}C$ values of -24.2 ‰ for phytoplankton and -20.0 ‰ for ice algae (Tamelander et al., in preparation). These results suggest that the major unidentified fraction of the export flux measured at the BC stations was freshly produced, labile material.

1.4.2 Export fluxes of biogenic matter in the absence of ice cover

1.4.2.1 Barrow Canyon

Ice cover decreased between the sampling periods, with ice concentrations from 10 to 20% at the BC stations during the second sampling. Chl-*a* fluxes at BC stations were low (<1.5 mg m^{-2} d^{-1}) while POC fluxes were high (175 to 800 mg C m^{-2} d^{-1}); Chl-*a*: POC ratios were therefore low and consistent with ice-free conditions. An apparent transition in composition of phytoplankton collected by traps was observed at BC stations, with a shift from diatom dominance under ice cover to an equal contribution of diatoms and heterotrophic dinoflagellates in ice-free conditions. The increased proportion of

heterotrophs in the mostly ice-free waters of the BC stations may partly explain the observed decrease in Chl-*a* fluxes, possibly resulting from higher grazing pressure. PPC contributed to 58.3 % of the POC fluxes, while FPC fluxes contributed to 20.2 % of the POC fluxes; the higher export of fecal pellets in ice-free water could be due to higher abundances of large copepods and better feeding conditions than under ice cover (Wexels Riser et al., 2002). Still, the large fraction of PPC contributing to the export fluxes suggests a mismatch between the phytoplankton and zooplankton communities, and the large biomass of *Fragilariopsis oceanica* hints at the rapid export of ice algae from the continuous melting of the ice. Relatively low C/N ratios (mean: 9.5) and enriched $\delta^{13}C$ values (-25.8 to -22.4 ‰), similar to values obtained under ice-covered conditions suggest a steady export of labile material at the BC stations.

1.4.2.2 East Hanna Shoal

The second sampling at the EHS stations was done in summer ice-free conditions. POC fluxes were higher (40 to 370 mg C m^{-2} d^{-1}) and Chl-*a* fluxes were lower (<1 mg m^{-2} d^{-1}) than under ice-covered conditions. A similar reduction in Chl-*a* fluxes has been observed in the Barents Sea, with Chl-*a* fluxes up to 38 mg m^{-2} d^{-1} in spring and generally <1 mg m^{-2} d^{-1} in summer (Olli et al., 2002). These low Chl-*a* fluxes may be due to higher consumption of Chl-*a* by heterotrophic dinoflagellates, which dominated the PPC fluxes at the EHS stations in ice-free conditions. PPC fluxes contributed 8.3 % of the POC fluxes and FPC contributed 17.8 % of the POC fluxes, suggesting that a larger proportion of the primary production was grazed by zooplankton later in the season, similar to

conditions observed at the BC stations. The composition of the sinking material was different in ice-free than in ice-covered conditions, with low C/N ratios (mean: 8.6) and relatively enriched $\delta^{13}C$ values (-27.4 to -23.2 ‰) suggesting the export of relatively labile biogenic matter, even though the FPC fluxes were larger than PPC fluxes. However, the FPC fluxes could have a relatively more labile signature due to recent zooplankton grazing and defecation of fresh labile material.

1.4.3 Chukchi Sea: an export or retentive ecosystem?

Most of the annual primary production and the subsequent vertical export of biogenic matter in the Chukchi Sea are limited to a few months because of seasonal ice cover. A decrease in ice cover would lessen the episodic nature of primary production on the Arctic continental shelves, resulting in an extended productivity period only constrained by light and nutrient availability, and therefore a potential increase in the annual export of biogenic matter. However, our results indicate that decreased ice cover would not necessarily lead to a significant increase in the export of biogenic matter, partly due to the variation in the composition of the export fluxes. Also, a previous study in the Greenland Sea indicate higher annual export fluxes in the marginal ice zone compared to areas with open waters that are never exposed to sea ice or melt water (Peinert et al., 2001). These results suggest that ice-covered export fluxes contribute significantly to the annual export flux on the Arctic continental shelves.

The POC fluxes measured in the Chukchi Sea during this study were 1.6 times higher in ice-free than in ice-covered conditions. The sediment trap results are within a factor of 2 of ^{234}Th-derived POC fluxes obtained in 2004 that indicated similar POC fluxes for both ice-covered and ice-free seasons (Lepore et al., submitted). In contrast, ^{234}Th-derived POC fluxes obtained in 2002 indicated a significant increase (~4 times) of POC export from ice covered to ice-free conditions (Moran et al., 2005). In 2004, trap-derived POC fluxes measured at the EHS stations indicated that sampling occurred in pre-bloom under ice-covered conditions and in late bloom in ice-free conditions, with a bloom probably occurring between the two sampling periods. It is notable that elevated POC fluxes associated with productive conditions were consistently observed at the BC stations that were sampled between the two sampling periods of the EHS stations. Hence, the estimated difference in POC export fluxes from ice-covered to ice-free conditions is much dependent on the time of sampling. The export fluxes on the Chukchi continental shelf and also most likely affected by high interannual variability, these results must therefore be interpreted with caution.

The seasonal variation in the composition of the sinking material, as indicated by C/N ratios and δ^{13}C values, was largely determined by variation in the PPC and FPC fluxes. PPC fluxes under ice cover were dominated by diatoms, while in ice-free conditions the contribution of dinoflagellates to the PPC flux increased at the BC stations and dominated the EHS stations. The proportion of PPC to the sinking POC at the EHS stations averaged 36.1 % under ice cover and only 8.3 % in ice-free water, suggesting a better retention of the phytoplankton in the upper water column in the absence of ice

cover. The opposite situation was observed at the BC stations, with PPC representing 7.5 % of the POC fluxes under ice cover and as much as 58.3 % in ice-free water, suggesting a larger export of phytoplankton in the absence of ice cover. FPC fluxes decreased at the EHS stations (38.7 % to 17.8 %) and increased at the BC stations (3.7 % to 20.2 %) from under ice cover to ice-free conditions; however, the export of FPC was similar at all stations in the absence of ice cover.

In the presence of ice cover, an average daily loss rate of 2.6 % of the suspended Chl-*a* and an average daily loss rate of 1.8 % of the suspended POC stock was observed at the EHS stations. At the BC stations, averaged daily loss rates of 1.7 % of the suspended Chl-*a* and of 5.8 % of the suspended POC were observed, indicating that BC may be a significant export area of POC even under ice cover. This supports the benthic biomass and sediment oxygen uptake patterns observed in the underlying benthos (Grebmeier et al., 2006). In ice-free water, an average daily loss rate of 3.1 % of the suspended Chl-*a* and an average daily loss rate of 4.0 % of the suspended POC was observed at the EHS stations. An average daily loss rate of 1.8% of the suspended Chl-*a* and of 5.4 % of the suspended POC fluxes were observed at the BC stations. Despite lower concentrations of Chl-*a* in ice-free water (Stockwell, unpublished data), daily loss rates of Chl-*a* were similar to under-ice daily loss rates, suggesting the retention of Chl-*a* in the upper water. Based upon our results and previous data (Moran et al., 2005), BC is an important area for carbon sequestration and export to the basin, as reflected by the daily loss rates of POC >5 % in both ice-covered and ice-free conditions.

1.5 Conclusion

The composition of the export fluxes of biogenic matter differed from ice-covered to ice-free conditions, mostly due to the variation in the contributions of PPC and FPC to the total POC fluxes. Although the composition of the sinking material was different seasonally, POC fluxes measured in the Chukchi Sea were of similar magnitude in the presence and in the absence of ice cover, indicating that export fluxes in the presence of ice cover contribute significantly to the annual export of biogenic matter in the Chukchi Sea. Relatively high daily loss rates of POC in both ice-covered and ice-free conditions at the BC stations suggest that BC is an important area of carbon export to the basin. This suggests that a reduction or disappearance of ice cover would not necessarily increase the annual export of POC over the Chukchi continental shelf.

Chapter 2

Export fluxes of particulate organic carbon in the Chukchi Sea: A comparative study using $^{234}Th/^{238}U$ disequilibria and drifting sediment traps

This chapter is a paper accepted for publication in Marine Chemistry (Lalande, C., Lepore, K., Cooper, L.W., Grebmeier, J.M., Moran, S.B. Export fluxes of particulate organic carbon in the Chukchi Sea: A comparative study using $^{234}Th/^{238}U$ disequilibria and drifting sediment traps). Kate Lepore was responsible for the ^{234}Th measurements and analysis, while I was responsible for the drifting sediment trap deployments and analysis. My contributions to the paper include the interpretation of data for the comparative study and the preparation of the manuscript, apart from the material and methods for the sampling of ^{234}Th written by Kate Lepore.

2.1 Introduction

Strong seasonal variability in solar irradiance influences the extent of sea ice formation and melting on the Arctic continental shelves. These seasonal extremes in light intensity and ice cover over the nutrient-rich waters of the Chukchi Sea cause rates of primary production to alternate from extremely low values under ice cover to extremely high values during ice edge and open water blooms (Springer and McRoy, 1993; Hill and Cota, 2005; Wang et al., 2005). This extreme seasonality nonetheless supports an estimated annual primary production of up to ~430 g C m^{-2} yr^{-1} in some regions of the Chukchi Sea (Hill and Cota, 2005), making the Chukchi Sea the most productive Arctic shelf sea, and one of the most productive areas in the world ocean (Sakshaug, 2004). The high rates of primary production during the open water season contribute to elevated carbon export fluxes over the Chukchi shelf and slope (Moran et al., 2005).

The episodic nature of export fluxes on the Arctic continental shelves can lead to uncertainty in the prediction of seasonal and annual rates of particulate organic carbon (POC) export (Wassmann et al., 2004). While there is still no ideal method to quantify the export of carbon in the upper ocean, the determination of POC export flux may be more tightly constrained by combining the ^{234}Th flux measured with *in situ* pumps or bottles with POC/^{234}Th ratios determined on material collected with drifting sediment traps (Murray et al., 1996; Charette et al., 1999; Benitez-Nelson et al., 2001; Amiel et al., 2002; Coppola et al., 2002; Moran et al., 2003).

^{234}Th/^{238}U disequilibria and drifting sediment traps are commonly used to determine POC export in the upper waters of the Arctic Ocean (Moran et al., 1997; Moran and Smith, 2000; Amiel et al., 2002; Coppola et al., 2002; Moran, 2004; Wassmann et al., 2004; Moran et al., 2005). Due to direct sampling of sinking particles, sediment traps have the advantage of providing material for biological composition analyses of exported particles. However, there are shortcomings such as hydrodynamic bias and inclusion of swimmers in the use of upper ocean sediment traps that can impact trapping efficiency, leading to under- or over-estimation of the sinking particle fluxes (Buesseler, 1991; Buesseler et al., 1994; Murray et al., 1996; Gardner, 2000; Buesseler et al., submitted).

In this regard, ^{234}Th ($t_{1/2}$ = 24.1 days) has been identified as the most promising independent tracer of particle export for trap calibration studies in the upper ocean (Gardner, 2000). ^{234}Th is a naturally occurring particle-reactive radionuclide produced continuously in seawater by decay of its parent ^{238}U, and is a useful tracer of upper ocean

particle export on a time-scale of days to months (Coale and Bruland, 1985; Coale and Bruland, 1987). ^{234}Th is removed from surface waters by particle export, creating a deficit relative to its soluble, conservative ^{238}U parent. POC fluxes are estimated by multiplying the depth-integrated ^{234}Th flux by the POC/^{234}Th ratio of sinking particles,

$$P_{POC} = (P_{Th})_z \left(POC/^{234}Th \right)_z \quad (1)$$

where P_{POC} is the flux of POC (mmol C m^{-2} d^{-1}), P_{Th} is the flux of ^{234}Th (dpm m^{-2} d^{-1}) at depth z, and $POC/^{234}Th$ is the ratio (mmol dpm^{-1}) at depth z (Buesseler et al., 1992a, Moran et al., 2003). The principal limitations of the ^{234}Th flux approach are the ability to define and measure the ^{234}Th flux and the POC/^{234}Th ratio on sinking particles (Moran et al., 2003). Discrepancies reported between results obtained using drifting traps and ^{234}Th measurements provide evidence of the uncertainty associated with the estimation of POC export fluxes in the upper ocean (Buesseler, 1991; Murray et al. 1996; Buesseler et al., submitted).

The goal of this study was to compare ^{234}Th and POC export fluxes obtained with large-volume *in situ* pumps and drifting sediment traps in the Chukchi Sea. The two independent means of estimating POC fluxes were evaluated in ice-covered and open water sites to investigate the processes that influence the export of carbon on the Chukchi Sea continental shelf and slope.

2.2 Material and Methods

Samples for POC and ^{234}Th determination were collected using *in situ* pumps and drifting sediment traps as part of the 2004 Western Arctic Shelf-Basin Interactions (SBI) spring (May 15-June 23) and summer (July 17-August 26) process cruises on board the *USCGC Healy*. Large-volume sampling of ^{234}Th and drifting sediment trap deployments were conducted simultaneously at five stations during the spring cruise and four stations during the summer cruise. All stations were located along East Hanna Shoal (EHS) and Barrow Canyon (BC) transects (Fig. 16).

2.2.1 Large-volume sampling by in situ pumps

Large-volume samples (200–1000 L) were collected using battery-operated *in situ* pumps (Challenger Oceanic Systems and Services, Surrey, U.K. and McLane Laboratories, Falmouth, MA, USA) at a flow rate of 2-4 L min^{-1}. Seawater was passed sequentially through a 142 mm 53 μm Nitex screen, a 1 μm prefilter cartridge (7.6 x 7.6 cm), and two MnO_2-impregnated cartridges (7.6 x 7.6 cm) connected in series to scavenge dissolved ^{234}Th. The accuracy of this method has been confirmed with measurements of ^{234}Th/^{238}U equilibrium in deep-water samples collected during previous cruises. Prefilter and MnO_2 cartridges were dried at 60˚C and ashed at 500˚C at sea.

