

Evaluation of the collection efficiency of upper ocean sub-photic-layer sediment traps: a 24-month in situ calibration in the open Baltic Sea using ^{234}Th

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Abstract

The collection efficiency of cylindrical sediment traps of common design was assessed in situ for more than 2 y in an offshore shelf regime using the ^{234}Th proxy and simultaneously collected hydrological and biogeochemical parameters. The traps were found to systematically record an undertrapping bias of ^{234}Th by, on average, a factor of three (range 0.8 to 10). Seasonal variations in trapping efficiency were related to the seasonally varying ballasting properties of the settling particle pool. Sediment trap ^{234}Th fluxes agreed within a factor of two of the estimated ^{234}Th export from the overlying surface waters in the winter-spring periods in both 1999 and 2000 and appeared related to a particle pool that included, presumably rapidly sinking, mineral particles and diatom tests acting as ballast. In contrast, discrimination against slowly settling organic-rich aggregates of apparent exudate origin resulted in undertrapping of ^{234}Th by factors of three to ten throughout the summer-fall seasons. These data are consistent with hydrodynamic predictions that the collection efficiency of sinking particles is inversely related to their intrinsic settling velocities. Recognition of changing particle composition along a settling velocity spectrum combine with carbon mass balance restrictions to suggest that these ^{234}Th -based collection efficiencies, ranging from 0.1 to 1, may not be directly applicable to “correct” sediment trap fluxes of other components, such as organic carbon. However, the ^{234}Th -derived insights of settling-velocity-related undertrapping may beneficially be taken into account when interpreting trap records both in studies of biogeochemical element fluxes and in phytoplankton ecology.

Much of our current understanding of upper ocean biogeochemistry and export fluxes is based on studies of the material caught by sediment traps. Deployments of these open cylin-

ders or cones as “rain gauges” have afforded spatial, temporal, and depth-varying studies of the changing flux and composition of settling matter. For instance, traps have been used to estimate the upper ocean settling export of carbon and other biogeochemically important elements (e.g., Martin et al. 1987; Knauer et al. 1990). Averaged over appropriate space and time scales, trap fluxes provide one means to estimate new production (e.g., Eppley 1989; Michaels et al. 1994). Trap-derived relationships of flux versus depth have also been used to estimate remineralization rates (e.g., Martin et al. 1987) and to parameterize large-scale biogeochemical models (e.g., Gnanadesikan 1999; Christian et al. 2002).

Knauer and Asper (1989) summarized many of the challenges facing accurate-flux recording with sediment traps that were discussed at the US Joint Global Ocean Flux Study (JGOFS) Sediment Trap Workshop held in 1988. Despite intensified use of upper ocean ocean sediment traps since then, the extent to which this technique provides unbiased estimates of verti-

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cal fluxes remains unresolved. Field data provide mixed diagnostics. The use of trap-derived particulate organic compound (POC) fluxes at the JGOFS Bermuda Atlantic Time Series (BATS) station resulted in a large upper ocean carbon imbalance (Michaels et al. 1994). Parallel deployment of traps with different designs have revealed that both absolute fluxes and the composition of the collected sinking material is a function of trap design and deployment conditions both in the Equatorial Pacific (Hernes et al. 1996; Murray et al. 1996) and in the BATS region (Gust et al. 1992; Buesseler et al. 2000; Stanley et al. unpubl. data unref.). However, other studies suggest that upper ocean trap fluxes are able to close the carbon mass balance within a factor of two (Emerson et al. 1997) and provide ecologically consistent flux patterns (e.g., Waite et al. 1992; Karl et al. 1996; Wassman 1998), leaving unresolved the question of collection efficiency.

Specific trap integrity studies have focused primarily on artifacts stemming from hydrodynamic biases (e.g., Gardner 1980; Blomqvist and Kofoed 1981; Butman et al. 1986; Gust et al. 1992; Gardner 1997), problems with preservation (Knauer et al. 1984; Wakeham et al. 1993; Kortzinger et al. 1994), and effects due to material entering the traps by other means than passive settling (i.e., “swimmers/surfers”; e.g., Lee et al. 1988; Michaels et al. 1990; Steinberg et al. 1998; Buesseler et al. 1994, 2000). Whereas significant mechanistic insights have been gained since the 1988 JGOFS Sediment Trap Workshop, several recent studies are stressing that key field-testing studies of sediment traps are still wanting (e.g., Gardner 1997, 2000; Buesseler et al. 2000).

More specifically, a major recommendation of the JGOFS Sediment Trap Workshop was to look for independent field-based tests of trapping efficiency, such as using the fluxes of the natural radionuclide ^{234}Th to calibrate in situ sediment trap fluxes (Knauer and Asper 1989). The tetravalent and thus particle-sorptive ^{234}Th ($\tau_{1/2} = 24$ d) is produced at a constant rate from the conservatively mixing ^{238}U and is thus ideal for tracing upper ocean particle processes on timescales from less than a week to months. Basically, the ^{238}U - ^{234}Th radioactive disequilibrium in the surface ocean is a reflection of the ^{234}Th flux on settling particles to strata below. Comparing this estimate of ^{234}Th export from the mixed surface ocean with the flux of ^{234}Th that is actually collected by a sediment trap positioned just below the mixed surface ocean provides an estimate of the in situ collection efficiency of the sediment trap:

$$\text{Eff}_{\text{trap}} = \frac{F_{\text{Th,trap}}}{F_{\text{Th,mix}}} = \frac{\{^{234}\text{Th}\} / (A_{\text{trap}} \cdot t)}{\lambda \cdot z_{\text{mix}} \cdot ([^{238}\text{U}_{\text{tot}}] - [^{234}\text{Th}_{\text{tot}}])} \quad (1)$$

where Eff_{trap} is the collection efficiency of the sediment trap, $F_{\text{Th,trap}}$ and $F_{\text{Th,mix}}$ ($\text{dpm m}^{-2} \text{d}^{-1}$) is the flux of ^{234}Th activity collected in the sediment trap and is estimated to have been exported from the mixed surface layer, respectively. $\{^{234}\text{Th}\}$ is the activity (dpm) of ^{234}Th in the trapped material decay-corrected to the midpoint of the deployment period, A_{trap}

(m^2) is the surface area of the trap mouth, t (d) is the deployment time, λ is the ^{234}Th radioactive decay constant (0.0288 d^{-1}), z_{mix} is the sub-photic-zone/mixed-layer trap deployment depth (m), $[^{238}\text{U}_{\text{tot}}]$ and $[^{234}\text{Th}_{\text{tot}}]$ (dpm m^{-3}) is the total radioactivity concentrations in the overlying water of ^{238}U and ^{234}Th , respectively. In some specific regimes, we need to consider non-steady state (e.g., Buesseler et al. 1992a) and other advection/dispersion processes (e.g., Gustafsson et al. 1998, 2000a; Benitez-Nelson et al. 2000) to correctly estimate the ^{234}Th export flux; this is assessed in detail for our particular study site below.