Dissolved ^{234}Th activities were measured by gamma spectrometry. Cartridge ash was packed into appropriate geometries for counting on a Canberra pure Ge well detector

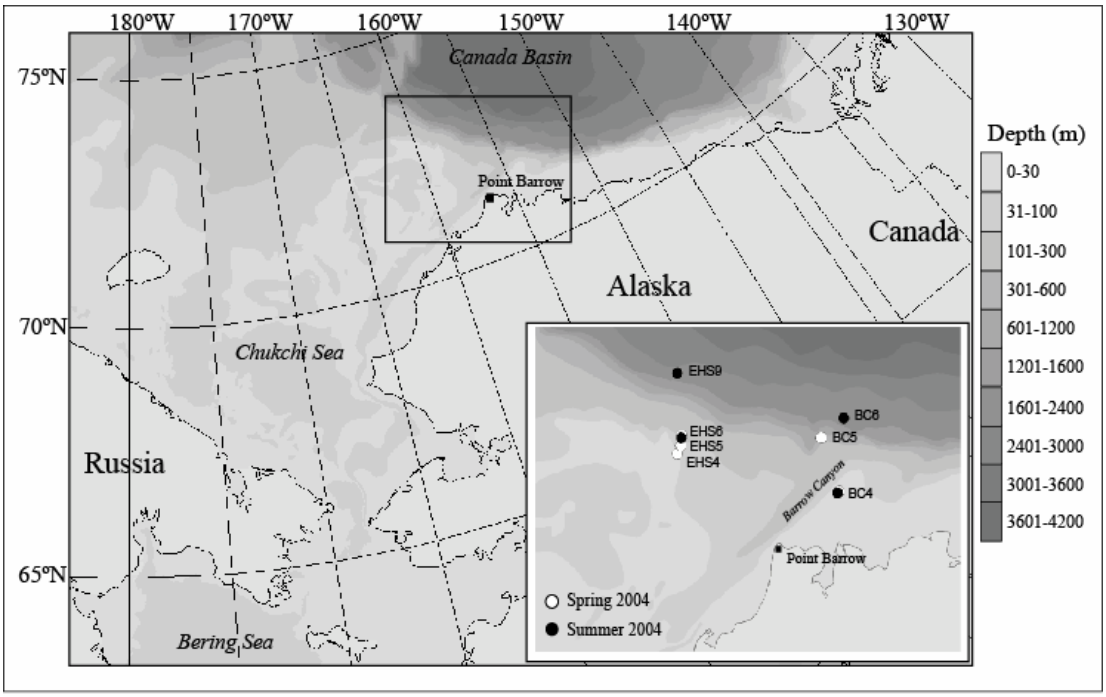

Figure 16. Stations sampled with sediment traps and *in situ* pumps in spring and summer 2004 in the Chukchi Sea. Stations are designated as BC (Barrow Canyon) and EHS (East Hanna Shoal)

(GL20203, 150 cm^3) or a Canberra pure Ge planar detector (GCW3023, 2000 mm^2). ^{234}Th activities were determined by gamma emission at 63.3 keV and decay-corrected to the midpoint of sample collection (Buesseler et al., 1992b). ^{234}Th activities on >53 μm particles were determined by beta emission of the ^{234}Pa daughter on a RISØ National Laboratory low-background beta detector. Particles collected on the Nitex screen were resuspended by sonication and collected on a Whatman GF/F filter. The filter was mounted on an acrylic planchet and covered with clear plastic (1.5 mg cm^{-3}) and Al foil (4.5 mg cm^{-3}) to shield alpha particles and low-level beta emitters (Charette and Moran, 1999; Cochran et al., 2000). Samples were counted a minimum of three times, with counting times no less than one week apart. ^{238}U activities were calculated from salinity according to the relationship ^{238}U (dpm L^{-1}) = salinity x 0.0708 (Chen et al., 1986).

POC was analyzed on GF/F filter subsamples containing particles collected on the 53 μm Nitex screen. Subsamples of known weight were placed in a dessicator with concentrated fuming HCl for 24 h to remove inorganic carbon, and dried for 24 h at 60˚C (Pike and Moran, 1997). POC was measured using an Exeter Analytical CE-440 elemental analyzer (University of Rhode Island). Blanks were collected at sea by passing ~100-200 mL GF/F-filtered seawater through a precombusted GF/F filter. The blank value included dissolved organic carbon (DOC) adsorption and the POC associated with the precombusted GF/F filter (average blank value = 9.3 ± 3.7 μmol C).

2.2.2 Sediment traps

A drifting array of sediment traps attached at five depths (30, 40, 50, 60, and 100 m) was deployed at each station for periods ranging from 11 to 20 hours due to the ship operations schedule and sometimes difficult weather conditions. The array was anchored to a drifting ice floe for deployments in ice cover and drifted during open water deployments. The water column depth at stations sampled ranged from 153 m to 2061 m, and a contribution of scavenging by resuspension or an addition of resuspended material in the sediment traps was not expected as the deepest trap was consistently deployed at least 90 m from seafloor. The sediment traps consisted of four cylindrical tubes (7.2 cm x 45 cm; height/diameter ratio: 6.25) mounted in a cross frame to ensure that the tubes remain vertical in the water (KC Denmark, Silkeborg, Denmark). No baffles were used in the tube opening and no poison was applied in the traps because solubilization of POC to DOC was assumed to be low for short deployment periods in cold Arctic waters. Upon recovery, contents of the four tubes deployed at each depth were mixed together into Nalgene® containers and kept cool and in the dark until processed within 10 hours. Two aliquots (~3 L and 200 mL) from each depth were filtered onto precombusted GF/F filters to measure particulate ^{234}Th activities and POC concentrations, respectively. Swimmers (zooplankton) were carefully removed from the filters with forceps and the filters were dried for 24 h at 60°C. Particulate ^{234}Th activities were determined both at sea and at the shore-based laboratory by direct non-destructive beta counting using the same RISØ National Laboratory low-background beta detector as for the large-volume ^{234}Th sampling. GF/F filters containing POC were stored until acidified ashore in a

dessicator with fuming concentrated HCl for 24 h to remove inorganic carbon. POC was then quantified using an Exeter Analytical CE-440 elemental analyzer at the Marine Science Institute (University of California, Santa Barbara). Blank filters exposed to 200 mL of filtered seawater were used to account for DOC adsorption onto precombusted filters and the trap-derived POC fluxes were corrected using the average blank value of 4.8 ± 1.4 μmol C.

2.3 Results

2.3.1 Large-volume sampling of ^{234}Th

$^{234}Th/^{238}U$ disequilibria were evident at every station during the spring and summer 2004 (Lepore et al., submitted), which indicates the export of ^{234}Th on sinking particles occurring on a time-scale of days to weeks. Large-volume sampling data are presented only for depths sampled in the upper 100 m so as to compare with depths sampled with the sediment traps (Table 3), although *in situ* pumps were deployed at larger depths than 100 m to measure equilibrium with ^{238}U (Lepore et al., submitted). The collection efficiency of the MnO_2 cartridges for ^{234}Th in the Chukchi Sea was 76% ± 15% (n=188). ^{234}Th fluxes derived from $^{234}Th/^{238}U$ disequilibria increased with depth at all stations, and the highest ^{234}Th fluxes were observed at BC during the summer (Fig. 17a). $POC/^{234}Th$ ratios were generally higher in surface waters and decreased with depth at both transects in both seasons (Fig. 17b). POC fluxes measured at 50 m along the BC transect averaged 14.0 ± 8.0 mmol C m^{-2} d^{-1} during the spring and 16.5 ± 6.5 mmol C m^{-2} d^{-1} in summer,

Table 3. *In situ* pump and sediment trap ^{234}Th fluxes, POC/^{234}Th ratios, POC fluxes and sediment trap collection efficiency measured in the upper 100 m of Barrow Canyon (BC) and East Hanna Shoal (EHS) during spring and summer 2004

Season	Station	Water depth m	Sample depth m	^{234}Th flux pump dpm m^{-2} d^{-1}	^{234}Th flux trap dpm m^{-2} d^{-1}	POC/^{234}Th pump µmol C dpm^{-1}	POC/^{234}Th trap µmol C dpm^{-1}	POC flux pump mmol C m^{-2} d^{-1}	POC flux trap mmol C m^{-2} d^{-1}	Efficiency trap Ratio ^{234}Th flux (trap / pump)
Spring	EHS4	153	10	323 ± 54		9.4 ± 7.1		3.0 ± 0.5		
			30	757 ± 173	962 ± 44	6.7 ± 5.1	6.8 ± 0.3	5.0 ± 1.2	6.5 ± 0.3	1.27 ± 0.25
			40	926 ± 178	986 ± 43	5.1 ± 3.9	4.8 ± 0.2	4.8 ± 1.0	4.7 ± 0.2	1.06 ± 0.24
			50	1149 ± 260	1368 ± 39	3.1 ± 2.4	3.4 ± 0.1	3.6 ± 0.9	4.6 ± 0.2	1.19 ± 0.15
			60	1427 ± 351	1458 ± 37	2.5 ± 1.9	2.2 ± 0.1	3.7 ± 1.0	3.3 ± 0.2	1.02 ± 0.11
	EHS5	247	10	475 ± 92						
			30	1143 ± 290	805 ± 71	1.8 ± 0.1	7.1 ± 0.6	2.0 ± 0.5	5.7 ± 0.3	0.70 ± 0.24
			40		1085 ± 69		6.9 ± 0.4		7.5 ± 0.4	
			50	1575 ± 405	1563 ± 61	0.6 ± 0.6	0.6 ± 0.1	1.0 ± 0.3	1.0 ± 0.1	0.99 ± 0.15
			60		1403 ± 60		0.2 ± 0.1		0.3 ± 0.1	
			75							
			100	2972 ± 726	2100 ± 57	0.0 ± 0.0	0.5 ± 0.1	0.0 ± 0.0	1.1 ± 0.1	0.71 ± 0.08
	EHS6	689	10	251 ± 48		53.4 ± 5.9		12.9 ± 2.9		
			30	737 ± 183	543 ± 37	2.5 ± 0.2	9.6 ± 0.7	1.9 ± 0.5	5.2 ± 0.3	0.74 ± 0.20
			40		1184 ± 31		4.9 ± 0.1		5.8 ± 0.3	
			50	1619 ± 349	1075 ± 31		3.1 ± 0.1	1.2 ± 0.3	3.3 ± 0.2	0.66 ± 0.09
			60		1257 ± 29		1.3 ± 0.1		1.6 ± 0.1	
			75	1714 ± 370		0.3 ± 0.1		0.5 ± 0.1		
			100	2311 ± 578	1429 ± 29		0.4 ± 0.1		0.5 ± 0.1	0.62 ± 0.05
	BC5	1184	10	174 ± 64		14.7 ± 1.1		2.6 ± 1.0		
			30	1000 ± 394	766 ± 50		17.0 ± 1.1		13.0 ± 0.7	0.77 ± 0.13
			40		1114 ± 47		38.0 ± 1.6		42.3 ± 2.1	
			50	1019 ± 402	1189 ± 44	21.5 ± 1.8	20.8 ± 0.8	21.9 ± 8.8	24.7 ± 1.2	1.17 ± 0.11
			60		1326 ± 43		22.9 ± 0.7		30.4 ± 1.5	
			75	1745 ± 423		17.4 ± 2.1		30.5 ± 8.2		
			100	2708 ± 851	1305 ± 44	22.3 ± 1.1	26.6 ± 0.9	61.0 ± 20.0	34.7 ± 1.7	0.48 ± 0.05
	BC4	545	10	231 ± 42		39.4 ± 4.9		9.1 ± 2.0		
			30	644 ± 156	1159 ± 43	9.1 ± 1.0	24.9 ± 0.9	5.9 ± 1.5	28.9 ± 1.4	1.80 ± 0.28

Table 3. continued.

Season	Station	Water depth m	Sample depth m	^{234}Th flux pump dpm m^{-2} d^{-1}	^{234}Th flux trap dpm m^{-2} d^{-1}	POC/^{234}Th pump µmol C dpm^{-1}	POC/^{234}Th trap µmol C dpm^{-1}	POC flux pump mmol C m^{-2} d^{-1}	POC flux trap mmol C m^{-2} d^{-1}	Efficiency trap Ratio ^{234}Th flux (trap / pump)
	BC4	545	40		1372 ± 44		19.3 ± 0.6		26.5 ± 1.3	
			50	999 ± 213	1271 ± 40	6.1 ± 0.4	29.8 ± 0.9	6.0 ± 1.3	37.9 ± 1.9	1.27 ± 0.19
			60		1357 ± 42		30.6 ± 0.9		41.5 ± 2.1	
			75	1548 ± 306		4.2 ± 0.4		6.5 ± 1.4		
			100	2215 ± 470	1647 ± 37	10.0 ± 0.8	21.0 ± 0.5	22.2 ± 5.0	34.6 ± 1.7	0.74 ± 0.08
Summer	BC4	326	10	340 ± 54		27.1 ± 1.9		9.3 ± 1.6		
			30	994 ± 233	1097 ± 29	37.3 ± 4.6	60.4 ± 1.6	37.1 ± 9.8	66.3 ± 3.3	1.10 ± 0.12
			40		855 ± 31		53.5 ± 1.9		45.8 ± 2.3	
			50	1750 ± 541	1227 ± 28	13.1 ± 1.4	31.9 ± 0.7	23.0 ± 7.5	39.1 ± 2.0	0.70 ± 0.05
			60		1367 ± 27		29.8 ± 0.6		40.8 ± 2.0	
			75	2774 ± 992		14.8 ± 2.1		41.0 ± 15.8		
			100	3801 ± 2661	1499 ± 26	11.4 ± 1.0	15.4 ± 0.3	43.6 ± 30.7	23.0 ± 1.2	0.39 ± 0.01
	BC6	2061	10	393 ± 86		22.3 ± 3.5		8.7 ± 2.3		
			30	1154 ± 327	990 ± 54	23.6 ± 4.1	45.2 ± 2.5	27.2 ± 9.0	44.7 ± 2.2	0.86 ± 0.17
			40		871 ± 55		61.8 ± 3.9		53.8 ± 2.7	
			50	1741 ± 478	1223 ± 51	5.7 ± 0.4	15.5 ± 0.7	10.0 ± 2.8	19.0 ± 1.0	0.70 ± 0.11
			60		1490 ± 48		9.9 ± 0.3		14.7 ± 0.7	
			75	2447 ± 763		6.4 ± 0.5		15.7 ± 5.0		
			100	3229 ± 977	2056 ± 44	5.2 ± 0.5	10.3 ± 0.2	16.9 ± 5.3	21.1 ± 1.1	0.64 ± 0.05
	EHS6	398	10	268 ± 61		33.3 ± 5.6		8.9 ± 2.5		
			30	596 ± 181	418 ± 56	15.7 ± 1.2	33.3 ± 4.4	9.4 ± 2.9	13.9 ± 0.7	0.70 ± 0.31
			40		484 ± 53		15.5 ± 1.7		7.5 ± 0.4	
			50	1313 ± 449	747 ± 47		11.4 ± 0.7	16.2 ± 5.8	8.5 ± 0.4	0.57 ± 0.10
			60		773 ± 47		6.6 ± 0.4		5.1 ± 0.3	
			75	1351 ± 462		8.2 ± 0.7		11.1 ± 3.9		
			100	2064 ± 747	1334 ± 42	1.1 ± 0.1	4.5 ± 0.1	2.3 ± 0.8	6.0 ± 0.3	0.65 ± 0.06
	EHS9	1938	10	207 ± 47		26.5 ± 3.2		5.5 ± 1.4		
			30	714 ± 212	459 ± 48	14.3 ± 2.0	7.6 ± 0.8	10.2 ± 3.3	3.5 ± 0.2	0.64 ± 0.23
			40		513 ± 49		13.8 ± 1.3		7.1 ± 0.4	
			50	1357 ± 368	948 ± 41	16.8 ± 1.5	18.5 ± 0.8	22.8 ± 6.5	17.5 ± 0.9	0.70 ± 0.11