The ^{234}Th trap calibration has been attempted in a few previous situations. Buesseler (1991) summarized the limited experiments with required simultaneous measurement of water-column ^{234}Th and sediment trap collection of ^{234}Th . Although most studies only involved 3 to 5 coupled observations, comparison of the surface ocean ^{234}Th export and the sediment trap ^{234}Th import fluxes suggested large and unidirectional over- or under-collecting biases, frequently by factors of three to ten (Buesseler 1991). Despite these worrisome trapping efficiency results, there have only been a few additional such in situ trap calibrations since then. The most complete study was conducted in a coastal fjord off northwest USA, where samples for ^{234}Th in both the water column and in traps were collected eleven times throughout a full year (Wei and Murray 1992), suggesting an average under-collection bias by a factor of two, but boundary scavenging effects could not be excluded. Buesseler et al. (1994) performed a 4-d three-dimensional trap calibration at BATS and reported overtrapping at low flux conditions. Murray et al. (1996) reported an average overtrapping of 3 to 4 for their 100-m trap and lower for deeper traps in their Equatorial Pacific trap calibration. Benitez-Nelson et al. (2001) performed a detailed ^{234}Th -based in situ calibration of the traps at station ALOHA in the North Pacific subtropical gyre during 9 cruises covering a full year. They found their cylindrical traps, deployed at 150 m, to under-collect the annual flux by nearly a factor of two, with most of the deduced missing flux being attributed to two single large export events. Also recently, Coppola et al. (2002) reported agreement within a factor of two for five stations during a summertime Barents Sea cruise (traps at 90 to 200 m depth). Given that accurately collecting and quantifying the settling flux out of the surface waters remain a central challenge in limnology and oceanography, the objective of the current study is to contribute to alleviating the current deficit of longer-term in situ trap calibrations. This article reports on a continuous upper ocean trap calibration spanning more than two years, performed at the well-studied offshore time series station BY31 in the open Baltic Sea proper.

Materials and procedures

Open Baltic Sea and the BY31 Landsort Deep time series station—The Baltic Sea is a semi-enclosed continental shelf sea. The selected open Baltic Sea time series station BY31 (Fig. 1;



Fig. 1. The northern European continental shelf with the location of the Baltic Sea time series station BY31 (Landsort Deep, $58^{\circ}35'N$ $18^{\circ}14'E$; 40 km off Swedish coast; 459 m depth) marked with a circle.

Landsort Deep, $58^{\circ}35'N$ $18^{\circ}14'E$; 40 km off Swedish coast; 459 m depth; away from any major rivers) has been intensively monitored for hydrographic, biological, and chemical parameters since the 1890s (see references in the reviews of Voipio 1981 and Fonselius and Valderrama 2003). A high-intensity time-series monitoring program with 22 to 25 observations per year has been operating since 1990 (e.g., HELCOM 1988; Larsson et al. 2001). The BY31 station has also been chosen for many specific research projects (e.g., Walve and Larsson 1999; Rahm et al. 2000; Gustafsson et al. 2000b; Larsson et al. 2001; Larsson et al. 2002; Sobek et al. 2003). Due to its brackishness, the open Baltic Sea is strongly stratified relative to other continental shelf seas, reducing effects of resuspended material on the trap fluxes. A permanent and strong halocline is centered on 60 to 80 m (e.g., Kullenberg et al. 1981). A strong seasonal pycnocline is developing at around 10 to 20 m deep (e.g., Stigebrandt 1985), below which density increases steadily with depth (Fig. 1). The upper mixed layer exhibits well-documented seasonal variations in biogeochemical parameters typical of temperate shelf areas (Elmgren et al. 1984; Larsson et al. 2001; Walve 2002; Hajdu 2002), making this site ideal for investigating mechanisms of putative sediment trap biases.

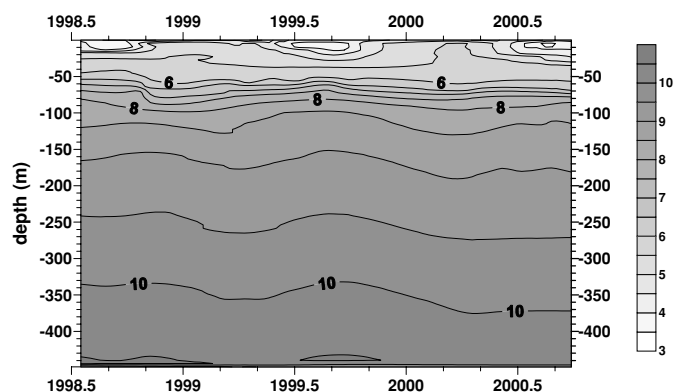


Fig. 2. The potential density field (σ_{ρ}) at the Landsort Deep BY31 time series station 1998–2000.

Sampling strategy

Water column sampling: High-volume water column sampling (500 to 800 L) for short-lived ^{234}Th was performed with in situ pumping from the middle of the mixed surface layer to a filtration and extraction unit located in a laboratory van, largely following previously described methodology (Gustafsson et al. 2000a). Briefly, water was passed at a flow rate of 5 to 8 L min^{-1} through a 100- μm nylon screen, a 0.2- μm polypropylene filter cartridge (Flotrex, Osmonics Inc.; 0.48 m^2 effective filter area), and two serially coupled MnO_2 -impregnated adsorbents (prepared according to Hartman and Buesseler 1994; here using 10 μm twined polypropylene filter cartridges) to adsorb dissolved ^{234}Th . The collection efficiency of the MnO_2 cartridges for ^{234}Th in these brackish surface waters was 0.75 ± 0.12 (1 standard deviation, $n = 28$).

Sediment traps: The employed cylindrical sediment trap system of Larsson et al. (1986) with modifications by Broman et al. (1990) is commonly used for upper ocean and continental shelf studies. To match the time scales of upper ocean particle processes and the half-life of ^{234}Th , the traps were deployed in periods of 3 to 4 weeks over the 2-y study period. The traps were bottom-anchored and arranged in tube holders that are constructed to be of a hydrodynamically stable, self-suspended, and buoyant design (Broman et al. 1990). They were positioned at 40 m below the surface to remain constantly below the seasonal pycnocline and photic zone, as well as away from direct influence of surface mixing (Fig. 2). There was only one trap per mooring and 1 to 3 parallel moorings were deployed at any given time. A string of small floats was used at the surface to minimize the effect of short period wave motion. Because most of the drag on a trap array is from the mooring line itself (Gust et al. 1992), a 3-mm thin nylon line was used. The straight cylindrical glass tubes (500 \times 100 mm) are arranged in polyvinyl chloride cylinders. The gimbaled construction is further equipped with turbulence generators and splitter planes to minimize vortex street formation. The trap design has been tested in wave tanks and been shown to

be hydrodynamically stable and the vertical alignment of the sediment collection vessels are retained both in laminar and moderately turbulent flow rates up to 45 cm s^{-1} (Broman et al. 1990). The horizontal current velocity at the deployment depth was low throughout the 24-month study period and ranged from 0.1 to 27 cm s^{-1} (median 2.8 cm s^{-1}).