Table 3. continued

Season	Station	Water depth m	Sample depth m	^{234}Th flux pump dpm m^{-2} d^{-1}	^{234}Th flux trap dpm m^{-2} d^{-1}	POC/^{234}Th pump µmol C dpm^{-1}	POC/^{234}Th trap µmol C dpm^{-1}	POC flux pump mmol C m^{-2} d^{-1}	POC flux trap mmol C m^{-2} d^{-1}	Efficiency trap Ratio ^{234}Th flux (trap / pump)
	EHS9	1938	60		737 ± 41		41.5 ± 2.3		30.6 ± 1.5	
			75	1648 ± 442		10.2 ± 0.7		16.8 ± 4.6		
			100	1933 ± 744	971 ± 39	1.4 ± 0.2	7.9 ± 0.3	2.8 ± 1.1	7.7 ± 0.4	0.50 ± 0.05

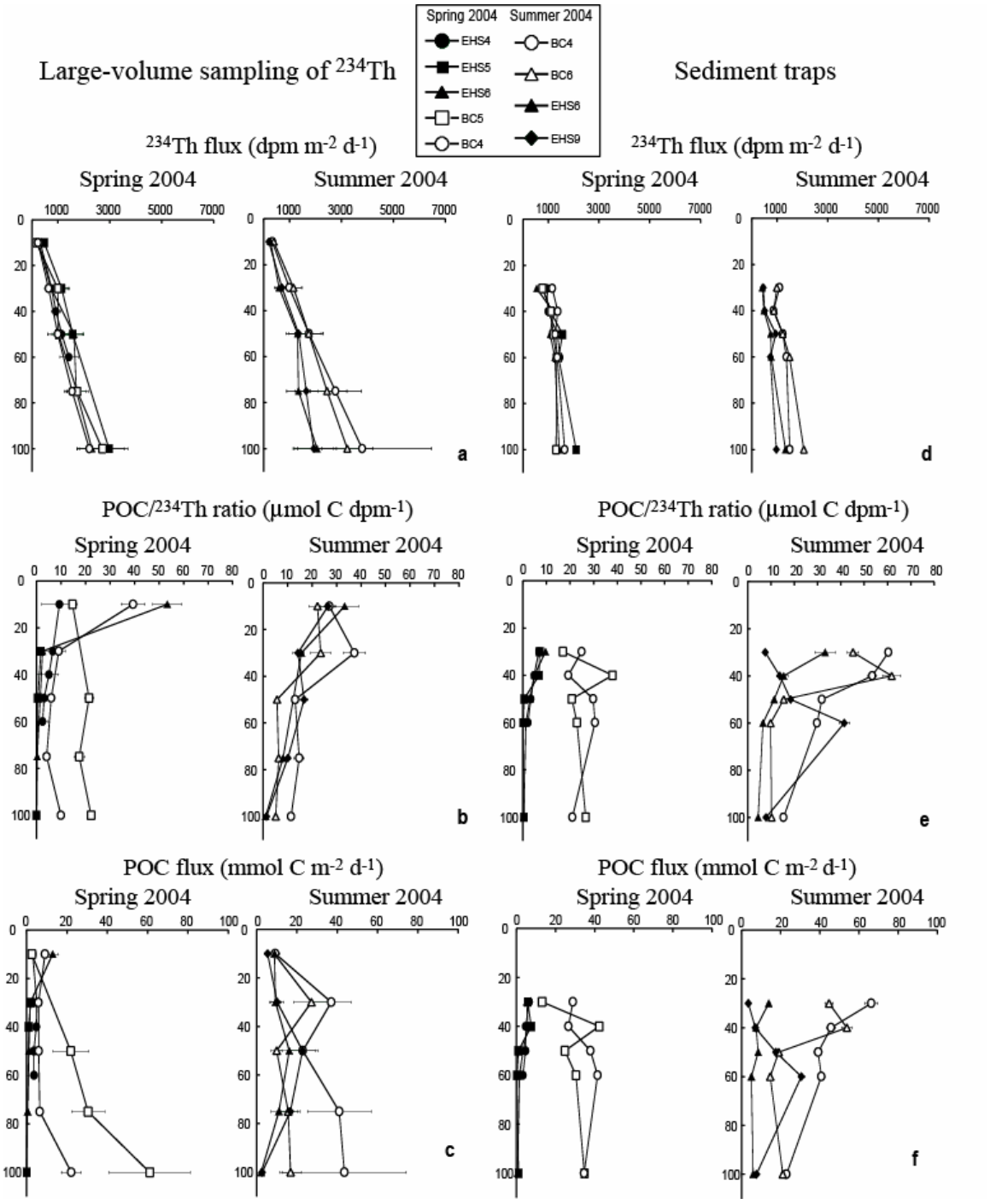

Figure 17. Depth profiles of ^{234}Th fluxes, POC/^{234}Th ratios and POC fluxes obtained from *in situ* pumps and sediment traps in spring and summer 2004 in the Chukchi Sea

while POC fluxes measured along the EHS transect averaged 1.9 ± 1.1 mmol C m^{-2} d^{-1} during the spring and 19.5 ± 3.3 mmol C m^{-2} d^{-1} in summer (Fig. 17c).

2.3.2 Sediment traps

Sediment trap ^{234}Th fluxes increased with depth at all stations during both seasons (Fig. 17d). ^{234}Th fluxes were similar among stations in spring, while ^{234}Th fluxes were higher along the BC transect than along the EHS transect during the summer (Fig. 17d). The collection efficiency of the sediment traps, obtained by comparing the ^{234}Th flux collected by sediment trap with the ^{234}Th export from the mixed surface ocean at corresponding depths, ranged from 0.39 ± 0.01 to 1.80 ± 0.28 (Table 3). POC/^{234}Th ratios and POC fluxes were higher in BC than along the EHS transect by at least a factor of 2 during both seasons (Fig. 17e and 17f). POC fluxes measured at 50 m along BC averaged 31.3 ± 9.3 mmol C m^{-2} d^{-1} during the spring and 29.1 ± 14.2 mmol C m^{-2} d^{-1} in summer, while POC fluxes measured along the EHS transect averaged 3.0 ± 1.9 mmol C m^{-2} d^{-1} during the spring and 13.0 ± 6.4 mmol C m^{-2} d^{-1} in summer (Fig. 17f).

2.3.3 Comparison of in situ pump-derived and sediment trap-derived export fluxes

Large-volume *in situ* pump measurements recorded higher ^{234}Th fluxes than sediment traps at depths greater than 60 m at every station for both seasons (Table 3). Both methods showed similar ^{234}Th fluxes among stations in spring and highest fluxes

occurring in BC during the summer (Fig. 17a and 17d). Both methods also indicated that POC/^{234}Th ratios were higher in BC than along the EHS transect, however the difference between transects was greater when measured with sediment traps than with *in situ* pumps (Fig. 17b and 17e). For both seasons, POC fluxes measured with sediment traps at 50 m in BC were approximately twice as high as POC fluxes measured with *in situ* pumps (31.3 ± 9.3 versus 14.0 ± 8.0 mmol C m^{-2} d^{-1} in spring and 29.1 ± 14.2 versus 16.5 ± 6.5 mmol C m^{-2} d^{-1} in summer, respectively), while the estimated POC fluxes were similar on the EHS transect at 50 m when measured either with *in situ* pumps or sediment traps during both seasons (3.0 ± 1.9 versus 1.9 ± 1.1 mmol C m^{-2} d^{-1} in spring and 13.0 ± 6.4 versus 19.5 ± 3.3 mmol C m^{-2} d^{-1} in summer, respectively) (Fig. 17c and 17f). Greater variability in POC fluxes (x 2 in spring and x 2.7 in summer) was observed in the euphotic zone when measured by sediment traps compared with *in situ* pumps. The export fluxes obtained from both methods were compared at 50 m because this depth was consistently sampled during both *in situ* pump and trap deployments and because it corresponded to the base of the euphotic zone at most stations (Hill et al., 2005; V. Hill, personal communication).

^{234}Th fluxes, POC fluxes and POC/^{234}Th ratios measured using both methods at corresponding stations and depths were plotted against each other (Fig. 18). ^{234}Th fluxes, POC/^{234}Th ratios, and POC export fluxes were within a factor of 2 at most stations and depths (Fig. 18a-c). A 2-way repeated measures ANOVA indicated that there were no significant differences observed between POC fluxes measured with *in situ* pumps and sediment traps. The exception was at station BC4 during the spring, where significantly

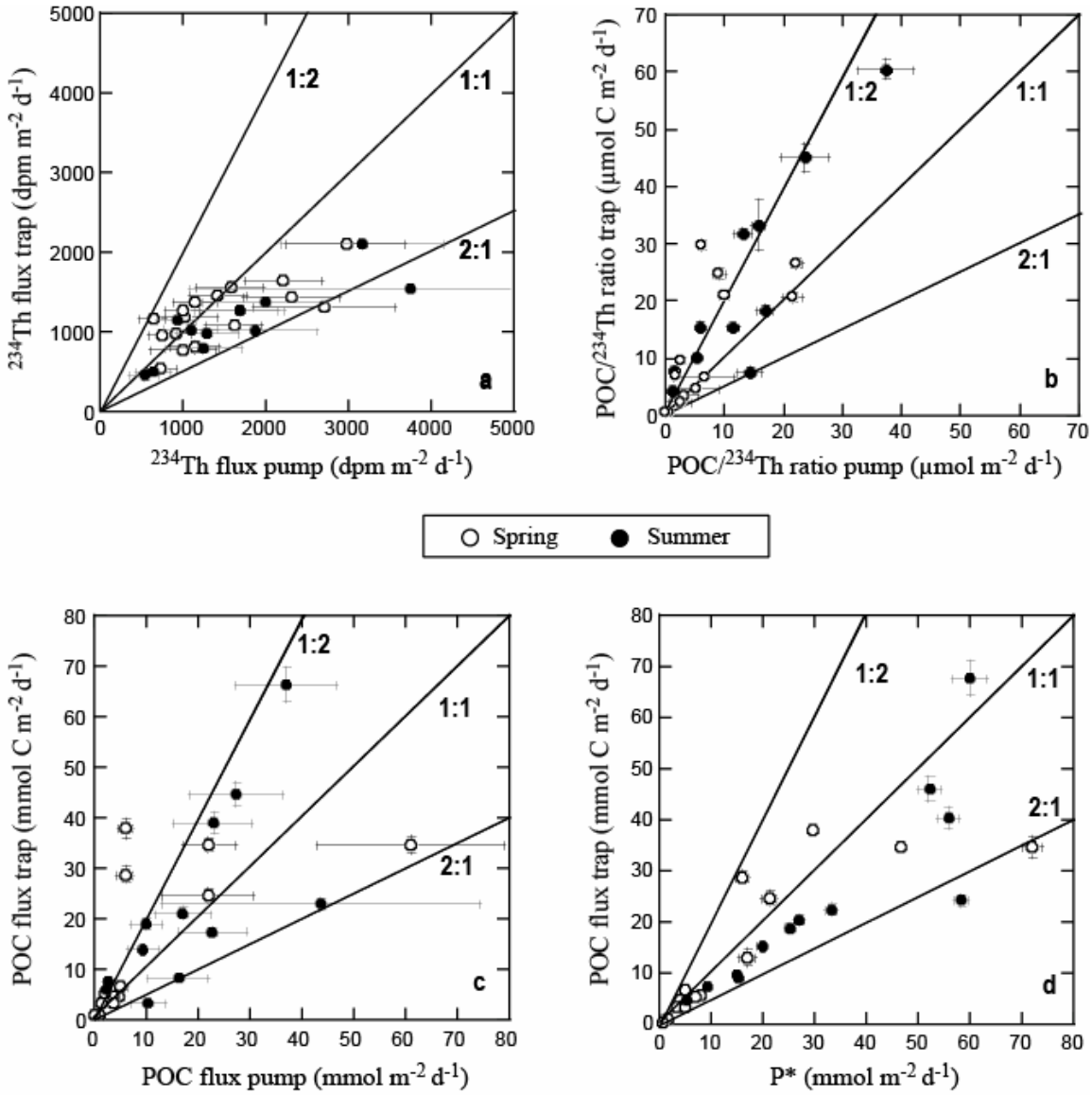

Figure 18. Comparison of ^{234}Th fluxes, POC fluxes, and POC/^{234}Th ratios determined with *in situ* pumps and sediment traps, as well as POC fluxes calculated using the pump-derived ^{234}Th flux and POC/^{234}Th ratios measured in sediment traps (P*) in spring and summer 2004 in the Chukchi Sea. Diagonal lines correspond to 1:1, 1:2 and 2:1 relations

higher fluxes were measured with sediment traps. POC fluxes calculated using the pump-derived ^{234}Th flux and POC/^{234}Th ratios measured in sediment traps (P^{*}) showed an increase from 70% to 93% of the measurements within a factor of 2 (Fig. 18d).

2.4 Discussion

^{234}Th-derived POC fluxes and sediment trap POC fluxes measured in the Chukchi Sea during spring and summer 2004 were similar to POC fluxes previously reported using either method over the central Barents Sea (Coppola et al., 2002; Olli et al., 2002), the northern Bering Sea (Fukuchi et al., 1993) and the Chukchi Sea (Moran et al., 1997; Moran et al., 2005), representing some of the highest POC fluxes reported in the literature (Moran et al., 2003). POC fluxes determined from either method were similar during spring and summer 2004 along the BC transect. This could be due to the fact that Barrow Canyon is one of the four main pathways through which nutrient-rich water flowing from Bering Strait exits the Chukchi Sea into the Arctic Ocean (Woodgate et al., 2005). The constant input of nutrients results in high primary production rates along the BC transect during spring and summer (Hill and Cota, 2005), which may explain the similar POC fluxes observed during both seasons. However, a significant increase in POC fluxes observed along the EHS transect from spring to summer, as well as a 3-fold increase in POC fluxes observed between spring and summer of 2002 (Moran et al., 2005) suggest that seasonal and interannual variability of POC export is important on the Chukchi Sea shelf. Variability in POC export fluxes throughout the Chukchi Sea was

also reflected in the composition of the export fluxes in the presence or absence of sea ice cover (Lalande et al., in preparation).