To minimize artifacts related to zooplankton herniation (e.g., Peterson and Dam 1990) and solubilization of collected POC into dissolved organic carbon (DOC) (Hansell and Newton 1994), we avoided using brines and any poison. Because this approach minimizes zooplankton swimmer accumulation in the trap (e.g., Lee et al. 1988), "swimmer picking" was not performed, which also led to avoiding the risk of any unintended removal of surface-active non-swimmer material during such manual handling. Microscopical observations suggested qualitatively that swimmers were a small fraction of the total floc material collected in the trap. Furthermore, any inclusion of swimmers would not have affected the ^{234}Th load in the traps as $^{234}\text{Th}/\text{C}$ ratios in swimmers have been found to be about a factor of 1000 lower than on non-swimmer carbon (Coale et al. 1990; Buesseler et al. 1994). Any potential loss of POC due to biological degradation appears to have been insignificant as a degradation-associated increase of C:N was not seen. It has previously been demonstrated that losses of trapped material due to biological degradation is slow for these time scales ($\sim 1\%$ d^{-1} ; average particle residence time in the traps = $0.5 \times$ deployment time = 7 to 15 d) and in situ temperatures (average temperature at trap depth was 3°C) (Lee et al. 1987; Heiskanen 1998). Even if such a process would have affected trapped POC values, the trapped ^{234}Th cannot be degraded and would have repartitioned to other surfaces of the abundant particle floc recovered in each trap.

Ancillary biogeochemistry—At the onset of each sampling occasion, a full conductivity-temperature-depth (CTD) profile (General Oceanics Inc.) was obtained to deduce the depth of the mixed layer and to select sampling depths. The CTD data were subsequently used to describe the hydrography and stability of the water column.

For enumeration of phytoplankton $> 2\ \mu\text{m}$, integrated samples (0 to 20 m) were taken with a plastic hose (inner diameter 25 mm) about 20 times per year (weekly during spring, biweekly after that and monthly during winter). A sub-sample of 200 mL was then preserved with 0.8 mL acid Lugol's solution and counted after sedimentation in a settling chamber (10 to 50 mL) using a NIKON inverted microscope with phase contrast and $100\times$ to $400\times$ magnification. Preservation, counting procedure, and cell volume calculation followed the recommendation of the Baltic Monitoring Programme (HELCOM 1988). Carbon values were estimated with the equations of Menden-Deuer and Lessard (2000).

Chlorophyll *a* (Chl *a*) data for the BY31 station were obtained from the SHARK (Svenskt HAVSarkiv) database of the Swedish national monitoring program (database host: Swedish Meteorological and Hydrological Institute). The ten-depth Chl

a water column profile is obtained approximately 30 times per year. The Chl *a* profiles for the years 1998 to 2000 were integrated trapezoidically to get an estimate of the seasonally and interannually varying biomass inventory in the photic zone of the open Baltic Sea.

Samples for analysis of total organic carbon (TOC) and optical parameters of the organic matter were collected in 12-mL plastic tubes and brown glass bottles at a sampling port split in the deckboard sampling system described above.

Analytical methods—The CTD salinities were used to estimate the activity of ^{238}U , as it has been shown that this conservative isotope can be estimated from salinity within a 1% certainty range (^{238}U [dpm/L] = $0.07061 \times \text{S}\%$; Chen et al. 1986; Andersson et al. 1995).

The short-lived isotope ^{234}Th was radiochemically purified from the filters, MnO_2 -impregnated adsorbers, and splits of the trapped material and quantified by either low-level β - or γ -counting techniques. The procedures largely followed that described by Buesseler et al. (1992b) with modifications for more organic-rich waters outlined in Gustafsson et al. (2000a). The measured ^{234}Th activities were corrected for detector background, method recovery, and U ingrowth and reported values were decay-corrected to the midpoint of the sample collection period. Errors (2% to 5% at the 95% confidence limit) were constrained by the goodness of the fit of the raw counts to the ^{234}Th decay curves.

TOC, optical properties, and major inorganic elements—The samples for TOC and optical characterization were analyzed as described previously (Gustafsson et al. 2001). Briefly, the TOC samples were acidified with 200 mL of 1.2 M HCl to remove inorganic carbon and quantified with a high-temperature catalytic oxidation instrument (Shimadzu TOC 5000). Fluorescence-based measures of humic substances (HS) were corrected for the inner filter effect and obtained fluorescence intensities were normalized to and reported as quinine sulfate equivalents (units of $\mu\text{g L}^{-1}$). The molar extinction coefficient at 280 nm (ϵ_{280}) was derived from normalizing the absorbance at 280 nm (A_{280}) to the TOC. This parameter represents the π - π^* transition of aromatic carbon atoms. Hence, ϵ_{280} reflects the composition of the suspended organic matter and has been shown to be higher for surface waters dominated by input of terrestrial humic matter and lower for regimes impacted by less aromatic polysaccharide-rich exudates from phytoplankton (Gustafsson et al. 2001).

For the determinations of Fe, Si, and Al in the sediment-trapped material the LiBO_2 digestion procedure of Burman et al. (1978) was followed by inductively-coupled plasma mass spectrometry–atomic emission spectrometry analysis. The accuracy and precision of the analyses were checked by analyzing reference sediments and was generally better than 5% (1 relative standard deviation) for the three elements.

Assessment

System description: hydrography and ecology patterns—The open Baltic Sea exhibits large seasonal variations in both hydrogra-

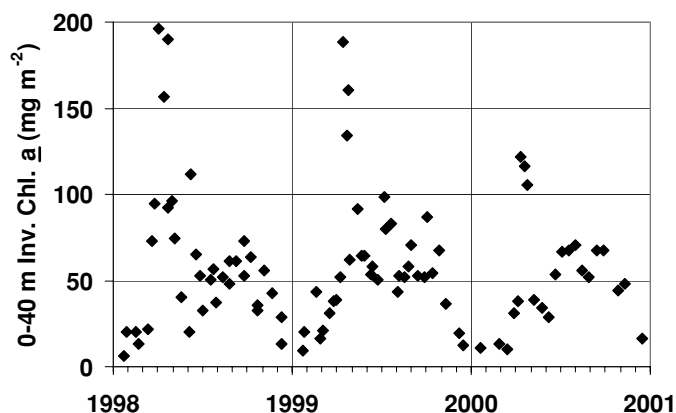


Fig. 3. The 0 to 40 m depth-integrated inventory of Chl *a* at the Landsort Deep BY31 time series station 1998–2000.

phy and biogeochemistry. The permanent halocline stayed rather invariant around 60 to 80 m (Fig. 2) throughout the two full seasonal cycles of the study period (July 1998–August 2000). A transient shallowing of the upper halocline to around 50 m was recorded in the fall of 1998. The well-pronounced seasonal thermocline was clearly seen to last through the summer, half of the year, in all 3 years, with the weaker stratification in the intermediate waters prevailing during the winters. The 8-m surface salinity and temperature ranged from 5.54‰ to 6.91‰ and 1.6°C to 16.1°C, whereas at the 40-m trap depth the annual ranges were 6.69‰ to 7.45‰ and 1.8°C to 6.7°C.

Chl *a* broadly followed a similar seasonal trend as the hydrography. The 0 to 40 m depth-integrated Chl *a* inventory was as low as 10 mg m⁻² in the winter but rapidly increased at the onset of stratification and solar heating to reach yearly maxima during the spring bloom (late March to early April) of 150 to 200 mg m⁻² (Fig. 3). A summertime standing stock biomass of 50 to 80 mg Chl *a* m⁻² was sustained in all 3 y into the month of October. A second but smaller Chl *a* maxima was observed in each year in late September to early October as the photic zone inventory reached 70 to 90 mg m⁻².