2.4.1 Discrepancies between ^{234}Th-derived and sediment trap-derived fluxes

The collection efficiency of the sediment traps suggested undertrapping by the sediment traps, with 70% of the ^{234}Th fluxes measured by the sediment traps lower than ^{234}Th fluxes obtained from *in situ* pumps (Table 3). However, the ^{234}Th and POC fluxes obtained with *in situ* pumps and drifting sediments traps were within a factor of 2 for 70% of measurements (Fig. 18a-c). This is a reasonable agreement between both techniques because differences of less than a factor of 2 are difficult to resolve when comparing methods for ascertaining export production (Ducklow et al., 2001) and because the resolution of either method may not be better than a factor of 2 to 3 (Emerson et al., 1997; Moran et al. 2003). Also, the estimation of 1-dimensional pump-derived ^{234}Th fluxes differed by less than a factor of 2 from 3-dimensional pump-derived ^{234}Th fluxes when averaged along a transect, which indicates that advective transport of the ^{234}Th deficit did not appreciably affect the estimation of the ^{234}Th flux by *in situ* pumps (Lepore et al., submitted). Despite reasonable agreement between *in situ* pumps and sediment traps, there are still discrepancies observed in POC fluxes obtained with both methods that may be best explained by differences in the estimated POC/^{234}Th ratios, which are a significant source of variability when calculating POC export fluxes (Amiel et al., 2002; Coppola et al., 2002; Moran et al., 2003; Buesseler et al., 2006; Gustafsson et al., 2006; Passow et al., 2006).

A possible bias in the use of upper ocean sediment traps that may impact trapping efficiency and explain some of the observed differences between methods is the inclusion of swimmers in the sediment traps (Gardner, 2000). The presence of swimmers in the traps increases the POC/^{234}Th ratios due to higher carbon content (Buesseler et al., 2006), while swimmers may avoid *in situ* pumps (Liu et al., 2005). Alternatively, swimmers may contribute to carbon remineralization within the trap prior to recovery. Swimmers were not observed in trap samples during the spring, but were observed prior to removal at all stations during the summer. Although swimmers were removed from the sediment trap samples upon recovery, their presence in the traps during deployment may still contribute to the discrepancy in POC/^{234}Th ratios observed between traps and pumps.

Differences in POC export fluxes measured with *in situ* pumps and traps may also be due to differences in the time-scale of the measurement techniques. ^{234}Th/^{238}U disequilibrium provides a temporally-integrated measurement of particle export over several days to weeks, while sediment traps collect sinking particles over a short, fixed period of time (11 to 20 hours in this study) that is less than the integrated time-scale recorded by ^{234}Th (Buesseler et al., 2006). It is therefore possible that the discrepancies observed between POC fluxes measured with both methods along the BC transect in spring may at least be partly due to the underestimation of the ^{234}Th-derived POC fluxes associated with the onset of the spring bloom. However, short sediment trap deployments provided a limited spatial and temporal coverage of the POC fluxes, which vary on a time-scale of days.

Discrepancies between the ^{234}Th- and sediment trap-derived POC fluxes may be due to natural variability in carbon export, rather than uncertainty in the POC flux measurement.

Discrepancies between *in situ* pump and sediment trap POC fluxes were greater at higher POC/^{234}Th ratios (Fig. 16b), as previously observed in the North Water polynya (Amiel et al., 2002). The estimated POC fluxes from both methods were more highly correlated at low carbon fluxes than at higher carbon fluxes, indicating an increased dissimilarity between both methods during periods of high primary productivity. The high primary productivity measured at station BC4 during spring (V. Hill, personal communication) is consistent with the significant difference between POC fluxes determined from *in situ* pumps and sediment traps at BC4 during the spring.

Ideally, the POC/^{234}Th ratios are representative of the sinking particle flux (Moran et al., 2003). Large-volume sampling by *in situ* pumps using 53 μm screens is intended to collect the larger, rarer, sinking material for determination of the POC/^{234}Th ratios (Bishop et al., 1978; Fowler and Knauer, 1986; Buesseler et al., 2006), because it is assumed that large particles (>53 μm) contribute to the majority of the sinking flux (Lal, 1977; Lal, 1980; Mccave, 1975; Mccave, 1984). It is however uncertain whether the POC/^{234}Th ratios obtained by large-volume filtration represent an accurate sampling of sinking particles because *in situ* pumps may also collect suspended matter that do not contribute substantially to the export flux. On the other hand, particles with very slow sinking speeds may be undercollected by cylindrical traps due to hydrodynamic discrimination (Gust and Kozerski, 2000; Gustafsson et al., 2004). However, the

deployment of a drifting array minimizes the flow past traps (Gardner, 2000), so there may be no significant decrease in trap efficiency even though high currents speeds (30-50 cm s^{-1}) were previously recorded in the Chukchi Sea (Weingartner et al., 2005). These processes are clearly potential sources of variation between POC/^{234}Th ratios measured with pumps and traps. For example, in the Barents Sea, POC/^{234}Th ratios measured on suspended particles were higher than trapped POC/^{234}Th ratios by a factor of 10 (52.0 ± 9.9 and 5.3 ± 2.2 μmol C dpm^{-1}, respectively); POC fluxes calculated using the high POC/^{234}Th ratios measured on suspended particles would therefore have been overestimated (Coppola et al., 2002).

Recent export fluxes obtained from sediment trap deployments in the Barents Sea indicated that the vertical flux of carbon associated with pico- (<2 μm), nano- (2-20 μm) and microplankton (>20 μm) contributed approximately half of the POC flux in the marginal ice zone (Olli et al., 2002). Also, the settling phytoplankton in the Barents Sea collected from sediment traps were dominated by a single-celled form of *Phaeocystis pouchetii* (5 μm) and flagellates (6-10 μm) (Olli et al., 2002). During the same study, carbon from flagellates was correlated with the scavenging rate of ^{234}Th, suggesting that small phytoplankton cells played a key role in ^{234}Th scavenging (Coppola et al., 2002), which could therefore affect POC/^{234}Th ratios. In addition, the dominant fraction of the particle flux collected in sediment traps on the Canadian Beaufort shelf was in the <63 μm size fraction, indicating the significant contribution of smaller particles to the POC flux, especially during periods of high flux (O'Brien et al., 2006).

Small particles (<53 μm) that contribute to the sinking flux of carbon may be missed by *in situ* pump filtration, but this will only result in an erroneous POC flux if the POC/^{234}Th ratio on these small particles is different than the ratio on large (>53 μm) particles. Previous studies reported that POC/^{234}Th ratios may decrease, remain constant, or increase with increasing particle size (e.g. Bacon et al., 1996; Buesseler et al., 2001; Moran et al., 2003), but thus far little difference in POC/^{234}Th ratios between large particles (>53 μm, >70 μm) collected with *in situ* pumps and sediment traps has been reported (Buesseler et al., 2006). In this study, variability in POC/^{234}Th ratios measured at 50 m was greater with sediment trap samples than with particles collected using *in situ* pumps (Fig. 19). POC/^{234}Th ratios measured on size-fractionated particles using *in situ* pumps during spring and summer 2004 in the Chukchi Sea were similar to within a factor of 2 on 20-53 μm, 53-100 μm, and >100 μm size particles (Fig. 19) (Lepore et al, submitted). Because sediment trap POC measurements were made on sinking particles larger than 0.7 μm, trap-derived POC/^{234}Th ratios represent an integration of the POC/^{234}Th ratios throughout the size spectrum of sinking particles. The greater range of POC/^{234}Th ratios in traps may then be due to higher sinking particle diversity collected by the sediment traps. However, no systematic offset was observed between POC/^{234}Th ratios on particles collected using *in situ* pumps or sediment traps. This suggests that particles collected with both methods had a similar size range, which may be due to the possible undercollection of small, slow-sinking particles by sediment traps (Gustafsson et al., 2006; Passow et al., 2006).

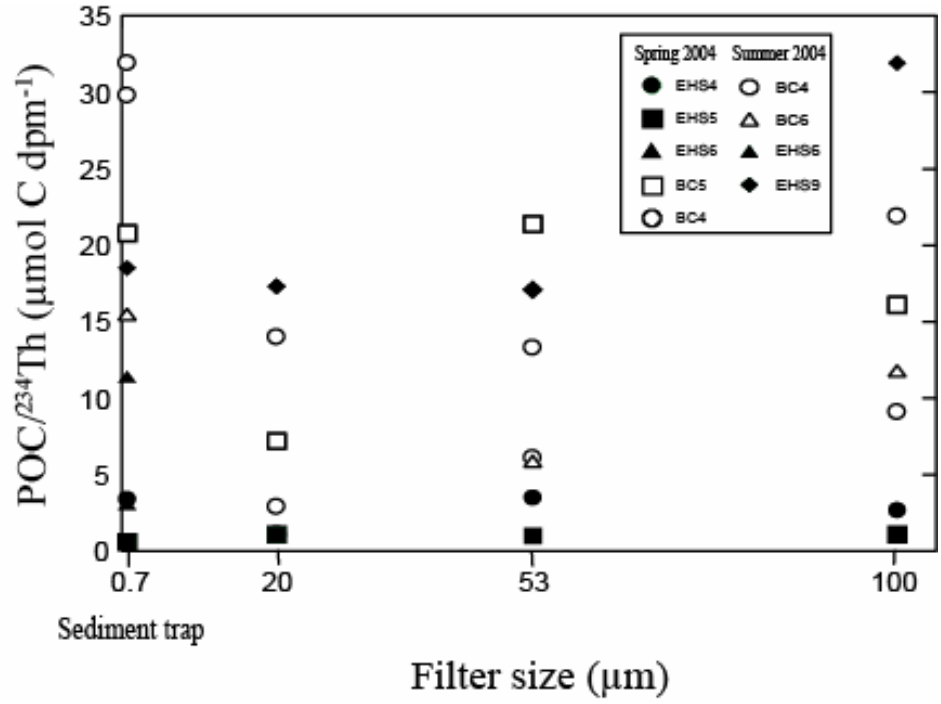

Figure 19. Plot of POC/^{234}Th ratio versus filter pore size for samples collected at 50 m in the Chukchi Sea. The 0.7 µm size fraction is the GF/F filter from the sediment traps

2.4.2 Comparison with other Arctic studies

Previous studies in the Arctic Ocean also suggested a good agreement between ^{234}Th-derived and trap-derived POC and ^{234}Th fluxes (Fig. 20). In the North Water polynya, the POC fluxes determined from ^{234}Th/^{238}U disequilibria and POC/^{234}Th ratios on large particles agreed to within a factor of 2 to 5 with sediment trap-derived POC export fluxes in the upper 100 m of the water column (Amiel et al., 2002). In the Barents Sea, model-derived ^{234}Th fluxes were similar to within a factor of 2 to ^{234}Th fluxes measured with sediment traps in the upper 200 m (Coppola et al., 2002). The collection efficiency of both methods does not seem to be affected by ice conditions, as the export fluxes were well constrained in the presence or the absence of ice cover in these Arctic studies.

In contrast, Buesseler (1991) concluded that shallow traps may not provide an accurate measure of particle flux based on observations from a variety of open ocean, coastal and semi-enclosed basin settings in which trap-derived and model-derived ^{234}Th fluxes differed by a factor of 3 to 10. Even though some of the regions sampled in the Arctic Ocean were characterized by relatively high current velocities, the agreement between methods is reasonably good compared with observations made in other oceanic regions.

2.5 Conclusions

In situ pump- and sediment trap-derived POC fluxes agreed to within a factor of 2 at the majority of stations sampled in spring and summer 2004 in the Chukchi Sea, with

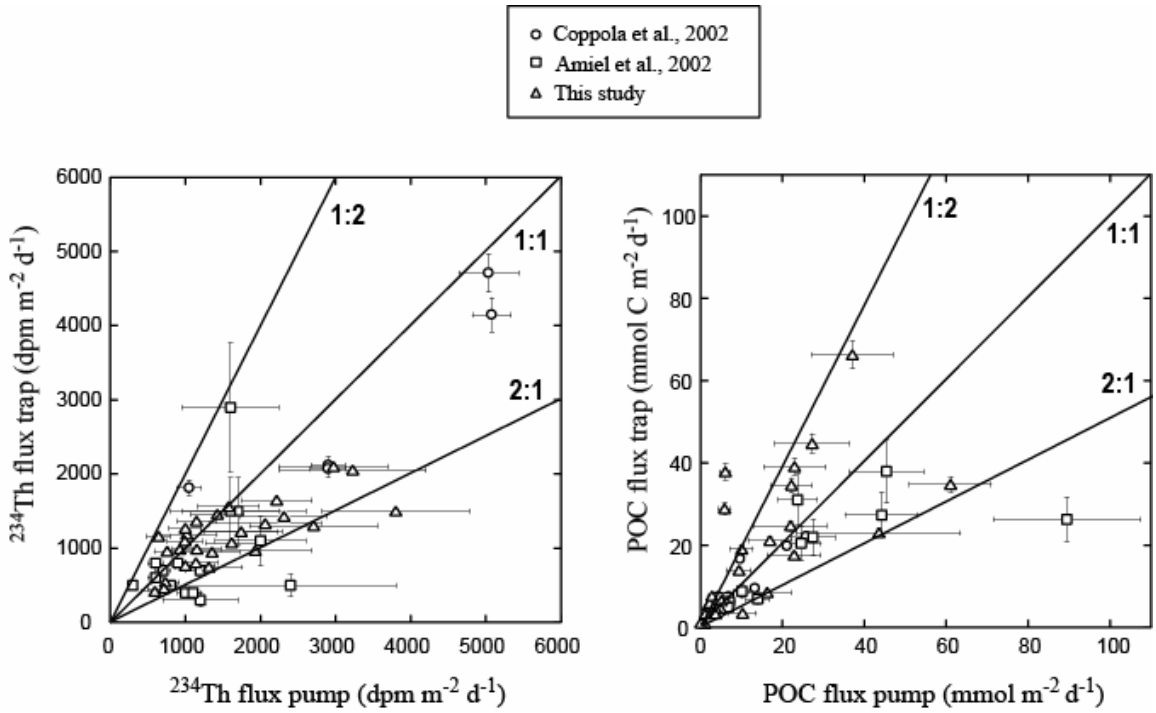

Figure 20. Comparison of ^{234}Th and POC fluxes determined from ^{234}Th/^{238}U disequilibria and sediment traps in the Barents Sea (Coppola et al., 2002), the North Water polynya (Amiel et al., 2002) and the Chukchi Sea (this study). Diagonal lines correspond to 1:1, 1:2 and 2:1 relations

significant differences between POC fluxes observed only at a highly productive station in Barrow Canyon during spring. Despite the reasonable agreement between both methods, discrepancies may be associated with the variability of the estimated pump and trap POC/^{234}Th ratios. This variability may be due to elevated primary production rates, presence of swimmers in traps during deployments, and/or to different time-scale measurement of each technique. The different properties (sinking versus suspended) and sizes of the particles collected with *in situ* pumps or sediment traps may also explain the discrepancies in POC/^{234}Th ratios. Overall, the ^{234}Th technique has the advantage of allowing greater spatial coverage than sediment traps, however, POC/^{234}Th ratios obtained with *in situ* pumps might not be as representative of the POC/^{234}Th ratios in sinking particles as POC/^{234}Th ratios obtained with sediment traps, although this did not appear to be the case in this study.