Phytoplankton composition also showed clear seasonal differences. The spring bloom was dominated by large dinoflagellates (*Scrippsiella hangoei* [Schiller] Larsen, *Peridiniella catenata* [Levander] Balech) with diatoms sub-dominant. In both years, diatoms (*Chaetoceros wighamii* Brightwell, *Thalassiosira baltica* [Grunow] Ostensfeld, *Skeletonema costatum* [Greville] Cleve, respectively) were abundant during the first half of the spring bloom and occurred in higher numbers in 1999 compared to 2000. In summer and early autumn, cyanobacteria (*Aphanizomenon* sp., *Nodularia spumigena* Mertens, and mucilaginous colony-forming picocyanobacteria) and small nanoflagellates (2 to 10 μm) were dominant. Diatoms were sparse in summer, but the small fast-growing diatom *Cyclotella choctawhatcheana* Prasad was present in 1999.

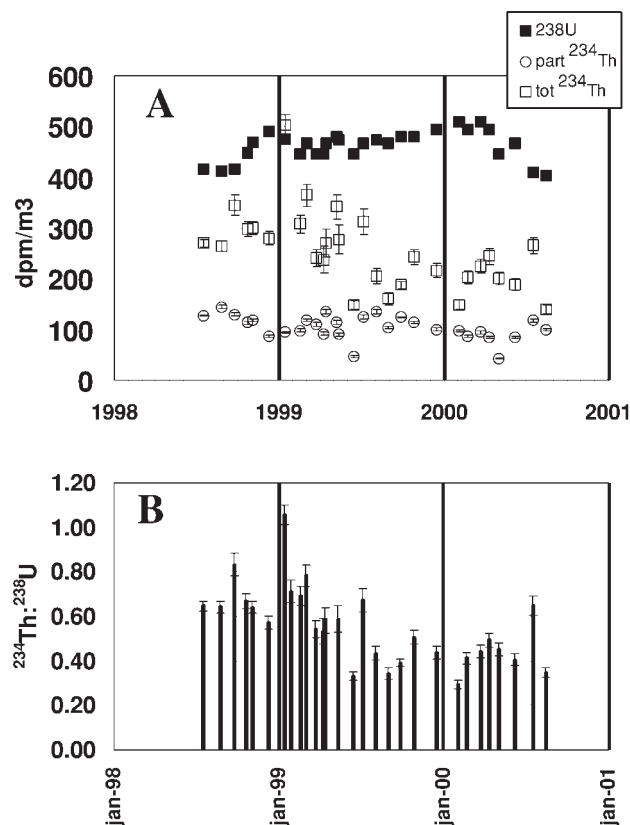


Fig. 4. Activity concentrations (A) of ^{238}U (■), total $^{234}\text{Th}_{\text{tot}}$ (□), and particulate $^{234}\text{Th}_{\text{part}}$ (○) and extent of ^{234}Th secular equilibrium (B) in the mixed surface layer of the Landsort Deep BY31 time series station during the 1998–2000 study period. The error bars represent 1 standard deviation of the propagated counting errors.

Water column ^{238}U and ^{234}Th dynamics—There is constantly a pronounced ^{238}U - ^{234}Th disequilibria in the mixed surface layer of the open Baltic Sea (Fig. 4; Table 1). The particulate fraction is varying between third to half of the total ^{234}Th . A certain influence of detrital particles of riverine origin on the scavenging fluxes must be expected for a semi-enclosed sea such as the Baltic Sea. This may have contributed to the attenuation of the “seasonal” signal in ^{234}Th scavenging, because such particles may be of greater relative importance and, thus, may compensate in the non-vegetative season. In addition to a slight seasonal variation in total ^{234}Th activity (Fig. 4a), there is also a suggestion of an interannual variation with a smaller deficit the first year compared to the second year of the study. Low scavenging in oligotrophic gyres yields very small ^{238}U - ^{234}Th differences (e.g., Buesseler et al. 1994), in many cases making the ^{234}Th technique less applicable to such regimes. In contrast, because the total disequilibria hovers around 50% on average in the open Baltic Sea (Fig. 4b; Table 1), the ^{234}Th proxy technique is much better fitted to be applied to such continental shelf sites. The steady-state $F_{\text{Th,mix}}$ ranged up to

Table 1. BY31 station water column ^{234}Th fluxes and residence times

Collection date	Salinity	Total ^{234}Th (dpm m^{-3})	$^{234}\text{Th}:^{238}\text{U}$	^{234}Th flux (dpm $\text{m}^{-2} \text{d}^{-1}$)	Residence time (d)
17 Jul 98	5.90	269.4 ± 8.1	0.65	169.6 ± 9.1	64
25 Aug 98	5.84	264.6 ± 10.6	0.64	170.2 ± 11.4	62
24 Sep 98	5.88	345.0 ± 20.7	0.83	80.9 ± 24.3	171
21 Oct 98	6.33	297.6 ± 14.9	0.67	172.1 ± 17.9	69
3 Nov 98	6.65	300.0 ± 12.0	0.64	195.3 ± 14.8	61
8 Dec 98	6.93	279.6 ± 14.0	0.57	241.6 ± 17.1	46
13 Jan 99	6.74	503.4 ± 20.1	1.06	-31.7 ± 23.8	—
27 Jan 99	6.80	341.4 ± 23.9	0.71	159.8 ± 28.1	85
17 Feb 99	6.29	307.8 ± 18.5	0.69	157.9 ± 21.9	78
3 Mar 99	6.63	364.8 ± 21.9	0.78	116.6 ± 25.8	125
23 Mar 99	6.31	241.8 ± 16.9	0.54	233.9 ± 20.2	41
8 Apr 99	6.26	237.0 ± 26.1	0.53	239.4 ± 30.5	40
14 Apr 99	6.58	270.0 ± 27.0	0.58	225.8 ± 31.6	48
12 May 98	6.70	277.8 ± 27.8	0.59	225.0 ± 32.5	49
15 Jun 99	6.33	147.6 ± 8.9	0.33	342.4 ± 11.4	17
6 Jul 99	6.61	313.2 ± 25.1	0.67	176.1 ± 29.4	71
4 Aug 99	6.72	205.2 ± 14.4	0.43	308.6 ± 17.4	27
31 Aug 99	6.59	159.6 ± 12.8	0.34	353.0 ± 15.7	18
28 Sep 99	6.80	187.2 ± 7.5	0.39	337.5 ± 10.2	22
27 Oct 99	6.78	243.0 ± 14.6	0.51	273.2 ± 17.7	36
16 Dec 99	7.01	216.0 ± 13.6	0.44	320.6 ± 16.7	27
2 Feb 00	7.23	148.8 ± 9.4	0.29	414.2 ± 12.3	14
22 Feb 00	7.04	203.4 ± 12.8	0.41	335.1 ± 15.8	24
23 Mar 00	7.18	224.4 ± 14.1	0.44	327.2 ± 17.3	27
11 Apr 00	6.99	244.2 ± 15.4	0.49	288.1 ± 18.6	34
02 May 00	6.32	199.8 ± 12.6	0.45	282.3 ± 15.4	28
06 Jun 00	6.61	189.0 ± 11.9	0.41	319.1 ± 14.7	24
17 Jul 00	5.81	265.2 ± 16.7	0.65	166.3 ± 19.8	64
15 Aug 00	5.72	139.8 ± 8.8	0.35	302.6 ± 11.2	19