Chapter 3

Particulate organic carbon export derived from ^{234}Th and comparison with drifting sediment traps fluxes in the Barents Sea

This chapter is a paper that will soon be submitted for publication by C. Lalande, S.B. Moran, P. Wassmann, J.M. Grebmeier and L.W. Cooper. My contributions to this paper include the large-volume sampling of ^{234}Th, preparation of the samples for beta and gamma counting, interpretation of data and preparation of the manuscript.

3.1 Introduction

The estimation of particulate organic carbon (POC) export fluxes in the Barents Sea is essential to evaluate the impact that climate change may have on export production over this highly productive continental shelf. In past decades, export fluxes of biogenic matter in the Barents Sea have been measured with drifting sediment traps, except in one instance where ^{234}Th was used to estimate POC fluxes and to calibrate drifting sediment traps (i.e. Coppola et al., 2002). There are some common biases associated with sediment traps that may affect collection efficiency, including the consumption of the trapped material by zooplankton during deployment, the solubilization of particulate matter to dissolved matter in the trap, and hydrodynamic effects possibly leading to the undercollection of sinking particles (Gust and Kozerski, 2000; Gardner, 2000; Gustafsson et al., 2004). Because of the uncertainties associated with sediment trap deployments, it is strongly recommended that the ^{234}Th deficit be measured in conjunction with short-term sediment trap deployments (Gardner, 2000). ^{234}Th ($t_{1/2}$=24.1 days) is a naturally occurring particle-reactive radionuclide produced continuously in the ocean by alpha

decay of ^{238}U. Because of its particle-reactive property and its short half-life, ^{234}Th is a useful tracer of scavenging and POC export occurring on a time-scale of days to months (Coale and Bruland, 1985; Coale and Bruland, 1987), and it is increasingly used for trap calibration studies in the upper ocean (e.g. Buesseler et al., 2006). Previous measurements in the Arctic Ocean indicated reasonably good agreement between ^{234}Th-derived and trap-derived POC fluxes in the North Water polynya (Amiel et al., 2002), the Barents Sea (Coppola et al., 2002) and the Chukchi Sea (Lalande et al., accepted). The objectives of this study were to estimate the POC export fluxes using ^{234}Th in the MIZ of the Barents Sea, and to compare these fluxes with direct POC export obtained from deployments of drifting sediment traps as part of the project CABANERA (*Carbon flux and ecosystem feedback in the northern Barents Sea in an era of climate change*).

3.1.1 Study area

The Barents Sea continental shelf sea is divided into northern and southern regions by the Polar Front. South of the Polar Front, the Barents Sea is permanently ice-free, with warm Atlantic surface waters (s>34.9; t=3-6ºC), while the region north of the Polar Front is characterized by seasonally ice-covered Arctic waters (s=34.3-34.8; t<0ºC) with maximum ice extent in March and minimum ice extent in September (Sakshaug, 1997; Serreze et al., 2000). The strong stratification that develops north of the Polar Front as ice melts and light becomes available establishes a 30-50 km wide highly productive phytoplankton bloom area that trails the receding ice edge. Primary production in the southern part of the Barents Sea is initiated by a weak stratification developing slowly

from solar radiation during the course of the summer (Reigstad et al., 2002; Sakshaug, 1997). Phytoplankton biomass and productivity in the Barents Sea is thus strongly related to ice cover and the relative distribution of Atlantic and Arctic waters.

In the Barents Sea, the inflow of warm Atlantic water significantly affects the extent of ice cover; reduced ice cover is observed for years with large Atlantic inflow (Sakshaug, 1997). The inflow of Atlantic water into the Barents Sea is likely to dramatically change as a result of global warming, possibly leading to an increase of the northward transport of Atlantic water into the Nordic Seas (Orvik et al., 2001). This "atlantification" of the Barents Sea implies that the current marginal ice zone (MIZ) will move northwards and that stratification will decrease in the region which is currently the MIZ region, and consequently function like most of the Atlantic water does at present (Wassmann et al., 2004). New production, i.e. the fraction of total primary production supported by supply of new nutrients (Dugdale and Goering, 1967), is more than twice as high in the southern Atlantic region of the Barents Sea (90 g C m^{-2} yr^{-1}) than north of the Polar Front (<40 g C m^{-2} yr^{-1}; Sakshaug, 1997). Hence, primary production in the Barents Sea is higher in years when the Atlantic water inflow is larger and the ice edge is located further to the north (Falk-Petersen et al., 2000). Moreover, model simulations in the Barents Sea indicate that primary production is 42-49 % greater during warm years than during cold years (Wassmann et al., 2006). The total primary production is therefore expected to increase in the Barents Sea in response to increases in Atlantic water inflow (Sakshaug, 2004; Wassmann et al., 2004).

New production is assumed to be equivalent to the organic matter that potentially can be exported out of the euphotic zone (Eppley and Peterson, 1979). Therefore, export production is expected to be higher in Atlantic than in Arctic water due to higher new production. Higher inflow of Atlantic water to the Barents Sea, as a result of global warming, may increase the rate of export production in the Barents Sea area. In this case, the Barents Sea may act as a seasonal carbon sink due to an increase in biological uptake of carbon in the surface layer. The estimation of POC fluxes in the MIZ of the Barents Sea is therefore important due to the potentially significant change in annual export production occurring in this region.

3.2. Material and Methods

3.2.1 Sampling

Sampling was conducted in the northern Barents Sea aboard *RV Jan Mayen* during a summer cruise from July 8-22, 2003 (Stations I, II, III, IV) and a spring cruise from May 18-June 5, 2005 (stations XIV, XVI, XVII, XVIII) (Fig. 21, Table 4). Large-volume samples (~500 L) were collected using a submersible sump pump lowered over the side of the ship at 10 and 20 m and from multiple CTD rosette casts (~280 L) at depths of 60, 90 and 120 m. A peristaltic pump (Cole-Parmer Instrument Co.) was used to empty the rosette. Seawater was pumped through two MnO_2-impregnated adsorbtion cartridges at every depth to scavenge dissolved ^{234}Th from seawater (Moran et al., 1997; Charette et al., 1999). At the depths of 20, 60 and 120 m, a 53 μm pore size (142 mm diameter)

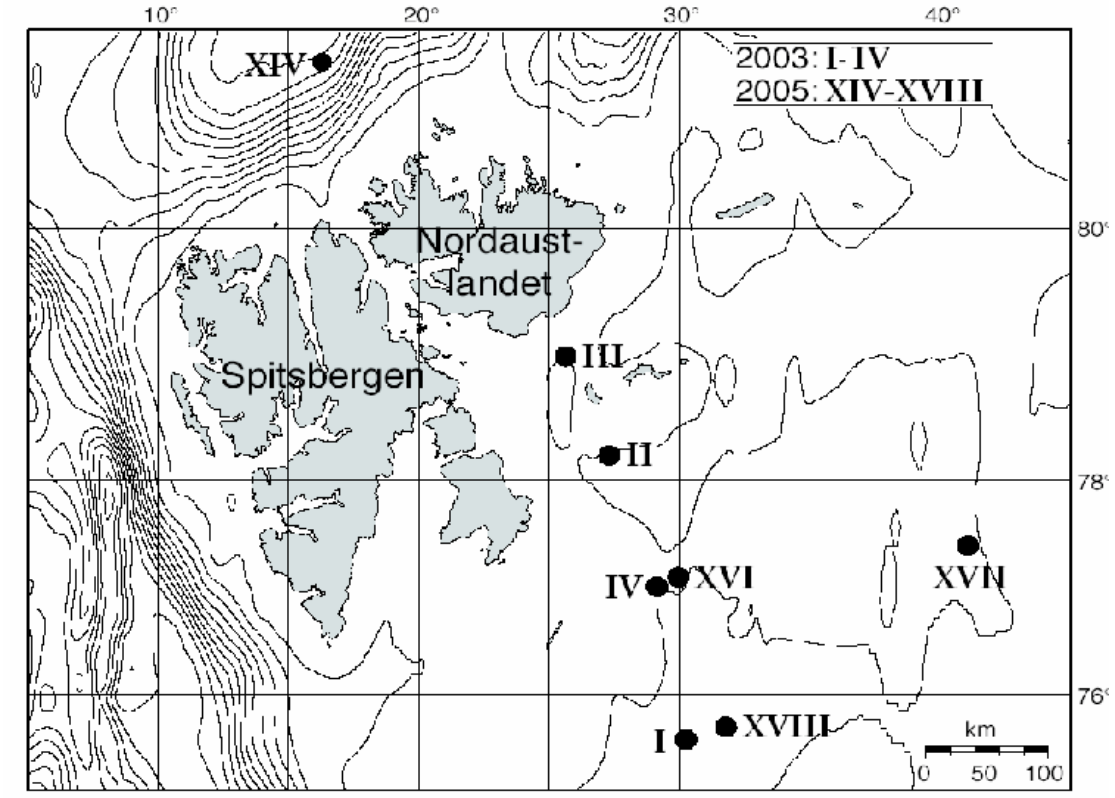

Figure 21. Study area and stations sampled in the northern Barents Sea in July 2003 and May 2005

Table 4. Sediment trap deployment and large-volume sampling stations, times, locations, water column and ice conditions

Station	Date	Location	Latitude ºN	Longitude ºE	Water depth (m)	Euphotic zone (m)	Chl-*a* max (m)	Ice concentrations (%)	Bloom conditions
I	July 10 2003	Hopen trench	75° 32.1	30° 16.6	361	50	37	40-70	late bloom
II	July 13 2003	South Kong Karlsland	78° 13.9	27° 19.2	317	40	24	40-70	bloom
III	July 15 2003	East Erik Eriksen stredet	79° 02.6	25° 41.5	212	50	28	50-70	bloom
IV	July 18 2003	Hopen Bank	77° 03.2	29° 09.7	229	20	10	40-70	early bloom
XIV	May 20 2005	Questrenna	81° 07.6	16° 19.0	2052	10	10	40-50	bloom
XVI	May 25 2005	North Hopen trench	77° 08.4	29° 56.7	203	10	20	80-90	late bloom
XVII	May 28 2005	East Storbanken	77° 25.7	41° 02.8	226	30	10	60-70	early bloom
XVIII	May 31 2005	Hopen trench	75° 40.5	31° 47.8	343	30	10	open water	bloom

Nitex screen was connected in series with the MnO_2-impregnated cartridges to collect POC and the particulate fraction of ^{234}Th. The MnO_2 cartridges were stored for subsequent measurements of dissolved ^{234}Th. Particles collected on the Nitex screens were resuspended into GF/F filtered seawater (~200 ml) by ultrasonication (10 min) and filtered onto precombusted GF/F filters (Buesseler et al., 1995; Charette and Moran, 1999; Charette et al., 1999). The GF/F filters were dried for 24 h at 60°C prior to particulate ^{234}Th and POC analysis. Blank filters exposed to 200 ml of GF/F filtered seawater were taken in 2005 to account for DOC adsorption onto filters (Moran et al., 1999; Gardner et al., 2003).

A drifting array of sediment traps was anchored on an ice flow or deployed in open water for 24 h at each station. The traps consisted of two parallel cylinders (diameter: 7.2 cm; height: 45 cm; height/diameter ratio: 6.25) mounted in a gimballed frame equipped with a vane to ensure that the traps remain vertical in the water (KC Denmark, Silkeborg, Denmark). No baffles were used in the tube openings and no poison was applied in the traps. Water samples for particulate ^{234}Th and POC analysis from the traps (~2 L) were obtained at 20, 60 and 120 m at each station, filtered onto precombusted GF/F filters that were then dried for 24 h at 60°C and stored for later analysis.

3.2.2 ^{234}Th and POC analysis

MnO_2 cartridges were dried at 60ºC for 24 h and ashed overnight at 500ºC. Dissolved ^{234}Th activities were counted by gamma spectrometry on the cartridges ashes using a

Canberra pure-Ge planar detector (Graduate School of Oceanography, University of Rhode Island). Particulate ^{234}Th activities (>53 μm) were determined on the GF/F filters by beta spectrometry using a RISØ National Laboratory low-background beta detector (Graduate School of Oceanography, University of Rhode Island). GF/F filters were mounted on an acrylic planchet and covered with clear plastic and Al foil to shield alpha particles and low-level beta emitters. ^{238}U activities were calculated from salinity according to the relationship ^{238}U (dpm L^{-1}) = salinity x 0.0708 (Chen et al., 1986).

Subsamples of known weight from the GF/F filters were placed for 24 h in a dessicator with fumes of concentrated HCl to remove inorganic carbon and dried for 24 h at 60ºC for subsequent POC measurements using an Exeter Analytical CE-440 elemental analyzer (MSI Analytical Laboratory, University of California, Santa Barbara and Graduate School of Oceanography, University of Rhode Island). POC fluxes were corrected using the average blank value of 4.8 ± 1.4 μmol C.

3.3 Results

3.3.1 Hydrography and primary production

Stations occupied during July 2003 and May 2005 were located in the MIZ and characterized by 40 to 90% ice cover, except for station XVIII that was located in Atlantic water and was not ice-covered during the 2004-2005 winter (Table 4). Stations sampled in July 2003 exhibited strong stratification due to ice melt, and nutrient concentrations at each station reflected the phytoplankton bloom stage (Sturluson et al.,

accepted; H. Hodal and C. Kivimäe, personal communication). Station I was nutrient depleted in the surface layer and a deep chlorophyll maximum, indicating a late stage bloom, while stations II, III and IV had well-developed blooms. Low primary production rates at station III suggested that the bloom was declining, whereas at station IV the bloom was in an earlier stage as nutrients still remained in the surface layer. In May 2005, stations XIV and XVI were influenced by Atlantic water (Sundfjord et al., submitted) and had a weak thermal stratification with lower nutrient concentrations in the upper water column. Stations XVII and XVIII had mixed water columns with high surface nutrient concentrations and early bloom stages.

3.3.2 Large-volume ^{234}Th activities, ^{234}Th fluxes, POC/^{234}Th ratios and POC fluxes

^{234}Th/^{238}U disequilibrium was evident in the upper 120 m at every station and the disequilibria were larger in 2005 (Fig. 22). The ^{234}Th deficit was similar at all stations in 2003, while more variation was observed among stations in 2005. The particulate fraction did not contribute significantly to the total ^{234}Th activities in 2003, with >99% of the ^{234}Th activities measured in the dissolved fraction (Table 5). Particulate ^{234}Th activities were higher in 2005, contributing up to 15% of total ^{234}Th activities (Table 5). The ^{234}Th activity measured at station III at a depth of 20 m was much higher than the activity of its parent ^{238}U; this result was therefore excluded from interpretation (Table 5).

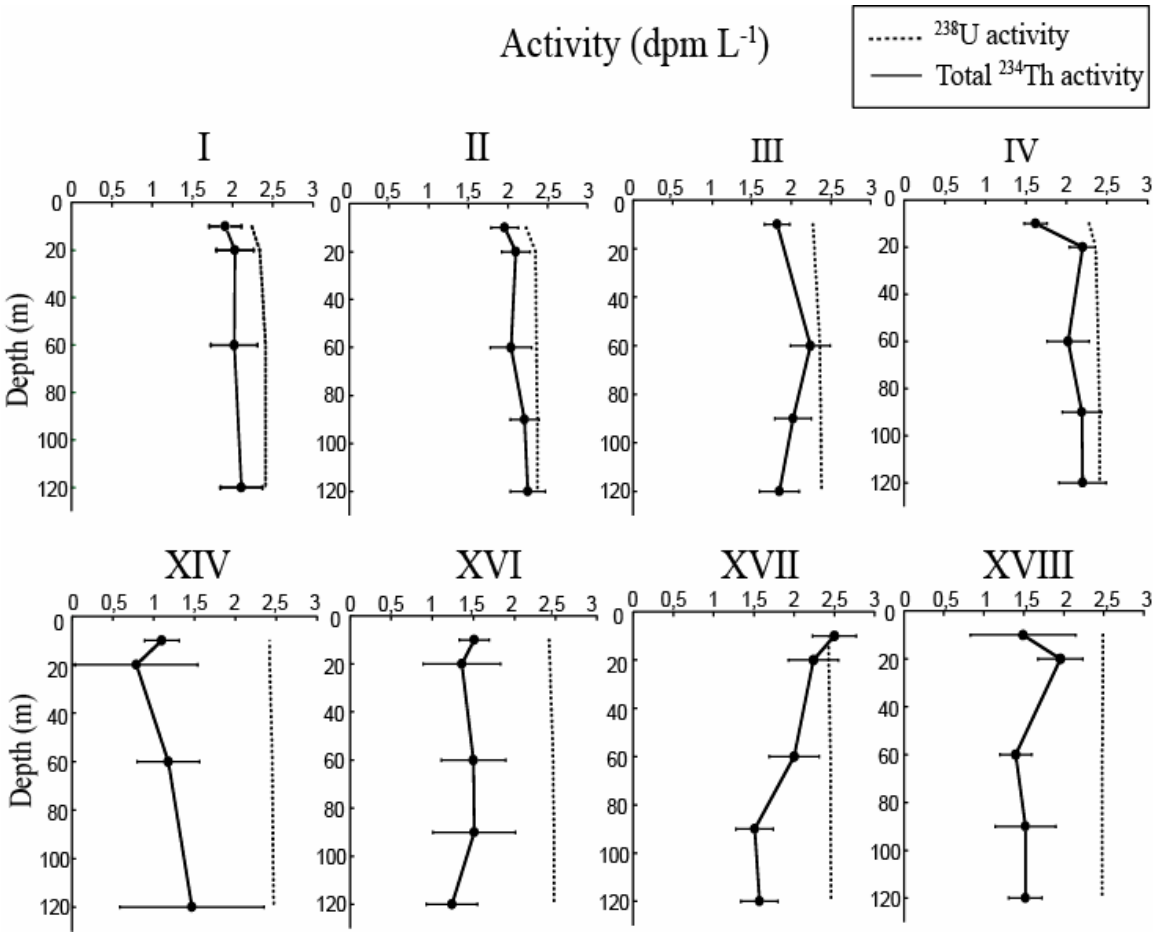

Figure 22. Activity profiles of ^{234}Th measured in the northern Barents Sea in July 2003 (I, II, III, IV) and May 2005 (XIV, XVI, XVII, XVIII)

Table 5. Salinity, ^{234}Th and ^{238}U activities in the northern Barents Sea in 2003 and 2005

Station	Depth m	Salinity psu	Dissolved ^{234}Th dpm L^{-1}	Particulate ^{234}Th (>53 μm) dpm L^{-1}	Total ^{234}Th dpm L^{-1}	^{238}U dpm L^{-1}	$^{234}Th/^{238}U$
July 2003							
Station I							
(75º33 N, 30º13 E, 355m)	10	32.53	1.91 ± 0.20		1.91 ± 0.20	2.30	0.83
	20	33.92	2.03 ± 0.20	0.0017 ± 0.0001	2.03 ± 0.23	2.40	0.85
	60	34.89	2.01 ± 0.27	0.0158 ± 0.0008	2.02 ± 0.29	2.47	0.82
	120	34.98	2.11 ± 0.23	0.0061 ± 0.0003	2.11 ± 0.26	2.48	0.85
Station II							
(78º13 N, 27º18 E, 313m)	10	32.38	1.96 ± 0.17		1.96 ± 0.17	2.29	0.85
	20	34.10	2.07 ± 0.14	0.0172 ± 0.0009	2.09 ± 0.18	2.41	0.87
	60	34.23	2.03 ± 0.24	0.0105 ± 0.0005	2.04 ± 0.26	2.42	0.84
	90	34.29	2.21 ± 0.18		2.21 ± 0.18	2.43	0.91
	120	34.38	2.23 ± 0.19	0.0148 ± 0.0007	2.25 ± 0.22	2.43	0.92
Station III							
(79º02 N, 25º38 E, 206m)	10	32.87	1.82 ± 0.16		1.82 ± 0.16	2.33	0.78
	20*	33.93	5.93 ± 0.45	0.0148 ± 0.0007	5.94 ± 0.54	2.40	2.47
	60	34.21	2.23 ± 0.23	0.0162 ± 0.0008	2.24 ± 0.25	2.42	0.92
	90	34.38	2.02 ± 0.23		2.02 ± 0.23	2.43	0.83
	120	34.49	1.84 ± 0.23	0.0075 ± 0.0004	1.85 ± 0.25	2.44	0.76
Station IV							
(77º03 N, 29º09 E, 224m)	10	33.03	1.62 ± 0.14		1.62 ± 0.14	2.34	0.69
	20	34.13	2.19 ± 0.12	0.0106 ± 0.0005	2.20 ± 0.16	2.42	0.91
	60	34.62	2.01 ± 0.24	0.0074 ± 0.0004	2.02 ± 0.26	2.45	0.82
	90	34.90	2.19 ± 0.24		2.19 ± 0.24	2.47	0.89
	120	34.96	2.19 ± 0.27	0.0081 ± 0.0004	2.20 ± 0.29	2.48	0.89

Table 5. continued

Station	Depth m	Salinity psu	Dissolved ^{234}Th dpm L^{-1}	Particulate ^{234}Th (>53 μm) dpm L^{-1}	Total ^{234}Th dpm L^{-1}	^{238}U dpm L^{-1}	^{234}Th/^{238}U
May 2005							
Station XIV							
(81º07 N, 16º19 E, 2052m)	10	34.22	1.10 ± 0.21		1.10 ± 0.21	2.42	0.45
	20	34.25	0.71 ± 0.75	0.0825 ± 0.0041	0.79 ± 0.75	2.42	0.33
	60	34.66	1.06 ± 0.38	0.1254 ± 0.0063	1.18 ± 0.38	2.45	0.48
	120	34.82	1.46 ± 0.88	0.0169 ± 0.0008	1.47 ± 0.88	2.47	0.60
Station XVI							
(77º08 N, 29º56 E, 203m)	10	34.17	1.51 ± 0.18		1.51 ± 0.18	2.42	0.63
	20	34.26	1.32 ± 0.47	0.0439 ± 0.0022	1.36 ± 0.47	2.43	0.56
	60	34.83	1.48 ± 0.39	0.0264 ± 0.0013	1.50 ± 0.39	2.47	0.61
	90	34.97	1.51 ± 0.50		1.51 ± 0.50	2.48	0.61
	120	34.99	1.23 ± 0.31	0.0104 ± 0.0005	1.24 ± 0.31	2.48	0.50
Station XVII							
(77º25 N, 41º02 E, 226m)	10	34.33	2.50 ± 0.27		2.50 ± 0.27	2.43	1.03
	20	34.34	2.23 ± 0.31	0.0137 ± 0.0007	2.24 ± 0.31	2.43	0.92
	60	34.62	1.99 ± 0.31	0.0045 ± 0.0002	2.00 ± 0.31	2.45	0.81
	90	34.66	1.51 ± 0.23		1.51 ± 0.23	2.45	0.61
	120	34.70	1.57 ± 0.23	0.0044 ± 0.0002	1.57 ± 0.23	2.46	0.64
Station XVIII							
(75º40 N, 31º47 E, 343m)	10	35.10	1.49 ± 0.66		1.49 ± 0.66	2.49	0.60
	20	35.10	1.81 ± 0.28	0.1517 ± 0.0076	1.96 ± 0.28	2.49	0.79
	60	35.10	1.20 ± 0.20	0.2024 ± 0.0101	1.40 ± 0.20	2.48	0.56
	90	35.10	1.52 ± 0.38		1.52 ± 0.38	2.48	0.61
	120	35.10	1.50 ± 0.21	0.0217 ± 0.0011	1.52 ± 0.21	2.48	0.61

* Station III - 20 m was excluded from interpretation

90 m depth was not sampled for dissolved ^{234}Th at station I and XIV

^{234}Th fluxes obtained from large-volume filtration in 2003 ranged from 410 to 495 and from 739 to 1092 dpm m^{-2} d^{-1} at 60 and 120 m, respectively (Fig. 23; Table 6). The ^{234}Th fluxes were higher and more variable in 2005 than in 2003, with values ranging from 386 to 2095 and from 1777 to 4057 dpm m^{-2} d^{-1} at 60 and 120 m, respectively (Fig. 23). ^{234}Th-derived POC fluxes obtained in 2003 ranged from 13.8 to 62.1 and from 8.2 to 125.4 mmol C m^{-2} d^{-1} at 60 and 120 m respectively, with the highest POC export occurring at station IV (Fig. 23). In 2005, POC fluxes ranged from 13.0 to 39.9 and from 40.6 to 110.1 mmol C m^{-2} d^{-1} at 60 and 120 m respectively, and POC fluxes were higher at 60 m than at 120 m at station II (Fig. 23). POC/^{234}Th ratios were much higher in 2003 than in 2005, with values ranging from 11.2 to 641.8 and from 11.4 to 47.8 μmol dpm^{-1} in 2003 and 2005, respectively (Fig. 24). Overall, ^{234}Th fluxes measured at 60 m increased from 435 ± 30 to 1272 ± 506 dpm m^{-2} d^{-1} from 2003 to 2005, while ^{234}Th fluxes measured at 120 m increased from 922 ± 121 to 2986 ± 669 dpm m^{-2} d^{-1} from 2003 to 2005 (Fig. 23). ^{234}Th-derived POC fluxes were similar for both years at 60 m with fluxes of 30.5 ± 16.0 and 26.8 ± 11.0 mmol C m^{-2} d^{-1} in 2003 and 2005 respectively, while the POC fluxes decreased from 2003 to 2005 when measured at 120 m, with fluxes of 120.6 ± 39.6 and 67.4 ± 21.4 mmol C m^{-2} d^{-1} in 2003 and 2005, respectively (Fig. 23).

3.3.3 Drifting sediment traps ^{234}Th fluxes, POC/^{234}Th ratios and POC fluxes

^{234}Th fluxes measured from the sediment traps in 2003 ranged from 547 to 1946 and from 847 to 1581 dpm m^{-2} d^{-1} at 60 and 120 m, respectively (Fig. 25; Table 6). In 2005, ^{234}Th fluxes ranged from 900 to 3444 and from 1174 to 4537 dpm m^{-2} d^{-1} at 60 and 120 m

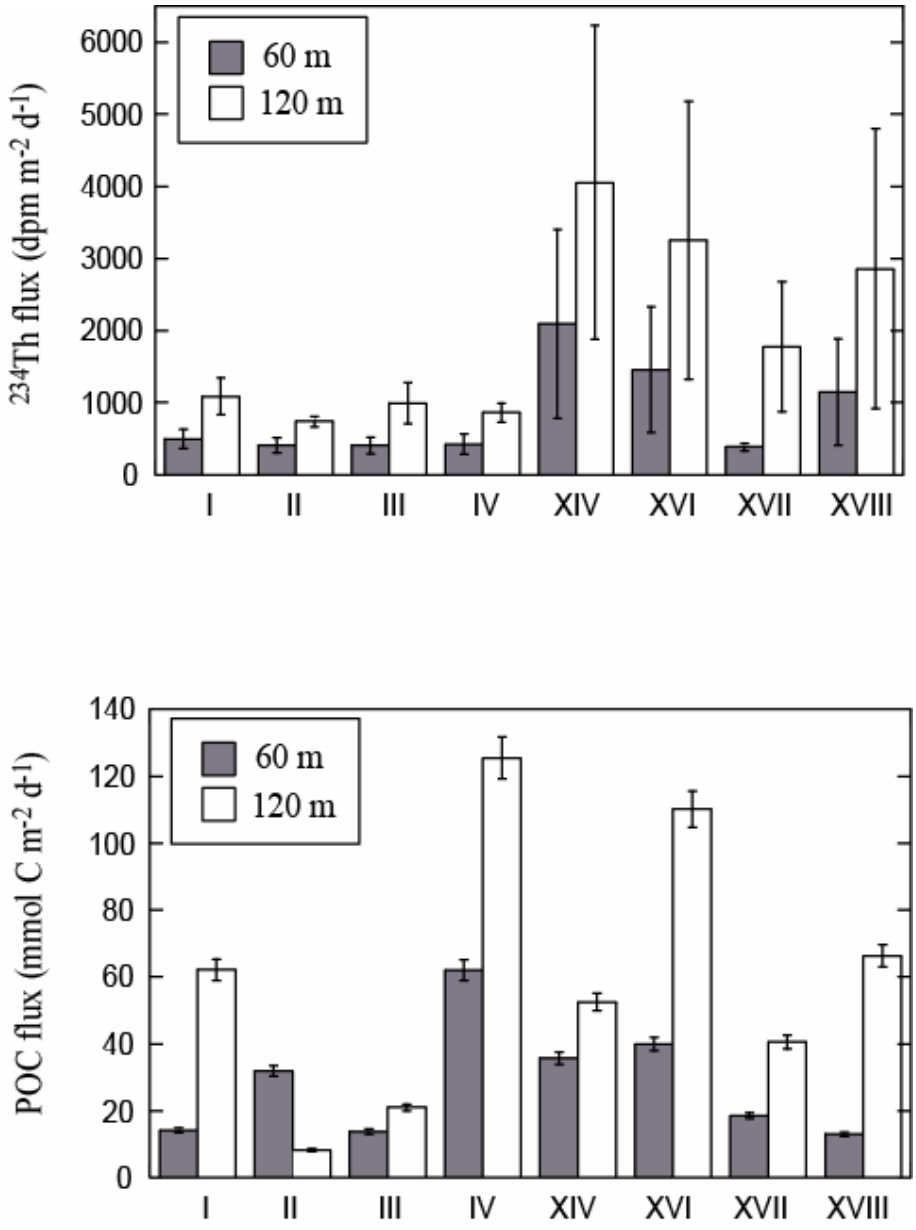

Figure 23. Large-volume ^{234}Th fluxes and ^{234}Th-derived POC fluxes; error bars indicate ± standard deviations