414 dpm $\text{m}^{-2} \text{d}^{-1}$ with a mean flux over the 25 months of 238 ± 96 dpm $\text{m}^{-2} \text{d}^{-1}$ (1 standard deviation; $n = 29$). Because of the brackish waters of the Baltic Sea, this quantity is not easily comparable with other coastal/shelf regimes. However, combined with the mixed layer inventory, this translates into year-round mean residence times of generally 30 to 60 d (range 15 to 170 d; Table 1), which is comparable to reports from other continental shelf regimes (e.g., Bhat et al. 1969; Tanaka et al. 1983; Moran and Buesseler 1993; Gustafsson et al. 1997, 1998; Benitez-Nelson et al. 2000; Charette et al. 2001; Coppola et al. 2002). Also consistent with our data, a $^{234}\text{Th}:^{238}\text{U}$ activity ratio of 0.6 and ^{234}Th residence time of 50 d was reported for another Baltic Sea Proper location (Gotland Deep) sampled in June 1995 (Porcelli et al. 2001).

Evaluation of non-steady state and horizontal effects on the estimate of ^{234}Th export flux—Before evaluating the trapping efficiency by comparing the above export fluxes with the trap-collected ^{234}Th , we need to assess the potential influence of non-steady state (NSS) conditions as well as effects of horizontal transport on the vertical ^{234}Th flux estimate. The absence of rapid changes in the $^{234}\text{Th}:^{238}\text{U}$ activity ratio throughout the

study period (Fig. 4b) suggest that NSS effects are likely to be only a minor influence for application of the ^{234}Th proxy in this regime. However, our long-term record affords the possibility to assess this aspect quantitatively. The NSS ^{234}Th export fluxes were thus calculated accordingly (Buesseler et al. 1992a):

$$F_{\text{Th,mix}} = z_{\text{mix}} \lambda \left[\frac{{}^{238}\text{U}_{\text{tot}}(1 - e^{-\lambda t}) + {}^{234}\text{Th}_{\text{tot},1}e^{-\lambda t} - {}^{234}\text{Th}_{\text{tot},2}}{(1 - e^{-\lambda t})} \right] \quad (2)$$

where ${}^{234}\text{Th}_{\text{tot},1}$ and ${}^{234}\text{Th}_{\text{tot},2}$ are the isotope radioactivity concentrations at the start and at the end of a period lasting t days between consecutive sampling occasions. Overall, the NSS estimates of $F_{\text{Th,mix}}$ were in close agreement with the steady state (SS) estimates espoused above. Two exceptions were September 1998 when the NSS estimate was a factor of six lower and February/March 1999 when the NSS estimate predicted a factor of three to four higher flux than the SS model. In the other 25 NSS-SS flux comparisons, the absolute difference between the two $F_{\text{Th,mix}}$ estimates (equally distributed in both directions) were, on average, 21%. This difference is much smaller than the offset between either of these $F_{\text{Th,mix}}$ estimates and the $F_{\text{Th,trap}}$ recorded below.

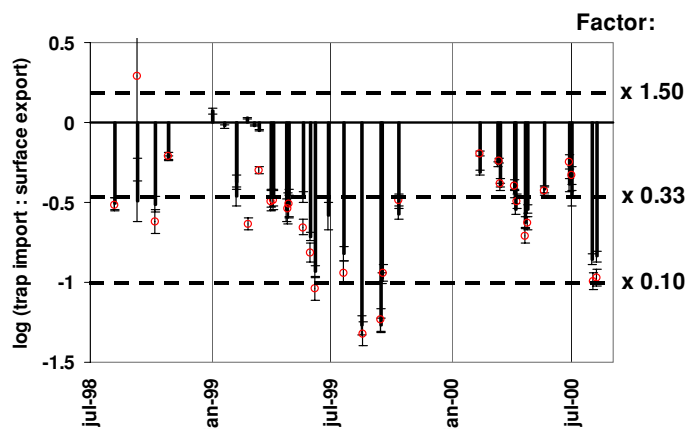


Fig. 5. Collection efficiency of the cylindrical 40-m sediment trap toward ^{234}Th at the Landsort Deep BY31 time series station during the 1998–2000 study period. The bars represent the steady-state model and the open circles the non-steady state model. The error bars represent 1 standard deviation of the propagated counting errors.

Although almost always neglected, it has been shown that horizontal gradients in surface water ^{238}U - ^{234}Th disequilibria may need to be considered in near-coastal environments with rapid water exchange (e.g., McKee et al. 1984; Gustafsson et al. 1998, 2000a; Benitez-Nelson et al. 2000). To test whether the local ^{238}U - ^{234}Th disequilibria at the BY31 station is affected by horizontal transport, we, on two occasions (23 March 1999 and 15 June 1999), sampled at three additional locations in the region, which together form a triangle with the BY31 station in the middle (the distance between BY31 and the control stations are 18 to 24 km). Only very small horizontal gradients in ^{234}Th activity were found. In March 1999, an activity of 242 ± 16 dpm m^{-3} was found at BY31 and an average of 203 ± 23 dpm m^{-3} at the reference stations. For the mid-June 1999 samples, the corresponding activities were 148 ± 9 dpm m^{-3} and 171 ± 11 dpm m^{-3} , respectively. The relative importance of horizontal and vertical transport for ^{234}Th , and thus other particle-reactive substances, may be assessed explicitly (Gustafsson et al. 1998):

$$\frac{\partial [^{234}\text{Th}]}{\partial t} = \lambda([^{238}\text{U}] - [^{234}\text{Th}]) - F_{\text{Th,mix}} + \frac{\partial}{\partial x} K_x \frac{\partial [^{234}\text{Th}]}{\partial x} - u_{\text{net}} \frac{\partial [^{234}\text{Th}]}{\partial x} \quad (3)$$

where K_x is the horizontal dispersion coefficient ($\text{m}^2 \text{d}^{-1}$) and u_{net} is the net horizontal advection ($\text{m} \text{d}^{-1}$).

The empirical ocean-mixing diagrams of Okubo (1971) were used to estimate the magnitude of the K_x parameter in the surface water of this open Baltic area (1.4 to $1.9 \cdot 10^6 \text{ m}^2 \text{d}^{-1}$ for this interstation spatial scale). The advection rate of the Baltic cyclonic surface current in the Landsort Deep region was estimated with a 6-h resolution using a dynamic baroclinic model of the Baltic Sea circulation (Funkquist 2001). The median advection estimated for 2-, 8-, and 40-m depths at BY31 during the study period were 5.1, 3.2, and 2.8 $\text{cm} \text{s}^{-1}$ with mean annual directions of 149° , 153° , and 183° from true

north (i.e., a SSE boundary current). Substituting the 8-m transport parameters into Eq. 3 yields that the horizontal dispersion fluxes of ^{234}Th between BY31 and any of the three reference stations in both seasons are always $<4\%$ of the estimated vertical export flux. Estimation of the role of advection to the ^{234}Th flux at BY31 suggested that this process (only assessable for the one reference station up-current from BY31) could affect the estimated vertical export flux of ^{234}Th by 0% to 50%, with a decrease in the resulting vertical flux in the single spring and an increase in the single summer observations. However, the relative paucity of such spatially distributed and coupled velocity- ^{234}Th data precludes any definite conclusions, and the observed effect is smaller than the offset in vertical ^{234}Th export between water column deficit and sediment traps observed in the summer periods of this study (see *Sediment trap collection efficiency*). Stigebrandt (1985) modeled the seasonal pycnocline in the open Baltic Sea and concluded that negligible horizontal advection, and diffusion is a good approximation for most constituents in the open Baltic Sea. Also suggesting that any two-dimensional effect was of minor importance in this study, the sediment trap collection efficiencies were not related to the average intensity of the boundary current ($P = 0.28$; $n = 23$ deployment periods). This evaluation suggests that the common one-dimensional model of ^{234}Th scavenging flux is reasonable in this assessment of the collection efficiency of sediment traps.

Sediment trap collection efficiency—The ^{234}Th assessed collection efficiency of the cylindrical traps over the 24-month study period ranged from a good flux agreement to undertrapping by a factor of 10 (Fig. 5; Table 2). As a result of the unique length and time resolution of this field assessment study, a pattern of consistent seasonal variations in the trapping efficiency was resolved. In both winter periods, either agreement between the water column export fluxes and the sediment trap import fluxes or only minor undertrapping (factor of two) was recorded (Fig. 5). However, from the end of the spring bloom through the summer period an increasing undertrapping developed which in both years peaked in August through September, with collection efficiencies in the range of 0.1 to 0.3 (Table 2; Fig. 5).

A summertime under-collection of cylindrical sediment traps in the open Baltic Sea is corroborated by another 3-y study of pelagic-benthic coupling in this region (Lehtonen and Andersin 1998). They found that secondary production of benthic amphipods were closely following sedimentation in time. However, the secondary production of macrobenthos were alone of the same magnitude as the measured sediment trap carbon fluxes over three consecutive years, leaving the associated respiration unsupported by the too small input. However, this imbalance between estimated carbon input to the benthos and its observed demand can be explained if the sediment trap fluxes were underestimated.

Sediment trap collection efficiency: evaluation of mechanisms for varying trapping bias—We further sought to understand the

Table 2. BY31 station 40-m sediment trap ²³⁴Th fluxes and collection efficiencies

Deployment interval	Trap flux ²³⁴ Th (dpm m ⁻² d ⁻¹)	Eff _{trap} *
17 Jul–25 Aug 98	53.2 ± 1.4	0.31 ± 0.02
25 Aug–24 Sep 98	26.0 ± 0.7	0.32 ± 0.08
24 Sep–21 Oct 98	52.9 ± 1.4	0.31 ± 0.03
21 Oct–3 Nov 98	116.8 ± 3.0	0.60 ± 0.04
8 Dec 98–27 Jan 99	75.7 ± 1.9	1.18 ± 0.33
13 Jan–27 Jan 99	60.4 ± 1.5	0.94 ± 0.33
27 Jan–17 Feb 99	67.1 ± 1.7	0.42 ± 0.05
27 Jan–17 Feb 99	54.4 ± 1.4	0.34 ± 0.04
17 Feb–3 Mar 99	124.4 ± 3.2	1.07 ± 0.21
17 Feb–23 Mar 99	167.3 ± 4.3	0.95 ± 0.12
3–23 Mar 99	209.1 ± 5.3	0.89 ± 0.07
23 Mar–8 Apr 99	80.6 ± 2.1	0.34 ± 0.04
23 Mar–14 Apr 99	81.5 ± 2.1	0.34 ± 0.04
8 Apr–12 May 99	63.5 ± 1.6	0.28 ± 0.04
14 Apr–12 May 99	67.7 ± 1.7	0.30 ± 0.04
12–26 May 99	96.2 ± 2.5	0.34 ± 0.02
12 May–18 Jun 99	66.1 ± 1.7	0.19 ± 0.01
26 May–18 Jun 99	39.9 ± 1.0	0.12 ± 0.01
18 Jun–6 Jul 99	45.8 ± 1.2	0.26 ± 0.04
6 Jul–4 Aug 99	46.5 ± 1.2	0.15 ± 0.01
4–31 Aug 99	19.1 ± 0.5	0.05 ± 0.01
31 Aug–28 Sep 99	18.2 ± 0.5	0.05 ± 0.01
31 Aug–28 Sep 99	35.7 ± 0.9	0.11 ± 0.01
28 Sep–27 Oct 99	73.0 ± 1.9	0.27 ± 0.02
2–22 Feb 00	163.1 ± 4.2	0.49 ± 0.02
22 Feb–29 Mar 00	178.6 ± 4.5	0.55 ± 0.03
22 Feb–29 Mar 00	129.3 ± 3.3	0.40 ± 0.02
29 Mar–11 Apr 00	104.1 ± 2.6	0.36 ± 0.02
29 Mar–11 Apr 00	82.6 ± 2.1	0.29 ± 0.02
11 Apr–4 May 00	67.1 ± 1.7	0.24 ± 0.01
11 Apr–4 May 00	81.1 ± 2.1	0.29 ± 0.02
2 May–6 Jun 00	121.6 ± 3.1	0.38 ± 0.02
6 Jun–19 Jul 00	67.8 ± 1.7	0.41 ± 0.04
6 Jun–19 Jul 00	55.9 ± 1.4	0.34 ± 0.04
19 Jul–15 Aug 00	42.2 ± 1.1	0.14 ± 0.01
19 Jul–15 Aug 00	44.1 ± 1.1	0.15 ± 0.01

*The water column ²³⁴Th export flux obtained on the closest date succeeding the trap midpoint deployment date was used in calculation. In a few cases where two water-column sampling dates were equally close, the average was used.

reasons for this seasonally varying trap-collection efficiency. Because the observed trap bias was toward under-collection, processes that would cause fewer particles to be trapped were of particular interest. It is well known that marine particles encompass sizes from nanometers to millimeters and cover broad non-linear ranges in both effective densities and geometry descriptions (e.g., Sheldon et al. 1972; McCave 1984; Knauer and Asper 1986; Alldredge and Silver 1988; Stolzen-

bach and Elimelech 1994; Johnson et al. 1996; Gustafsson and Gschwend 1997; Gustafsson et al. 2000b; Archambault et al. 2001). Variations in these key particle properties result in a complex settling velocity distribution that can only be sampled accurately in the ocean with highly specialized techniques (Gustafsson et al. 2000b). Importantly, hydrodynamic studies have suggested that the collection efficiency of cylindrical sediment traps is governed by an interrelationship between the horizontal current across the trap mouth (approach velocity) and the intrinsic particle settling velocity (e.g., Butman et al. 1986; Baker et al. 1988; Gust et al. 1996; Gust and Kozerski 2000). Lower collection efficiency is expected for higher horizontal current and for particles of lower settling velocity. For instance, it is predicted that for an approach velocity of ≥ 12 cm s⁻¹ the commonly employed multiPIT (cylindrical) trap is rejecting $\geq 95\%$ of all particles settling at ≤ 5 m d⁻¹ (Gust and Kozerski 2000).