Table 6. Large-volume and sediment trap ^{234}Th fluxes, POC fluxes and POC/^{234}Th ratios in the northern Barents Sea in 2003 and 2005

Station	Depth	^{234}Th flux - pump	POC flux - pump	POC/^{234}Th ratio - pump	^{234}Th flux - traps	POC flux - traps	POC/^{234}Th ratio - traps
	m	dpm m^{-2} d^{-1}	mmol C m^{-2} d^{-1}	µmol C dpm^{-1}	dpm m^{-2} d^{-1}	mmol C m^{-2} d^{-1}	µmol C dpm^{-1}
I	0-60	495 ± 133	14.2 ± 0.7	28.6 ± 1.6	547 ± 37	5.6 ± 0.3	10.3 ± 0.2
	0-120	1092 ± 254	62.1 ± 3.1	56.9 ± 7.9	920 ± 34	5.6 ± 0.3	6.1 ± 1.0
II	0-60	410 ± 107	31.9 ± 1.6	77.7 ± 5.9	1946 ± 42	27.1 ± 1.4	13.9 ± 0.9
	0-120	739 ± 72	8.2 ± 0.4	11.2 ± 0.6	1581 ± 41	20.6 ± 1.0	13.0 ± 3.1
III	0-60	410 ± 115	13.8 ± 0.7	33.6 ± 1.6	1331 ± 44	19.4 ± 1.0	14.6 ± 11.6
	0-120	994 ± 284	21.0 ± 1.1	21.1 ± 2.4	1398 ± 45	11.6 ± 0.6	8.3 ± 5.7
IV	0-60	423 ± 138	62.1 ± 3.1	146.6 ± 17.4	783 ± 50	8.1 ± 0.4	10.3 ± 0.1
	0-120	864 ± 134	125.4 ± 6.3	145.1 ± 15.8	847 ± 46	7.2 ± 0.4	8.5 ± 0.9
XIV	0-60	2095 ± 1306	35.7 ± 1.8	17.0 ± 0.7	1056 ± 50	16.8 ± 0.8	15.9 ± 1.1
	0-120	4057 ± 2179	52.5 ± 2.6	12.9 ± 0.2	1174 ± 41	9.9 ± 0.5	8.4 ± 0.4
XVI	0-60	1460 ± 871	39.9 ± 2.0	27.3 ± 0.3	900 ± 47	12.2 ± 0.6	13.5 ± 1.2
	0-120	3253 ± 1930	110.1 ± 5.5	33.9 ± 0.3	2325 ± 71	17.7 ± 0.9	7.6 ± 0.3
XVII	0-60	386 ± 55	18.5 ± 0.9	47.8 ± 0.5	1377 ± 37	5.9 ± 0.3	4.3 ± 0.1
	0-120	1777 ± 904	40.6 ± 2.0	22.9 ± 0.3	1316 ± 39	7.7 ± 0.4	5.8 ± 0.2
XVIII	0-60	1148 ± 736	13.0 ± 0.7	11.4 ± 0.7	3444 ± 33	38.0 ± 1.9	11.0 ± 0.1
	0-120	2858 ± 1941	66.3 ± 3.3	23.2 ± 0.5	4537 ± 28	30.4 ± 1.5	6.7 ± 0.1

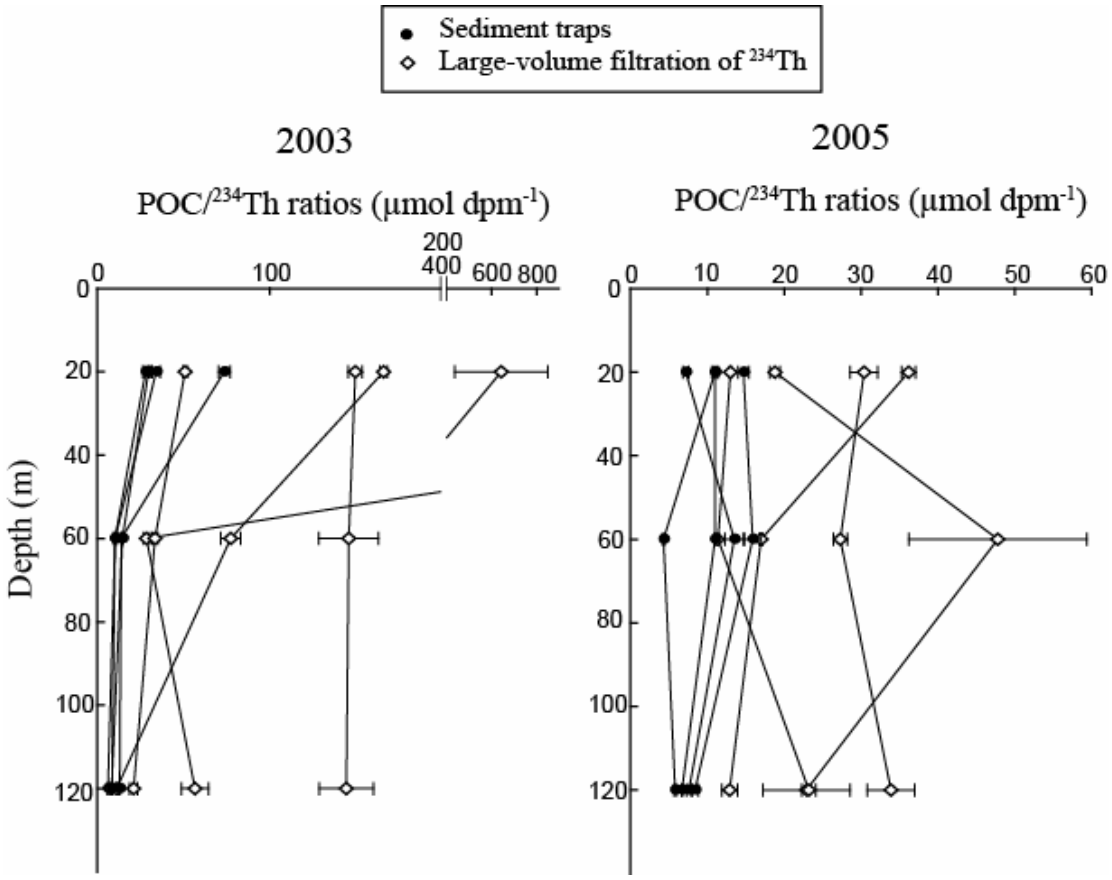

Figure 24. Large-volume and sediment trap POC/^{234}Th ratios as a function of depth; error bars indicate ± standard deviations

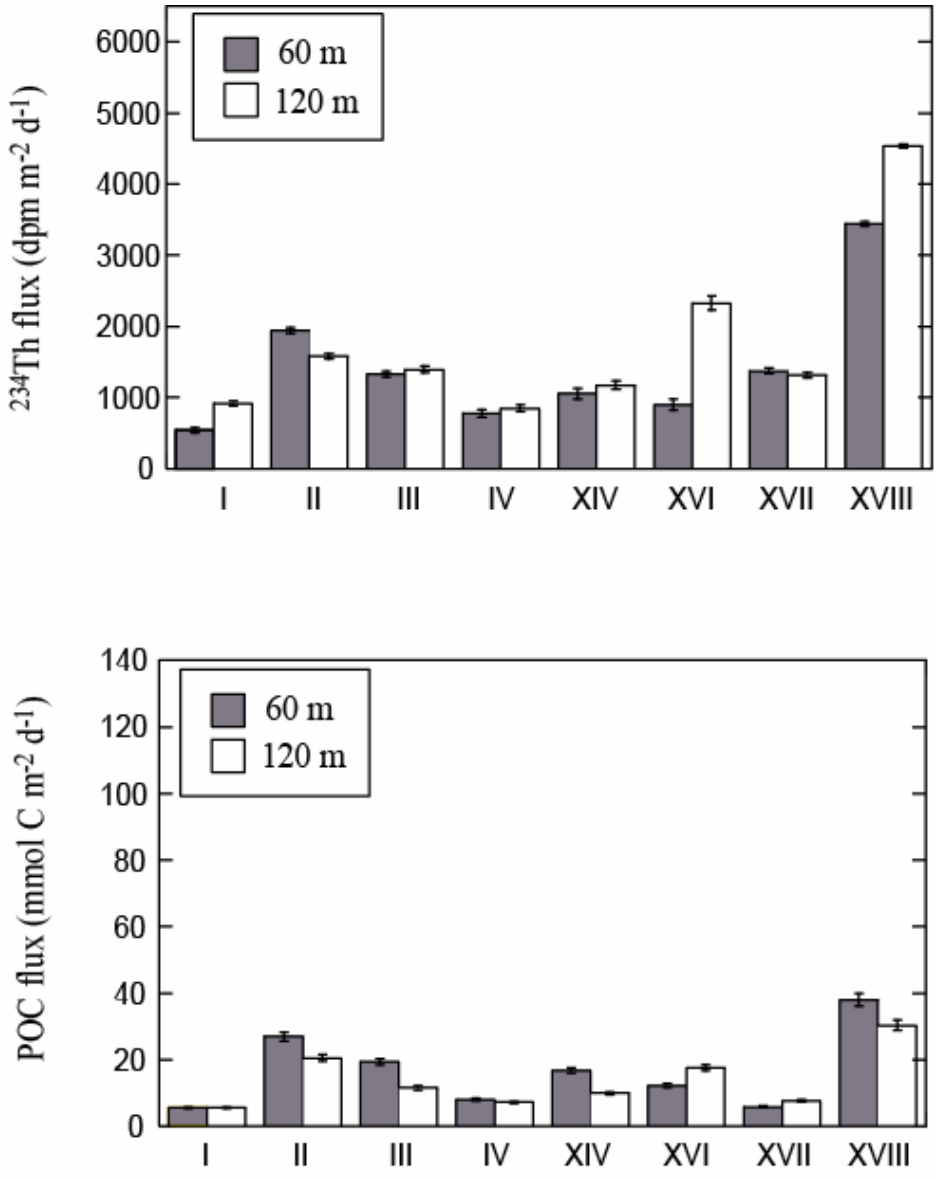

Figure 25. Sediment trap ^{234}Th and POC fluxes; error bars indicate ± standard deviations

respectively, and the highest ^{234}Th fluxes were observed at station XVIII (Fig. 25). In 2003, POC fluxes ranged between 5.6 and 27.1 and from 5.6 to 20.6 mmol C m^{-2} d^{-1} at 60 and 120 m, respectively (Fig. 25). POC fluxes were similar in 2005 with values ranging from 5.9 to 38.0 and from 7.7 to 30.4 mmol C m^{-2} d^{-1} at 60 and 120 m, respectively (Fig. 25). In contrast with POC fluxes obtained from large-volume filtration, sediment trap POC fluxes were generally higher at 60 m than at 120 m. Sediment trap POC/^{234}Th ratios were similar among stations and depths in 2003 and in 2005, with values ranging from 6.1 to 74.0 and from 4.3 to 15.9 μmol dpm^{-1} in 2003 and 2005, respectively (Fig. 24). Overall, trap-derived ^{234}Th fluxes at 60 m increased from 1152 ± 487 to 1694 ± 875 dpm m^{-2} d^{-1} from 2003 to 2005, and from 1186 ± 303 to 2338 ± 1099 dpm m^{-2} d^{-1} at 120 m (Fig. 25). POC fluxes were similar at both depths and for both years, with values at 60 m equal to 15.1 ± 8.2 and 18.2 ± 9.9 mmol C m^{-2} d^{-1} in 2003 and 2005 respectively, and values at 120 m of 11.3 ± 4.9 and 16.4 ± 7.6 mmol C m^{-2} d^{-1} in 2003 and 2005, respectively (Fig. 25).

3.4 Discussion

Seasonal and interannual variations in ice cover, relative distribution of Atlantic and Arctic waters, primary production, as well as recycling and retention of organic matter contribute to the variability in vertical POC fluxes determined at station locations. The stage of the phytoplankton bloom at stations occupied in 2003 varied from early to late bloom stages, although ^{234}Th activities and associated fluxes were similar among stations, suggesting similar longer-term particle export (days to weeks) in the upper ocean.

However, highly variable and elevated POC/^{234}Th ratios resulted in POC fluxes that varied significantly among stations and reached maximum values at station IV where an early bloom was underway. In 2005, bloom conditions also ranged between early and late bloom stages. ^{234}Th/^{238}U disequilibria and ^{234}Th fluxes were higher in 2005 and showed more variation among stations than in 2003 suggesting higher particle export in 2005 than in 2003, although lower POC/^{234}Th ratios resulted in POC fluxes with a similar range of variation than in 2003. POC export flux determinations from large-volume filtration of ^{234}Th in the MIZ of the Barents Sea indicated that POC fluxes were similar for both years at 60 m, but decreased at 120 m from 2003 to 2005. ^{234}Th-derived POC fluxes were in the same range as POC fluxes obtained previously in the MIZ and the central Barents Sea, where POC fluxes ranged from 500 – 1500 mg C m^{-2} d^{-1} (42 – 125 mmol C m^{-2} d^{-1}) in spring and 150 – 300 mg C m^{-2} d^{-1} (12.5 – 25 mmol C m^{-2} d^{-1}) in summer (Olli et al., 2002).

In contrast to the large-volume pumping data, trap-derived ^{234}Th and POC fluxes and POC/^{234}Th ratios varied less among depths and between 2003 and 2005. Although POC fluxes obtained with sediment traps were lower than those estimated from large-volume filtration of ^{234}Th, the trap fluxes more directly reflected the bloom conditions that were observed at each station within a season. POC fluxes were lower at stations in early or late bloom stages compared to stations experiencing well-developed blooms. Also, ^{234}Th and POC fluxes obtained from the drifting sediment traps were significantly higher at station XVIII, located in Atlantic water, than at the MIZ stations. The elevated sediment trap fluxes obtained at station XVIII were consistent with deep mixing of the water

column associated with active downward transport of POC. Despite these differences, estimated ^{234}Th fluxes obtained using each independent method agreed within a factor of 2 at most stations and depths sampled (Fig. 26). However, the agreement between the two methods was not as good for POC fluxes. Sediment trap POC fluxes were much lower than large-volume POC fluxes at almost every station (Fig. 26). The offset observed between the two methods is largest for POC fluxes measured at 120 m, and appear to result from significantly different POC/^{234}Th ratios obtained using the two different methods.