The estimated horizontal current velocities (6-h average) at the 40-m trap deployment depth were low and ranged from 0.1 to 27 cm s⁻¹ (median of 2.8 cm s⁻¹) (Funkquist 2001). For these gimbaled bottom-tethered traps, the trap-associated approach velocities must be near equal to this macroscopic current speed. Because a link between the observed seasonal variations in trapping efficiency (Fig. 5) and the sluggish trap-depth current was statistically ruled out (see also above; $P = 0.28$, $n = 23$ deployment periods), the recorded undertrapping must instead be related to a changing composition of the particles across the settling velocity spectrum.

Consequently, we hypothesize that the good/acceptable trapping efficiencies (within a factor of two) observed in the winter-spring periods are associated with dominance in the settling flux of faster-settling mineral particles and higher-density diatom tests acting as ballasts. The Fe/Al ratio in the trap-collected matter indicates continuous presence of detrital material (Fig. 6a). The mineral contribution to the total particle flux was much higher in the winter periods of good collection efficiencies, as indicated by the Al concentration in the trapped material, reaching 500 to 900 $\mu\text{g/gdw}$ for those periods, whereas values < 100 $\mu\text{g/gdw}$ were observed during vegetative seasons associated with under-collection (Fig. 6b). Also consistent with this ballasting hypothesis, Si/Al (mass) ratios were elevated well above the 3 to 5 range of background winter values and average crust in both spring periods, reaching Si/Al values of 8 to 11 in three spring-to-early-summer deployments in 1999 and recorded a Si/Al ratio of 13 in a springtime deployment in 2000 (Fig. 6c). This biogenic Si/Al signal suggests a significant influence of rapidly settling diatoms at these times, explaining the good trapping efficiencies. Indeed, these high Si/Al trap ratios—and associated good collection efficiencies—coincided with, or were just preceded by, high diatom abundances in the water column. The longer sustained and elevated Si/Al ratios in 1999 compared to 2000 reflected the higher diatom occurrence observed this year. The late-March to mid-May 1999 and the late April 2000 trap deploy-

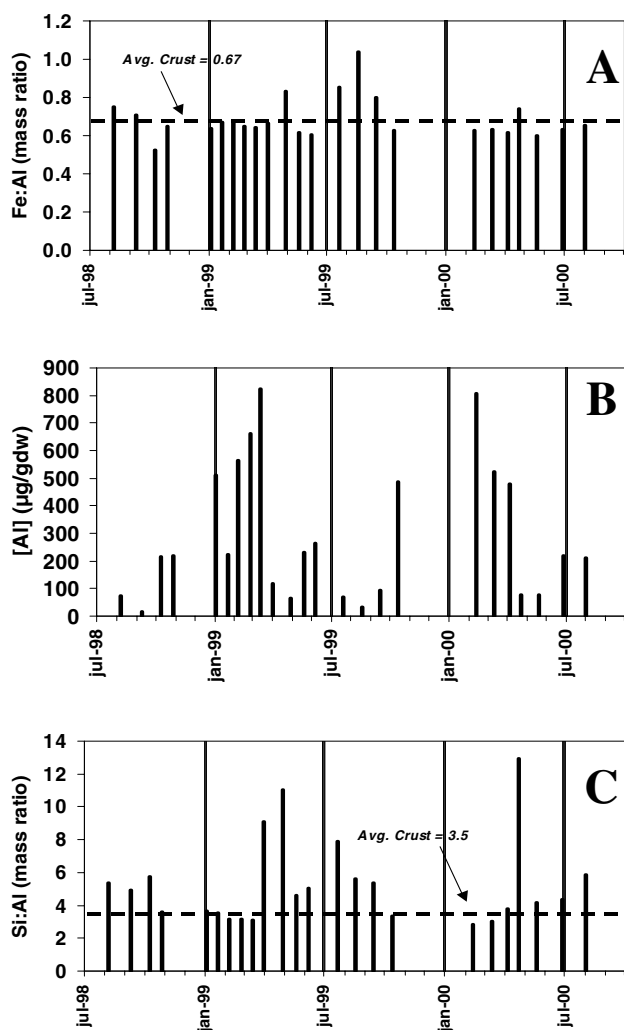


Fig. 6. Source-diagnostic composition of the particles collected in the sediment traps at the Landsort Deep BY31 time series station during the 1998–2000 study period: Fe:Al (A), Al concentration (B), and Si:Al (C). The horizontal broken lines in A and C represent typical values of average crust (Krauskopf and Bird 1995).

ments, which all had high Si/Al ratios, were associated with high water column abundances of the diatoms *Thalassiosira baltica*, *Chaetoceros wighamii*, and *Skeletonoma costatum*. The single elevated Si/Al of 8 in the July 1999 trap may be explained by the presence of the fast-growing small diatom *Cyclotella choctawhatcheeana* observed at that point.

Conversely, the lower trapping efficiencies obtained in the (late) summer periods likely reflect a settling regime dominated by slow-sinking, loosely aggregated, organic matter, such as marine snow (Allredge and Silver 1988), lacking mineral ballasts. There are clear seasonal signals in both TOC and the 280 nm molar extinction coefficient (ϵ_{280} ; reflecting the aromaticity of the organic matter) that are consistent with the hypothesis of ballasting affecting the sediment trap collection

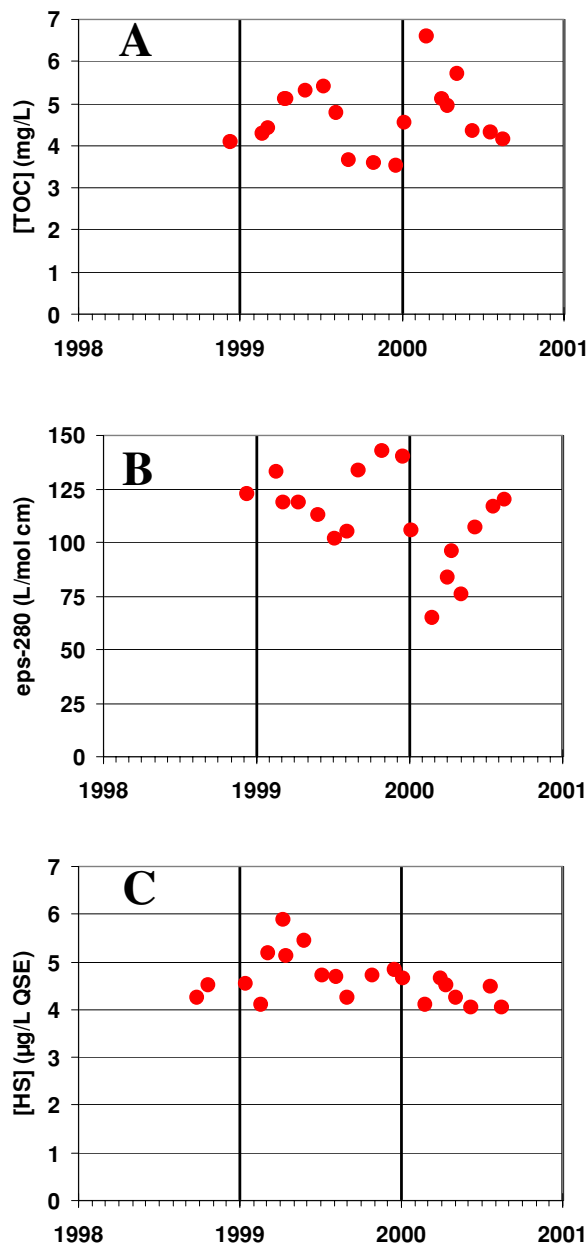


Fig. 7. Characteristics of the suspended organic matter, total organic carbon (TOC) (A), molar absorptivity at 280 nm (ϵ_{280}) (B), and humic substance abundance (C) at the Landsort Deep BY31 time series station during the 1998–2000 study period.

efficiencies. Mirroring the patterns of the organic matter characteristics observed in a nearby coastal Baltic Bay during a 5-month tri-daily study (Gustafsson et al. 2001), TOC increased from dormant winter values of 4 mg L⁻¹ during early spring to summer to 5 to 6 mg L⁻¹ in late spring to middle of the summer (Fig. 7). Thereafter TOC decreased to approach the dormant winter values, presumably reflective of near-constant year-round background levels of humic substances.

Intriguingly, the ϵ_{280} in the surface water shows an inverse trend of TOC, with decreasing values during the early spring to summer vegetative season, followed by increasing values thereafter. It is likely that the inverse TOC- ϵ_{280} relationship is reflecting the buildup and subsequent slow sedimentation of 280-nm transparent polysaccharide-rich exopolymeric substances (e.g., Passow and Alldredge 1995; Gustafsson et al. 2001), which may be hydrodynamically discriminated against near the trap mouth (e.g., Gust and Kozerski 2000). Such transparent exopolymer particles (TEP) would act to “dilute” the ϵ_{280} signal and could contribute to the TOC buildup until some threshold level was achieved where aggregation-settling becomes important and aggregates held together by these sticky exudates are sinking out of the surface waters. Given the slow settling velocities of such organic-rich aggregates (e.g., Alldredge and Silver 1988; Gustafsson et al. 2000b), a low collection efficiency of this material and associated substances throughout these summer to early fall study periods is synchronous with low ^{234}Th -based collection efficiencies (Fig. 5). Because on a carbon-atom basis, such exopolymer particles have been found to complex Th much stronger than bulk organic matter (Niven et al. 1995; Quigley et al. 2002; Guo et al. 2002), this undertrapping effect may be exacerbated in a ^{234}Th -based tracer study. Whereas coincident undertrapping of POC most certainly is taking place, it is likely that the undertrapping factor of POC is smaller than that for ^{234}Th . Taken together, ancillary biogeochemical data support the hypotheses that good ^{234}Th -based collection efficiencies are related to periods of predominant faster-settling detrital/mineral and diatom test particles (ballasting), whereas significant undercollection biases are related to slower-settling organic-rich aggregates. We stress that variable affinity of ^{234}Th for different forms of organic matter (e.g., Quigley et al. 2002) prohibits direct application of any ^{234}Th -based trap “calibration factor” to any other component of the settling flux such as carbon.

Discussion

Studies with hydrodynamic focus (e.g., Baker et al. 1988; Gust and Kozerski 2000) and studies diagnosing flux behavior through geochemical signals (Buesseler et al. 2000; this study) are now combining to suggest that cylindrical traps may undercollect slow-settling particles under hydrodynamic conditions that are common for upper ocean trap deployments. Knowledge of the potential for undercollecting the slow-settling particles may help explain some existing inconsistencies. For instance, not accounting for components of the slow-settling vertical particle flux may account for a significant part of the 80% imbalance in the upper ocean carbon budget at BATS (Michaels et al. 1994). Also, the observation of a secondary macrobenthic production in the open Baltic Sea of apparent equal magnitude as the trap-estimated total carbon export (Lehtonen and Andersin 1998) may be understood if the traps are undercollecting.

The use of upper ocean sediment traps undoubtedly adds useful fundamental information about upper ocean biogeochem-

istry and plankton ecology. Because data from sediment traps have played large roles in establishing several existing paradigms, the field should continue to strive toward a fuller knowledge of the limitations and possible biases of existing sediment trap methods, seek ways to minimize the risk of artifacts, and look for complementary techniques to obtain and support the type of data on settling-influenced processes that traps are attempting to track. Many of the sediment-trap specific considerations have been detailed elsewhere (e.g., Gardner 1997, 2000). Two new techniques, which may avoid any significant hydrodynamic discrimination among particles settling with different intrinsic fall velocities, are neutrally buoyant sediment traps (Buesseler et al. 2000) and techniques such as split flow thin-cell fractionation, which allows separation of particles based directly on their varying settling velocity in a laminar flow (Gustafsson et al. 2000). Initial results from these two distinct methods both suggest that particles from different segments of the settling velocity spectrum have different composition.

Discrimination against the slowest settling organic-rich fraction indicated by this 24-month in situ trap test calls into question the validity of the practice of correcting fluxes of biogeochemically important components, such as carbon, based on in situ calibration factors derived from Th isotope tracers (e.g., Murray et al. 1996, Scholten et al. 2001); an approach that relies on the assumption that the trapping efficiency is equal for all elements and substances. In fact, particularly strong ^{234}Th complexation with the transparent acidic polysaccharide component of the particulate organic matter has recently been indicated (Niven et al. 1995; Guo et al. 2002; Quigley et al. 2002). Our record of optical properties suggest that the period of most severe ^{234}Th undertrapping was likely associated with the presence of a slowly sedimenting component, likely containing such strongly complexing transparent exopolymeric material. A much lower POC/ ^{234}Th on such a subcomponent relative to the bulk POM, would hold that the collection efficiency of POC was higher than the 0.1 to 0.3 of ^{234}Th recorded under those periods. Carbon system mass balance constraints also support that the undertrapping was less for POC than for ^{234}Th (Gustafsson et al. in prep. unref.).

Taken together, this 2-y study demonstrates that cylindrical upper ocean sediment traps, even when positioned in a sluggish flow regime of a few cm s^{-1} , record consistent undertrapping of ^{234}Th -complexing particulate matter. Whereas collection efficiencies were good during winter-spring periods, the extents of undertrapping during the slow-settling dominated summer regimes were a factor of three to ten. System considerations suggest that this ^{234}Th -based collection efficiency is not quantitatively applicable to other flux components, but the magnitude is such that the trap-derived fluxes of any other settling components should be treated with caution and critically evaluated.

Comments and recommendations

The results of this study lead to three major recommendations: (1) The ^{234}Th proxy may be beneficially applied to assess

the seasonally varying direction and magnitude of in situ collection efficiency of any upper ocean sediment trap program, (2) the obtained ^{234}Th -based collection efficiencies should not be applied quantitatively and uncritically to "correct" obtained trap fluxes for other settling components, and (3) previous recommendations focusing mostly on limits of current speed to ensure unbiased trap collections (e.g., 15 cm s⁻¹, Gardner 1980; Butman et al. 1986) should probably be revised to place a larger emphasis on the settling velocity of the components of interest. Careful consideration of the operational limits and behaviors of sediment traps will lead to improved interpretations of the potentially valuable biological and geochemical data that are obtainable with this technique.

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