POC/^{234}Th ratios of marine particles may vary significantly with region and season in association with changes in primary and secondary production, plankton community structure, export production, particle size, particle aggregation-disaggregation, and food web dynamics (Moran et al., 2003; Buesseler et al., 2006). Differences between trap and large-volume measurements of the POC/^{234}Th ratios may also be due to the trapping efficiency, the accuracy of sampling sinking particles by pumps, and the differences in time scale of measurement of both methods (Amiel et al., 2002; Buesseler et al., 2006; Lalande et al., accepted). In this study in 2003 and 2005, some ^{234}Th-derived POC/^{234}Th ratios were unusually high and may possibly be error-associated. These high POC/^{234}Th ratios may be due to the filtration of large amount of suspended material when using the surface pump and rosette. Previous studies conducted in the Barents Sea indicate that POC concentrations of suspended matter are higher (6 - 31 μmol L^{-1}) there than in other regions of the Arctic Ocean (0.1 - 5 μmol L^{-1}) (Moran et al., 1997; Moran and Smith, 2000; Coppola et al., 2002). Coppola et al. (2002) also observed that flagellates

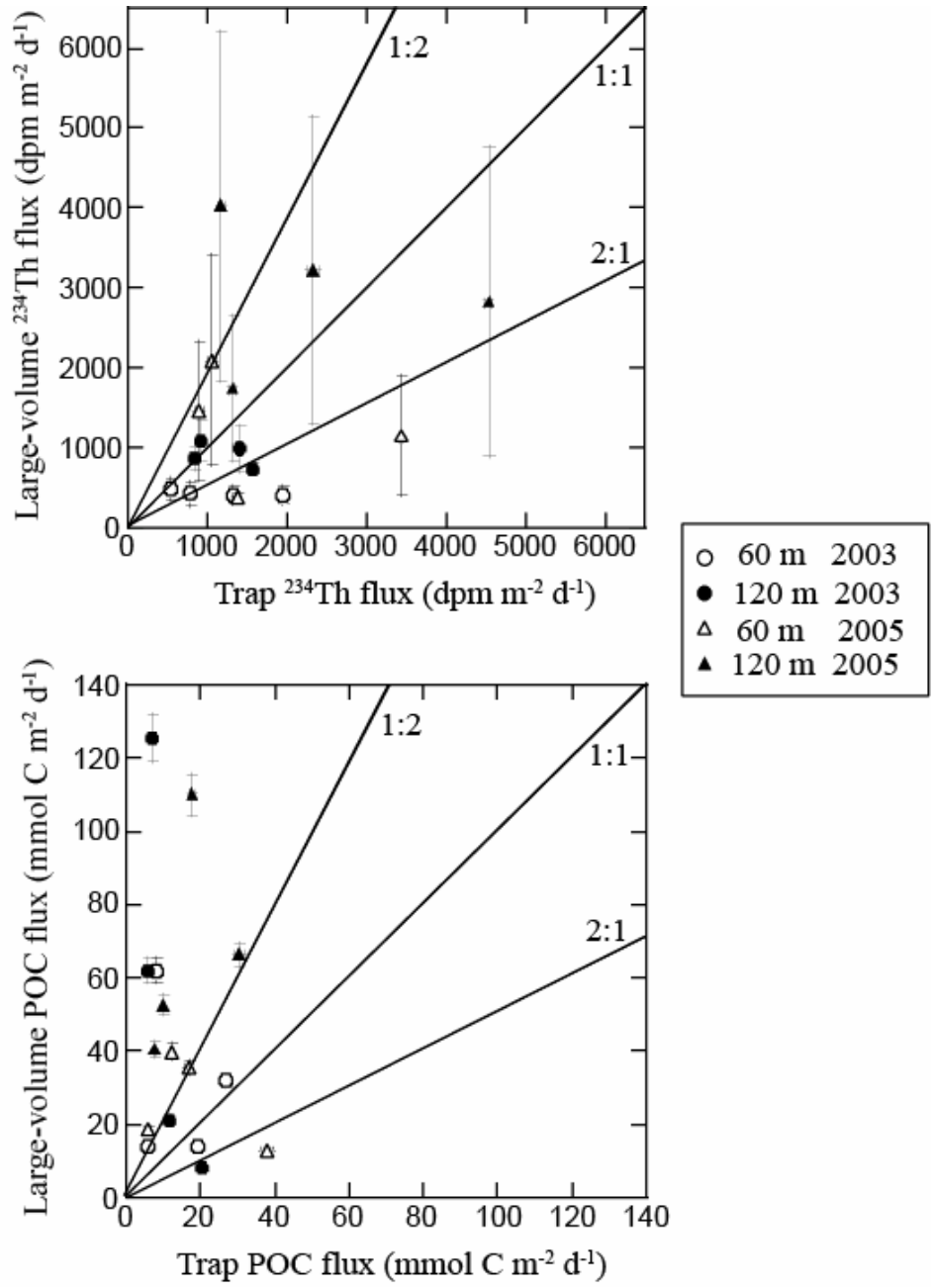

Figure 26. Comparison of large-volume and sediment trap ^{234}Th and POC fluxes

represented 30 to 50% of the suspended POC and suggested that small phytoplankton cells play a key role in thorium scavenging. This may partly explain the large discrepancies in the POC/^{234}Th ratios measured, as flagellates are not considered important for the vertical carbon flux due to their small size and low sinking rate (Reigstad et al., 2002).

In particular, the prominent presence of the prymnesiophyte *Phaeocystis pouchetii* in the Barents Sea may cause the large variation observed in the POC/^{234}Th ratios obtained from large-volume sampling of seawater. The colonial form of *P. pouchetii* has the ability to produce large, multilayered, mucilaginous envelopes and massive accumulation of this gelatinous material has been reported to clog fishing nets (Chang, 1984; Wassmann et al., 2005). Therefore, it is possible that the large mass of organic carbon present in the mucous envelopes of *P. pouchetii* colonies has the potential to introduce significant biases in the determination of large-volume POC/^{234}Th ratios due to the large amount of carbon associated with low activities of particulate ^{234}Th. By comparison, sediment trap POC/^{234}Th ratios would not be greatly affected by this process, as *P. pouchetii* does not contribute significantly to the vertical export of biogenic matter when measured with sediment traps in the Barents Sea (Riebesell et al., 1995; Reigstad and Wassmann, submitted). In the Barents Sea, the spring bloom is usually dominated by diatoms and/or *P. pouchetii* (Wassmann et al., 1999; Ratkova and Wassmann, 2002). *P. pouchetii* cells were dominant in terms of abundance at stations I, IV, XIV and XVI and important at station III (M. Reigstad, personal communication) during the field work in 2003 and 2005, suggesting that the presence of *P. pouchetii* may be a key factor

increasing the large-volume POC/^{234}Th ratios observed in the Barents Sea. ^{234}Th-derived POC/^{234}Th ratios were at least 4 times higher than trap-derived POC/^{234}Th ratios at stations I, II, IV, XVI and XVII, including most stations dominated by *P. pouchetii*. This is also consistent with observations by Coppola et al. (2002), who reported ^{234}Th-derived POC/^{234}Th ratios that were 4 to 16 times higher than those measured in sediment traps. In their study, the ratio between ^{234}Th fluxes measured in traps and calculated by a steady-state model was largest where a high *P. pouchetii* concentration was observed (Coppola et al., 2002). In addition, the largest differences between ^{234}Th-derived and trap-derived POC fluxes were observed at stations I, IV, XIV and XVI, where *P. pouchetii* was dominant. Therefore, the application of ^{234}Th to determine POC export in regions where *P. pouchetii* is dominant yield relatively high, and possibly incorrect, POC fluxes. This may be significant for the application of the ^{234}Th method as *Phaeocystis* spp. is one of the most widespread marine genera (Wassmann et al., 2005). It further suggests that the precision of the ^{234}Th method depends to an unknown degree on the phytoplankton species composition, i.e. ^{234}Th particle reaction is not uniform over time scale of days to months.

3.5 Conclusions

The relative magnitude of POC export fluxes in the Barents Sea depends on the method applied to determine the export fluxes. Higher fluxes were obtained at the weakly stratified Atlantic water station than in the MIZ by the sediment traps; however, there was no significant difference when determined from large-volume filtration of ^{234}Th.

Sediment trap POC fluxes were similar in 2003 and 2005, while ^{234}Th-derived POC fluxes were similar for both years at 60 m, but decreased from 2003 to 2005 at 120 m. In regions where *P. pouchetii* is dominant, the application of the ^{234}Th method yielded relatively high POC/^{234}Th ratios and hence overestimates of POC fluxes. In the case of the Barents Sea, the use of drifting sediment traps may be more reliable to measure the vertical export of biogenic matter, although additional studies of the influence of *P. pouchetii* on POC/^{234}Th ratios are needed to verify this hypothesis.

Conclusions

C.1 Summary of results

The first objective of this dissertation project was to compare the magnitude and the composition of the export of biogenic matter in the presence and absence of ice cover in the Chukchi Sea. POC fluxes obtained in ice-covered and ice-free conditions showed a different composition but a similar magnitude, indicating that the export fluxes in the presence of ice cover contribute significantly to the annual export of biogenic matter in the Chukchi Sea. Our results suggest that a reduction or disappearance of ice cover on the Chukchi continental shelf would not necessarily increase the annual export of POC, as POC fluxes were similar in the presence and absence of ice cover. Therefore, it remains uncertain if there will be an increase in uptake of atmospheric CO_2 following a reduction of ice cover and associated increased production in the Arctic Ocean.

However, it is important to note that the variations in export flux observed from ice-covered to ice-free conditions also reflected temporal variations that were imposed by the sampling program. Hence, a different spatial and temporal sampling coverage of the Chukchi Sea could have led to different results. Interannual variations may also have a significant impact on the annual export flux. Therefore, results should be interpreted with caution and additional investigations are needed to confirm or contradict the pattern observed in ice-covered and ice-free conditions in the Chukchi Sea in 2004.

The second objective was to compare POC export obtained using $^{234}Th/^{238}U$ disequilibria and sediment traps in the Chukchi Sea. ^{234}Th- and sediment trap-derived POC fluxes agreed within a factor of 2 for the majority of measurements taken in the Chukchi Sea. Despite the reasonable agreement between both methods, discrepancies were associated with the variability of the estimated ^{234}Th-derived and trap-derived POC/^{234}Th ratios. This variability may be due to elevated primary production rates, presence of swimmers in traps during deployments, different time-scale measurement of each method, and/or different properties (sinking versus suspended) and sizes of particles collected with both methods. Overall, the ^{234}Th technique has the advantage of allowing greater spatial coverage than sediment traps, however, POC/^{234}Th ratios obtained from ^{234}Th measurements might not be as representative of the POC/^{234}Th ratios in sinking particles as the POC/^{234}Th ratios obtained with sediment traps, although this did not appear to be the case in this study since there was a reasonable agreement between methods.

The third objective was to estimate POC export fluxes using ^{234}Th in the marginal ice zone of the Barents Sea and to compare these fluxes with direct POC export obtained from drifting sediment trap deployments. In contrast to the Chukchi Sea results, the magnitude of POC export fluxes in the northern Barents Sea depended on the method used to determine the export fluxes. ^{234}Th-derived POC fluxes were much higher than sediment trap POC fluxes at almost every station. The offset between the two methods was particularly large at stations dominated by *Phaeocystis pouchetii*, a flagellate that secretes large amounts of extracellular carbon. The utilization of the ^{234}Th technique in the Barents Sea where *P. pouchetii* is dominant may yield relatively high and possibly

incorrect POC/^{234}Th ratios and POC fluxes. In this case, the use of drifting sediment traps may be more reliable to measure the vertical export of biogenic matter. Overall, results obtained using ^{234}Th and drifting sediment traps in the Chukchi and northern Barents Seas are encouraging. However, the ^{234}Th method should be used with caution in some areas, as biological processes may affect POC/^{234}Th ratios.

C.2 Export fluxes on Arctic continental shelves and climate change

The similar magnitude of export fluxes measured in the presence and absence of ice cover suggests that the export of carbon might not significantly increase following a decline of sea ice due to climate change in the Chukchi Sea. Indeed, under-ice export fluxes were relatively high and probably contributed significantly to the annual export flux. However, it is important to note that the similar export fluxes measured under ice-covered and ice-free conditions mostly reflected the elevated export fluxes that were consistently observed along the BC transect. Due to highly dynamic hydrographic conditions allowing high productivity rates, Barrow Canyon is an important area for shelf to basin export in the presence and absence of ice cover. Since the conditions observed along Barrow Canyon are not representative of the majority of the Arctic continental shelves, the potential change in export fluxes from ice-covered to ice-free conditions may be better evaluated by comparing export fluxes over a more "typical" continental shelf, similar to conditions observed along the EHS transect. By considering export fluxes measured only at stations along the EHS transect, there was an increase in export fluxes from ice-covered to ice-free conditions in 2004. Also, the export fluxes measured during

this project were constrained in time and space by the sampling program of the SBI project. Therefore, it is reasonable to presume that variations in the timing and location of the measurements could have led to different patterns in export fluxes. For these reasons, the results obtained during this project should be interpreted with caution and further measurements should be taken to determine the impact of sea ice reduction on export fluxes. Ideally, a larger temporal and spatial coverage in export flux measurements would improve our understanding of the carbon export over the Arctic continental shelves.

C.3 Implications for future export production studies on Arctic continental shelves

It was previously thought that sediment traps would overestimate export fluxes over the shallow Arctic continental shelves because of the potentially important resuspension of sediments affecting the estimation of the export flux. However, the reasonable agreement between ^{234}Th fluxes obtained using drifting sediment traps and large-volume filtration in the Chukchi and Barents Seas suggests that resuspension is not a major problem in the determination of export fluxes over these Arctic continental shelves. Thus, both large-volume filtration of ^{234}Th and drifting sediment traps are effective methods to measure export production over Arctic continental shelves, and further measurements with both methods would clearly improve our knowledge of carbon export in the Arctic Ocean. Also, since both methods provided satisfactory results in the Chukchi and Barents Seas, it is also possible that moored sediment traps could properly estimate export fluxes over

these continental shelves, which could potentially be an important contribution to the investigation of export fluxes under different ice conditions.

However, there was a limitation in the application of the large-volume sampling of ^{234}Th to determine POC fluxes in the Barents Sea, possibly associated with the dominance of *P. pouchetii* that was observed at several stations. In order to resolve this complexity, future research should document POC/^{234}Th ratios of *P. pouchetii* to confirm that the species introduces a large volume of extracellular carbon and cause the higher and possibly incorrect POC/^{234}Th ratios and POC fluxes observed in the Barents Sea. Additional measurements of POC/^{234}Th ratios on different algal species would also provide important information concerning potential biological processes affecting the determination of POC fluxes with the ^{234}Th method.

Finally, because this project was conducted as part of two interdisciplinary projects, substantial data will be available to provide a comprehensive picture of the changes occurring on the continental shelves of the Chukchi and Barents Seas due to climate change. Once the complete dataset will be available, a potential additional project would be to integrate the export fluxes measured with drifting sediment traps as part of the SBI project to obtain a carbon budget indicating the importance of shelf to basin export in the Chukchi Sea.

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Vita

Catherine Lalande was born in 1977 in Montréal, Québec. She obtained a bachelor of science (B.Sc.) degree in Biology with a minor in Ecology from the Université du Québec à Montréal in 1999 and a masters (M.Sc.) degree in Oceanography from the Université du Québec à Rimouski in 2003.